

Persistent Organic Pollutants in British Columbia Grizzly Bears: Consequence of Divergent Diets

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Nitrogen and carbon stable isotope signatures in growing hair reveal that while some British Columbia grizzly bears (*Ursus arctos horribilis*) rely entirely on terrestrial foods, others switch in late summer to returning Pacific salmon (*Oncorhynchus* spp.). Implications for persistent organic pollutant (POP) concentrations and patterns measured in the two feeding groups of grizzly bears were profound. While the bears consuming a higher proportion of terrestrial vegetation ("interior" grizzlies) exhibited POP patterns dominated by the more volatile organochlorine (OC) pesticides and the heavier polybrominated diphenyl ethers (PBDEs: e.g., BDE-209), the bears consuming salmon were dominated by the more bioaccumulative POPs (e.g., DDT, chlordanes, and BDE-47). The ocean-salmon-bear pathway appeared to preferentially select for those contaminants with intermediate partitioning strength from water into lipid ($\log K_{ow} \sim 6.5$). This pattern reflects an optimum contaminant $\log K_{ow}$ range for atmospheric transport, deposition into the marine environment, uptake into marine biota, accumulation through the food web, and retention in the bear tissues. We estimate that salmon deliver 70% of all OC pesticides, up to 85% of the lower brominated PBDE congeners, and 90% of PCBs found in salmon-eating grizzly bears, thereby inextricably linking these terrestrial predators to contaminants from the North Pacific Ocean.

Atmospheric transport readily delivers contaminants from Asia and other sources to North America and the North East Pacific Ocean (1, 2). Subsequent deposition of contaminants into marine and terrestrial environments introduces persistent organic pollutants (POPs) into the lipid compartment of food webs (3), where the POPs may readily bioaccumulate, particularly through aquatic food webs, to top predators (4–6).

Grizzly bears (*Ursus arctos horribilis*) in British Columbia (BC), Canada, are typically regarded as terrestrial predators, consuming a wide variety of plants, berries, insects, mam-

mals, and carrion. Therefore, grizzly bears might be considered unlikely to accumulate significant concentrations of POPs as a result of the lower concentrations that typify the base of terrestrial food webs and the shorter food chains that limit POP amplification (7–9). In this way, grizzlies have been overlooked in contaminant studies. However, some grizzly bears rely heavily on Pacific salmon in the fall (10), and recent reports highlight the role that migratory Pacific salmon play as biological vectors for ocean contaminants to coastal North American watersheds (6, 11). Given that North American grizzly bear populations continue to face increased habitat loss, decreased food availability, and mortality associated with human settlements (12), POP exposure may present an additional conservation concern.

The obvious challenges associated with studying grizzly bears (e.g., their elusive nature, difficulty in capture, and potentially dangerous disposition) have largely precluded a detailed assessment of their foraging ecology, a critical foundation for any contaminant exposure assessment. Stable isotope analysis of various animal tissues, such as blood and hair, has been used as a surrogate for the assessment of both short- and long-term diet, respectively, in wildlife (13–16). Carbon (^{13}C : ^{12}C ; $\delta^{13}\text{C}$) and nitrogen (^{15}N : ^{14}N ; $\delta^{15}\text{N}$) are the most widely utilized stable isotopes in ecological applications. While $\delta^{13}\text{C}$ values indicate the extent of marine influence in diet, elevated $\delta^{15}\text{N}$ provides relative trophic position of the consumer, as there is a general enrichment in $\delta^{15}\text{N}$ of 3 to 4‰ with every increase in trophic level (17).

Available stable isotope information for grizzly bears is limited to homogenized whole hair strands to gather integrated dietary information over extended periods (e.g., annual) (15, 16, 18). While it is useful to observe gross differences in diet preferences, whole hair sheds little light on seasonal diet variation. Hair is a metabolically inert tissue and therefore records stable isotopes chronologically along the length of the strand (19), where the root represents the most recent diet prior to sample collection. Studies on variation in stable isotopes along the hair length are limited to captive animals with relatively homogeneous diets (19) and free-ranging wolves (for which two sections were used) (20). By conducting stable isotope analysis in multiple hair sections, especially in animals that undergo large seasonal dietary shifts, we would obtain better resolution of temporal and individual dietary variation. Hair segmentation stable isotope analysis becomes an essential foundation for interpreting the relative contributions of two food webs to POP burdens in grizzly bears in this study.

We studied three classes of POPs in BC grizzly bears: polybrominated diphenyl ethers (PBDEs), organochlorine (OC) pesticides, and polychlorinated biphenyls (PCBs). While OC pesticides and PCBs are legacy contaminants that are largely regulated in the industrialized world, current use PBDEs are presently increasing exponentially in wildlife and humans (21–24).

Our objectives in this study were to (1) characterize seasonal variation in the diet of BC grizzly bears using carbon and nitrogen stable isotope analysis, (2) estimate the proportion of salmon consumed by grizzly bears using a diet-to-consumer stable isotope fractionation model (15), (3) quantify PBDE, OC pesticide, and PCB concentrations in grizzly bears, and (4) characterize the linkage between POP burdens of individual bears and their dietary preferences. The diverging feeding habits (i.e., marine and terrestrial) of two grizzly bear populations provide novel insight into pathways of exposure and accumulation of contaminants of global concern.

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TABLE 1. Summary of Individual Grizzly Bear Samples in British Columbia, Canada, and Their Putative Feeding Strategy

bear ID # ^a	sex	age	tissue analyzed for POPs ^b	percent (%) lipid	feeding group
1	f	3	fat	97.6	interior ^{c,e}
2	f	unknown	fat	71.7	interior
3	m	15	fat	100.7	interior
4	m	1	fat	88.7	interior
5	m	10	fat	71.4	interior
6	m	5	fat	26.8	maritime ^d
7	m	12	muscle	6.2	maritime
8	m	unknown	fat	83.8	maritime
9	f	5	fat	83.2	maritime
10	f	5	fat	97.2	maritime
11	m	unknown	fat	92.7	interior
12	f	8	fat	100.4	maritime

^a Bear identification numbers (ID #) can be cross-referenced with Figure 2 for location and contaminant pattern information. ^b Persistent organic pollutants (POPs). ^c Interior = non-salmon-eating. ^d Maritime = salmon-eating. ^e Bear #1 is considered our herbivorous "baseline" grizzly bear.

Materials and Methods

Sample Collection. In collaboration with the BC Ministry of Water, Land and Air Protection (MWLAP), compulsory inspectors, and conservation officers, we obtained (where possible) fat, muscle, skin, and hair samples from 12 legally hunted or management ("problem") grizzly bears (Table 1) from various locations in BC during the fall 2003. Mule deer (*Odocoileus hemionus*; $n = 4$) and moose (*Alces alces*; $n = 7$) hair samples were also obtained (Terrace, BC) as proxies for purely herbivorous mammals. Additionally, Chinook salmon (*Oncorhynchus tshawytscha*) were collected from Johnstone Strait (2000; $n = 6$), Harrison Lake (2000; $n = 6$), Duwamish River (2001; $n = 6$), and Deschutes River (2001; $n = 6$) in Coastal BC (unpublished data, P. S. Ross). Samples were directly placed in hexane-rinsed aluminum foil and sealed in water-tight Ziploc bags. All samples were shipped frozen and stored at -20°C immediately upon delivery. Information on grizzly bears was cross-referenced with the BC MWLAP and, where possible, included age (determined using tooth cementum analysis), sex, sampling date, weight, general condition, and geographic location.

Stable Isotope Analysis. Grizzly hair was plucked from skin samples (bears #1–10) and subdivided into 1 cm segments commencing at the root to 5 cm, with each of six segments reflecting approximately 20 days of growth (25). For bear #12, enough hair was available to measure only whole hair stable isotopes. Bear #11 had only skin available to conduct stable isotope analysis. Deer and moose hair samples were not segmented. All hair samples were washed with 2:1 chloroform:methanol solution three times to remove surface oils and debris and then ground with a mortar and pestle to a powder using liquid nitrogen. Each hair sample was then freeze-dried at -50°C for at least 24 h. The skin sample for bear #11 was homogenized using a scalpel and freeze-dried at -50°C for 48 h.

Stable isotope measurements of subsamples (0.5 ± 0.08 mg) were carried out at the Biogeochemistry Facility (School of Earth and Ocean Sciences, University of Victoria, BC) using a Fisons NA 1500 Elemental Analyser-Isotope Ratio Mass-Selective (Milano, Italy) interfaced to a FinniganMAT 252 Isotope Ratio Mass Spectrometer (Bremen, Germany). Results are reported using standard isotope ratio notation (parts per thousand, ‰)

$$\delta X = [(R_{\text{SAMPLE}}/R_{\text{STANDARD}}) - 1] \times 1000 \quad (1)$$

where δX is $\delta^{13}\text{C}$ (‰ vs PDB) or $\delta^{15}\text{N}$ (‰ vs air N_2), and R

is the $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$ ratio, respectively (17). Carbon and nitrogen measurements were made relative to runs of acetanilide (an in-house standard with known isotope ratios) and blanks. Replicates were conducted on random samples to (1) observe within sample stable isotope variation, (2) measure any deviation of stable isotope values over time, and (3) measure differences from one sample rack to another. Isotopic values were adjusted to the standards if any deviation occurred.

Contaminant Analyses. Approximately 3 g of fat ($n = 11$) or when this tissue was not available, 20 g of muscle ($n = 1$) was analyzed for 39 PBDE congeners and 28 organochlorine pesticides [α -hexachlorocyclohexane (α -HCH), β -HCH, δ -HCH, γ -HCH, hexachlorobenzene (HCB), 2,4'-dichlorodiphenyl dichloroethane (DDD), 4,4'-DDD, 2,4'-dichlorodiphenyl ethylene (DDE), 4,4'-DDE, 2,4'-dichlorodiphenyl trichloroethane (DDT), 4,4'-DDT, heptachlor epoxide, heptachlor, methoxychlor, oxychlorane, γ (*trans*)-chlordane, α (*cis*)-chlordane, *cis*-nonachlor, *trans*-nonachlor, α -endosulfan, β -endosulfan, endosulfan sulfate, dieldrin, endrin, endrin aldehyde, endrin ketone, aldrin, and mirex].

A second set of fat samples pooled by feeding categories (determined following stable isotope analysis) was analyzed for 160 congener-specific PCBs ($n = 2$ pools) to use as a reference contaminant containing congeners with a wide range of octanol/water partition coefficient ($\log K_{ow}$) values (i.e., $\log K_{ow} \sim 4.2$ – 8.5) (26) that spanned those of the OC pesticides (27, 28) and PBDE congeners (29). One sample was a homogenate of 6 interior (non-salmon-eating) grizzly bears (#1–5, 11) and the other sample was a homogenate of 4 maritime (salmon-eating) bears (#6, 8–10). Bears #7 and #12 were not included in the maritime homogenate sample for PCB analysis, as #7 was a muscle sample and #12 had insufficient fat for analysis.

Samples were analyzed using high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) by AXYS Analytical Services, Sidney, BC, according to their laboratory procedures and criteria using an Ultima HRMS equipped with a Hewlett-Packard 5890 GC and a DB-5 Durabond capillary column (60 m \times 0.25 mm, 0.10 μm film). Percent of lipid in samples was determined at AXYS Analytical Services using the gravimetric lipid determination by weight of extract method with dichloromethane (DCM).

Samples were spiked with ^{13}C -labeled surrogate standards ($n = 12$ PBDEs; $n = 29$ PCBs; $n = 21$ OC pesticides) and then ground with anhydrous sodium sulfate. Samples were transferred to a Soxhlet thimble, surrogate standard was added, and samples were refluxed for 16 h with DCM. The extract was eluted through a gel permeation column with 1:1 DCM:hexane. The extract was applied to a partially deactivated Fluorisil column and eluted with hexane followed by 15:85 DCM:hexane. Eluates were then combined and eluted with 1:1 DCM:hexane and each fraction was concentrated.

Mono- and di-BDE data were not used for interpretation as surrogate recoveries were less than 10%. Since the isotope dilution method of quantification produces data that are recovery-corrected, the slight variances from the method acceptance criteria of some analytes are deemed not to affect the quantification.

Included with each batch of samples was a procedural blank. The lab blank had concentrations slightly above detectable levels (<20 pg/g) for 11 PBDE and 38 PCB congeners. BDE-47, 99, and 209 were detected at 92.5, 67.9, and 167 pg/g, respectively. There were no PCB congeners detected above 12.8 pg/g. Trace amounts (nondetectable ranges; NDR) of eight OC pesticides were found in the lab blank. HCB was detected at a concentration of 0.021 ng/g.

Detection limit substitutions were made for PBDE and OC pesticide analytes that were not detected in cases where

at least 8 out of 12 individual bears (>67%) had detectable values for that contaminant. Where less than 8 bears had detectable concentrations of an analyte, 0 ng/kg was substituted for nondetect concentrations. Contaminants were not reported if there were low NDRs in combination with nondetectables (below detection limit) in all bear samples. Detection limits for PBDE congeners were consistently <10 pg/g wet weight and, in most cases, <5 pg/g, with exception to BDE-209 which had detection limits ranging from 2.5 to 562 pg/g. Whenever the determined concentration of native BDE-209 in samples was not significantly different from that in the lab blank (167 pg/g wet weight), the detection limit for BDE-209 in samples was elevated to the concentration of the detected analyte and considered not detected. For PCB congeners, detection limits were consistently <1 pg/g and, in most cases, <0.25 pg/g. For OC pesticides, detection limits were consistently <0.05 ng/g and, in most cases, <0.01 ng/g. Results are expressed on a lipid weight basis and expressed as mean ± 1 standard deviation (SD).

While variable reporting of higher brominated PBDE congeners (e.g., BDE-206 to -209) partly reflects analytical difficulties (30), the inclusion of these congeners is considered important (31). We report here ΣPBDEs (all congeners detected including BDE-206 to -209), as most recoveries were considered within acceptable limits set by AXYS, and the reported concentrations were adjusted based on both those recoveries as well as concentrations found in the lab blank.

For PCB homogenate samples, the toxic equivalency quotient (TEQ) was calculated based on toxic equivalency factors (TEFs) of specific PCB congeners (32) in the following formula:

$$TEQ = \sum [PCB_i] \times TEF_i \quad (2)$$

Theoretical Calculations. Grizzly bears are large mammals with extensive home ranges (33) and their omnivorous diet in coastal areas of BC is poorly described. In general, their diets depend on opportunity and habit. A baseline would provide the basis for an internally consistent algebraic approach to define food item end-members that encapsulate the data field. We chose the whole hair isotopic value of bear #1 to act as our “baseline” or “anchor” for all BC grizzlies ($\delta^{15}N = 3.5\text{‰}$, $\delta^{13}C = -23.0\text{‰}$), as this bear most closely resembles the relative trophic position of the sampled herbivores, i.e., moose and deer; $\delta^{15}N = 3.8 \pm 0.9\text{‰}$. The 100% herbivore reference point then enables the estimation of deviations from an herbivorous diet for each of the other grizzly bears samples.

Although both $\delta^{13}C$ and $\delta^{15}N$ were measured in the grizzly bear hair, only $\delta^{15}N$ is required to calculate the estimated diet because of the following: (1) there was a significant linear correlation between $\delta^{13}C$ and $\delta^{15}N$ (see results), implying that terrestrial meat and salmon diets result in similar changes in $\delta^{13}C$ in relation to their trophic position ($\delta^{15}N$); (2) due to a resultant two end-member diet model, results from only one stable isotope are necessary to estimate diet (13); and (3) the use of $\delta^{15}N$ in characterizing trophic levels in food web-based contaminant studies is well-established. The two end-members for the model were vegetation and Chinook salmon. Although some bears do not consume salmon, by using Chinook as the meat end-member (which is the highest trophic-level salmon species), we are in fact calculating what might be considered a meat percent (%) “Chinook Equivalent” (CE). As we cannot accurately determine the composition of salmon species, or terrestrial species consumed by a particular bear, we have simply used the Chinook salmon as the index of meat consumed. This approach is supported by the strong correlation between $\delta^{15}N$ and $\delta^{13}C$ for bears (also observed by Hilderbrand et al. (15)), and by strong correlations

observed between $\delta^{15}N$ (trophic level) and POPs in aquatic food webs (34, 35).

First, stable isotope deviations ($\Delta\delta^{15}N_{SEG}$) were calculated from the herbivore baseline (3.5‰) in each hair segment ($\delta^{15}N_{SEG}$) for bears #2–10 using

$$\Delta\delta^{15}N_{SEG} = \delta^{15}N_{SEG} - 3.5 \quad (3)$$

This calculation was not conducted on bears #11 and 12, for which segmented hair samples were unavailable. Cumulative deviation in $\Delta\delta^{15}N_{SEG}$ from the baseline herbivore diet over the 4-month period ($\Sigma\Delta\delta^{15}N$) for bears #2–10 was calculated as

$$\sum \Delta\delta^{15}N_{HAIR} = \Delta\delta^{15}N_{SEG1} + \Delta\delta^{15}N_{SEG2} + \dots + \Delta\delta^{15}N_{SEG6} \quad (4)$$

Using stable isotope data from black bear feeding trials with known diets, Hilderbrand et al. (15) derived a linear relationship between the stable isotope values in diet with those of bear plasma (which they suggest is appropriate for all bear tissues except adipose tissue). Generalizing this relationship from plasma to bear hair, we assume the relationship

$$\delta^{15}N_{HAIR} = 4.76 + 0.91(\delta^{15}N_{DIET}) \quad (5)$$

to calculate the estimated 100% Chinook Equivalent end-member (Chinook: $\delta^{15}N = 15.4 \pm 0.6\text{‰}$; P. S. Ross, unpublished data). Using the 100% CE calculated from that model ($\delta^{15}N_{HAIR} = 18.8\text{‰}$) and substituting it into eqs 3 and 4 (as a value for each hair segment), we estimate 100% CE diet over 4 months equated to $\Sigma\Delta\delta^{15}N$ of 91.8‰. By definition, 100% vegetation (baseline) end-member over the sampling period equated to $\Sigma\Delta\delta^{15}N$ of 0‰. Both vegetation and meat CE end-members were then incorporated into a mass balance to obtain relative proportions of meat (P_{MEAT}) and vegetation (P_{VEG}) for each grizzly bear (#1–10)

$$\sum \Delta\delta^{15}N_{HAIR} = P_{VEG}(\sum \Delta\delta^{15}N_{VEG}) + P_{MEAT}(\sum \Delta\delta^{15}N_{MEAT}) \quad (6)$$

which can be simplified to

$$P_{MEAT} = \frac{\sum \Delta\delta^{15}N_{HAIR}}{91.8} \quad (7)$$

where

$$P_{VEG} = 1 - P_{MEAT} \quad (8)$$

We estimated the vegetation-derived contaminant concentrations for each grizzly bear ($[POP]_{VEG}$) using

$$[POP]_{VEG} = [POP]_{BASELINE}(P_{VEG}) \quad (9)$$

where $[POP]_{BASELINE}$ is the contaminant concentration in the anchor bear (bear #1). For PCBs, $[POP]_{VEG}$ is calculated by substituting $[POP]_{BASELINE}$ with the contaminant concentration of the interior bear homogenate, where P_{VEG} is the average proportion of vegetation consumed by the four maritime bears used in the homogenate sample.

To obtain the concentration of each contaminant attributed to meat ($[POP]_{MEAT}$), the $[POP]_{VEG}$ value calculated for each bear was incorporated into

$$[POP]_{MEAT} = [POP]_{TOTAL} - [POP]_{VEG} \quad (10)$$

where $[POP]_{TOTAL}$ is the contaminant concentration measured in the tissue sample of that individual.

The $[POP]_{MEAT}$ values were plotted against the proportion of meat (P_{MEAT}) in the diet of individual bears to produce “bioaccumulation slopes”, which were used to assess contaminant-specific bioaccumulative potential in grizzly bears.

To calculate the proportion of contaminants coming from salmon to the maritime grizzly bears ($P_{[POP]}$), we established which grizzlies had, in highest likelihood, consumed salmon (as opposed to terrestrial meat) by comparing both $\delta^{15}N$ and $\delta^{13}C$ stable isotopic values in the hair with realistic diets of the captive bears from Hilderbrand et al. (15), as well as considering opportunity to access salmon based on geographic location. The proportion of contaminants from salmon was calculated in the salmon-eating bears only using the following equation:

$$P_{[POP]} = \frac{[POP]_{MEAT}}{[POP]_{TOTAL}} \quad (11)$$

For PBDEs and OC pesticides, the POP proportion from salmon was averaged for the four maritime bears. There is only one value for PCBs since there were only two homogenate samples to conduct the calculation. Table S1 (Supporting Information) provides an example of how to use the theoretical calculations to obtain the proportion of contaminants transported from salmon to grizzly bears.

Statistical Analysis. Regression analyses were applied to relationships between (1) total contaminant concentrations and $\Sigma\Delta\delta^{15}N$, (2) $[POP]_{MEAT}$ and proportion of meat (P_{MEAT}) in diet for each grizzly (bioaccumulation slopes), and (3) proportion of PBDE, OC pesticide, and PCB contaminants (arcsine transformed) attributed to salmon and $\log K_{ow}$. T-tests (two-tailed) assuming unequal variances were conducted to compare contaminant concentrations between feeding groups. The criterion for significant effects was $\alpha = 0.05$. Normality and constant variance were assessed and data were transformed if those tests resulted in $\alpha < 0.05$. Statistical analysis was not conducted on PCB data between interior and maritime bears, as there was only one homogenized sample from each feeding group.

Results and Discussion

Stable Isotopes and Feeding Ecology in Grizzly Bears. Changes in $\delta^{15}N$ and $\delta^{13}C$ isotope ratios along the hair strands reflect chronological change in the assimilated diets for individual bears over the course of approximately 4 months (Figure 1). Five bears (#1–5) exhibit low $\delta^{15}N$ and $\delta^{13}C$, with little variation over time, consistent with a diet of vegetation and, possibly, a small supplement of terrestrial meat. Sharp rises in hair $\delta^{15}N$ and $\delta^{13}C$ toward the fall indicate a fundamental dietary shift in five other individual bears (#6–10), coincident with the return of adult Pacific salmon in coastal watersheds (36). The correlation between $\delta^{15}N$ and $\delta^{13}C$ ($r^2 = 0.88$; $p < 0.01$) suggests a marine origin for the observed increase in trophic position.

While interior bears range in cumulative changes in $\delta^{15}N$ ($\Sigma\Delta\delta^{15}N$) from 6.7 to 13.5‰, the maritime bears show both greater and more varied shifts ranging from 12.3 to 55.6‰ in $\Sigma\Delta\delta^{15}N$. We did not have adequate hair samples from two individuals (#11 and #12) to conduct hair segmentation assessment. Whole hair stable isotope ratios for bear #12 are $\delta^{13}C - 19.4$ ‰ and $\delta^{15}N 14$ ‰, consistent with values observed in maritime study bears. Skin stable isotope ratios for bear #11 are $\delta^{13}C - 22.5$ ‰ and $\delta^{15}N 9.4$ ‰, suggesting the diet of this bear is terrestrial, but fairly high trophically.

We estimate that the average diets during the period captured by hair growth ranged from 0 to 19% meat (as estimated using CE; see methods) for interior bears and from 13 to 61% meat for maritime bears. The remaining diet of all bears was assumed to consist of vegetation.

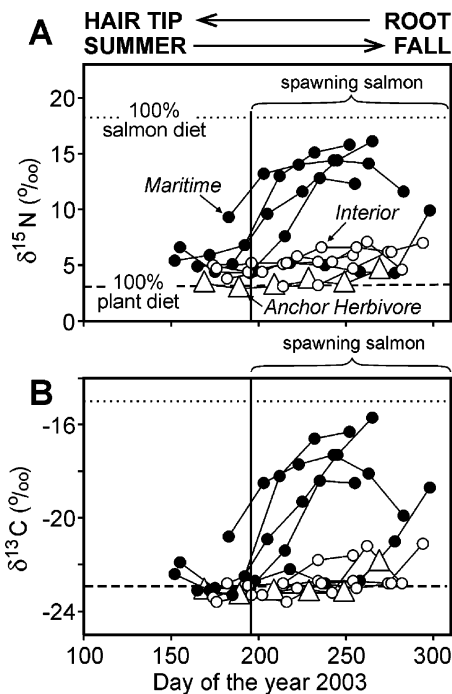


FIGURE 1. Seasonal changes in diet of individual grizzly bears as revealed by stable isotope ratios in growing hair. Interior bears (○), maritime bears (●), and the herbivorous anchor grizzly bear (△) are plotted, with the latter used to estimate diet proportions of other bears. The lower dashed line denotes a theoretical 100% vegetation diet, while the upper dotted line denotes theoretical 100% Chinook salmon diet. In British Columbia, salmon generally spawn in coastal watersheds after July 15 (Day 196). (A) Increasing $\delta^{15}N$ toward the fall indicates a shift to higher trophic positions by maritime bears. (B) Corresponding $\delta^{13}C$ increases provides additional evidence that this shift relates to marine sources (i.e., salmon).

Contaminant Concentrations in Grizzly Bears. Overall, maritime bears were more contaminated with many POPs than the interior bears. The maritime grizzly bears had higher concentrations of ΣDDT (t-test, $p = 0.046$), ΣCHL ($p = 0.017$), dieldrin ($p = 0.044$), and $\Sigma PCBs$ (t-test not done, as $n = 2$ pools) than the interior bears. $\Sigma PBDE$ concentrations did not differ between the two groups (t-test, $p = 0.313$).

Surprisingly, total PBDEs dominate in contaminant concentration rankings of the interior grizzlies: $\Sigma PBDEs > \Sigma PCBs > HCB > \Sigma HCH > \Sigma CHL > \Sigma DDT$, where $\Sigma PBDEs$: $\Sigma PCBs$ is 2.34:1. Contaminant profiles in these bears are dominated by both the heavier PBDE congeners (e.g., BDE-209, which constitutes up to 83% of $\Sigma PBDEs$ for these bears) and the lighter, more volatile pesticides, including HCB and ΣHCH . The relatively low trophic levels occupied by interior bears suggest that air-to-plant partitioning may play an important role in contaminant exposure for this feeding group; their generally low POP concentrations indicate that these levels, for the most part, can be considered as “baseline” for all grizzlies. The dominance of $\Sigma PBDEs$ in this baseline suggests that vegetation and the terrestrial food web may presently be the important pathway for the heavier congeners of this emerging contaminant of concern (e.g., BDE-209).

For maritime grizzly bears, $\Sigma PBDEs$ are not as prominent in the overall contaminant rankings, where $\Sigma PCBs > \Sigma CHL > HCB > \Sigma DDT > \Sigma PBDEs > \Sigma HCH$. Rather, these salmon-eating bears are dominated by legacy bioaccumulative contaminants, where the ratio $\Sigma PBDEs$: ΣPCB is 0.12:1. Contaminant patterns observed in these maritime bears likely reflect the seasonal shift to a higher trophic level through salmon consumption.

Although we observed significant differences in POP concentrations between these two feeding groups of grizzly

TABLE 2. Polybrominated Diphenyl Ether (PBDE), Organochlorine (OC) Pesticide, and Polychlorinated Biphenyl (PCB) Concentrations in Sampled Grizzly Bears, and the Correlation Statistics (Variation, r^2 ; Significance, p -Value) between Contaminant Concentration and Cumulative Changes in Trophic Position ($\Sigma\Delta\delta^{15}\text{N}$) over the Four-Month Period Captured by Segmented Hair Stable Isotope Analysis

contaminant	concentration range (ng/kg lipid weight) ^g	mean concentration \pm S.D. ^g	r^2 for regression with $\Sigma\Delta\delta^{15}\text{N}^h$	p -value for regression with $\Sigma\Delta\delta^{15}\text{N}^h$
Σ PBDE ^a	1121–53470	10794 \pm 16222	0.03	0.651
Σ DDT ^b	28–20277	4461 \pm 6243	0.58	0.010
Σ CHL ^c	213–27606	9179 \pm 8918	0.73	0.002
Σ HCH ^d	304–3779	1322 \pm 1364	0.51	0.020
DIEL	25–3354	982 \pm 1175	0.65	0.005
HCB	1023–21811	5963 \pm 5980	0.29	0.112
Σ PCB ^e	6948–43167	25058	n/a	n/a
Σ PCB TEQ ^f	0.42–2.01	1.22	n/a	n/a

^a This Σ PBDE includes the 20 congeners detected out of 39 tested. ^b Σ DDT includes 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT. ^c Σ CHL includes heptachlor epoxide, oxychlordane, α -chlordane, *trans*-nonachlor, γ -chlordane, and *cis*-nonachlor. ^d Σ HCH includes α -, β -, δ -, and γ -hexachlorocyclohexane (HCH). ^e Σ PCB includes all 132 congeners detected out of 160 tested; used as reference to other POPs, where only two pools were analyzed. ^f Toxic equivalency quotient (TEQ). ^g Concentration range and mean concentrations based on all sampled bears ($n = 12$). ^h Regression statistics based on bears that had $\Sigma\Delta\delta^{15}\text{N}$ values calculated ($n = 10$).

bears, large variation within each group was also evident. Since diet represents the major contributor to POP contaminant burdens in mammals, the variation likely reflects individual differences in diet. Studies of other mammalian top predators, such as killer whales (5), show strong relationships between age/sex and contaminant concentrations found in individual animals. No statistically significant relationships between age, sex, or percent lipid content of the grizzly bears and their contaminant concentrations could be found (results not shown), although our sample size was small. Therefore, we evaluated our contaminant results on an individual basis using only the individual variation in food choices, as measured by stable isotopes in hair.

For most POPs measured, total concentrations increased with an increasing trophic position ($\Sigma\Delta\delta^{15}\text{N}$) of individual bears (Table 2), suggesting that salmon consumption explains the increases in the concentrations of these POPs in the maritime grizzly bears. Increases in total POP concentrations were also observed in interior bears, likely reflecting individual-based increases in the consumption of terrestrial meat.

Contaminant Patterns in Grizzly Bears. Maritime grizzly bears that deviate from a terrestrial to a marine food web not only have increased contaminant concentrations but also show marked differences in contaminant patterns from the bears that feed exclusively within a terrestrial food web (i.e., interior grizzly bears).

Maritime bears were characterized by a pattern of top PBDE profile of 47 > 209 > 99 > 100 > 153, while interior bears were dominated by the higher brominated PBDEs: 209 > 206 > 47 > 207 > 208 (Figure 2). The predominance of the lighter congeners, such as BDE-47, in the maritime bears suggests that this congener may be attributed to marine foods, such as salmon, and/or enhanced atmospheric transport with subsequent accumulation through the terrestrial food web in coastal areas. The heavier PBDE congeners, such as BDE-209, appear to be delivered to the bears through their consumption of terrestrial vegetation, as bears with higher proportions of vegetation reliance (i.e., interior) are dominated by these congeners. The dominance of heavier PBDE congeners in interior bears may also indicate an increasing influence of local (North American) sources in bears inhabiting the interior portions of British Columbia (e.g., Deca-BDE currently at highest production for PBDE formulations (37)).

Interior and maritime grizzly bears had differing OC pesticide patterns in their tissues: interior bears were dominated by HCB > oxychlordane > α -HCH > β -HCH > dieldrin > heptachlor epoxide (Figure 2), consistent with observations in terrestrial herbivores where volatile contaminants (e.g., Σ HCH and HCB) dominate and Σ DDT is

generally low (7, 38), whereas maritime bears were dominated by oxychlordane > HCB > DDE > *trans*-nonachlor > dieldrin > α -CHL, a pattern that is more reflective of contaminants that bioaccumulate through aquatic food webs and is consistent with patterns observed in salmon (39). Metabolism may affect some OC pesticides, such as *cis*- and *trans*-chlordane: Hites et al. (39) documented these parent compounds in wild B.C. salmon, and yet they are absent in salmon-eating grizzly bears. Oxychlordane (a major metabolite of chlordane), on the other hand, is found in high concentrations in our maritime bears.

Two exceptions to the contaminant patterns were observed. The maritime bear #7 and the interior grizzly #11 had contaminant profiles that did not resemble those predicted isotopically. Switching feeding strategies between years by these individuals may explain these anomalies. In addition, contaminant results from bear #7 may have differed somewhat as muscle was used in place of fat.

Both interior PCB (153 > 118 > 180 > 99 > 138) and maritime grizzly bear PCB (153 > 118 > 180 > 138 > 99) patterns were dominated by the same congeners, although the patterns differed slightly. The relative proportions of non- and mono-ortho PCBs were similar between the feeding groups; however, PCB-156/157 contributed the most to total TEQ in maritime bears (ca. 39%), while PCB-126 contributed the most in interior bears (ca. 38%). TEQ values for both maritime and interior bears are low compared to those found in studies of high trophic level aquatic biota (5, 32, 40, 41).

Bioaccumulation of Individual PBDE Congeners and OC Pesticides. Most contaminants had significant bioaccumulation slopes (i.e., relative increase in contaminant concentrations with increasing consumption of meat by individual bears; Table 3). Positive slopes suggest that certain contaminants are transported to the grizzly bears through increased consumption of salmon (maritime grizzlies) or terrestrial meat (interior grizzlies). The slope itself is a reflection of the degree of contaminant bioaccumulation, where oxychlordane and 4,4'-DDE are the most bioaccumulative contaminants, while BDE-47 is the most bioaccumulative PBDE congener. Contaminants with steeper bioaccumulation slopes represent POPs that bioaccumulate more readily through aquatic food webs to grizzly bears, whereas contaminants with less accentuated slopes are more likely to be evenly distributed across food webs (terrestrial = marine) or are readily metabolized by the grizzly bears.

Rankings of these bioaccumulation slopes for OC pesticides and PBDEs are consistent with the observed contaminant pattern in maritime grizzly bears, supporting the conclusion that their contaminant profiles are dominated by those POPs that bioaccumulate in aquatic food webs.

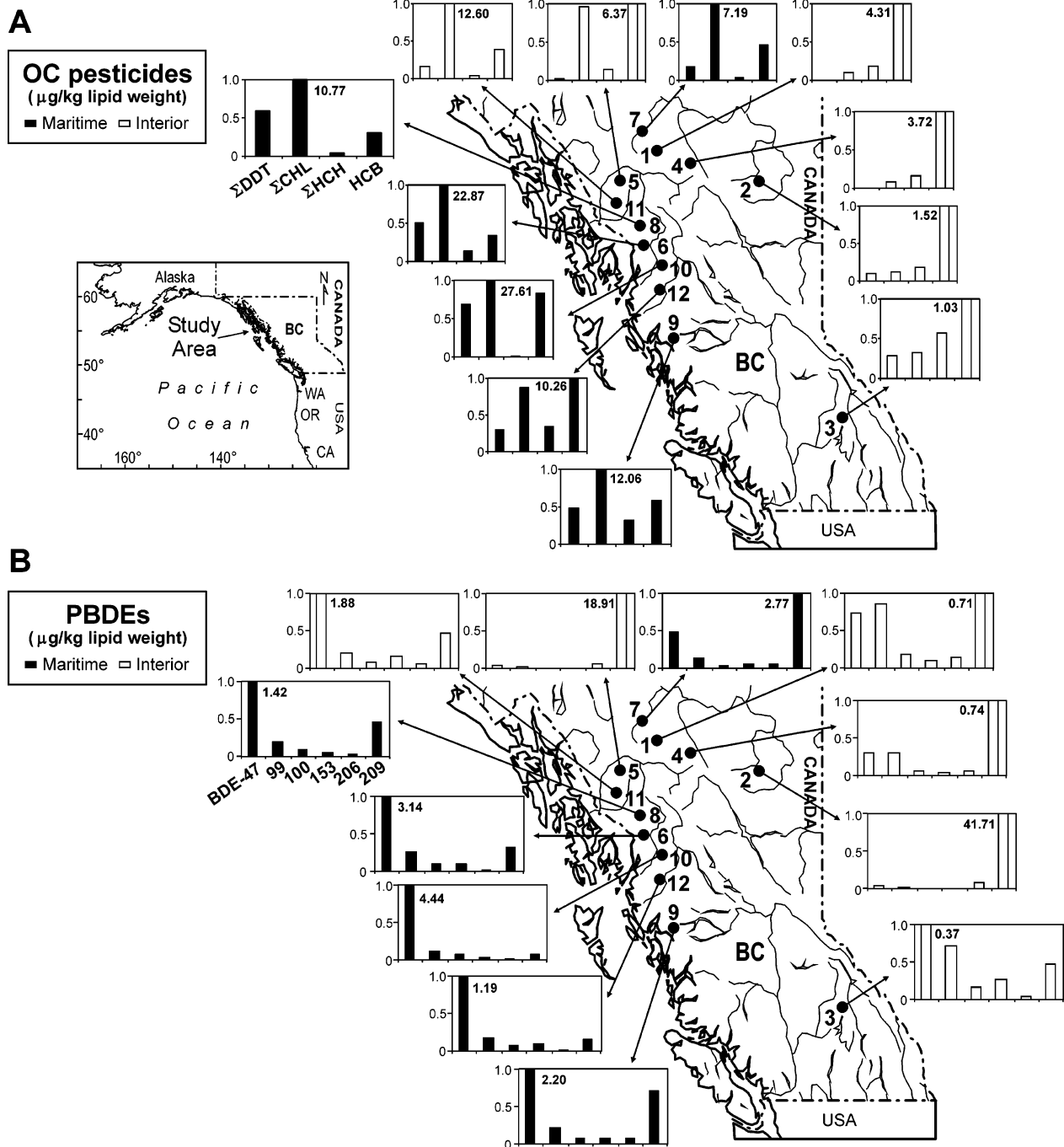


FIGURE 2. Grizzly bear sampling locations in British Columbia and their persistent organic pollutant (POP) patterns. (A) The patterns of the most dominant organochlorine (OC) pesticides (from left bar to right): ΣDDT , ΣCHL , ΣHCH , and HCB. (B) The patterns of top 6 polybrominated diphenyl ether (PBDE) congeners (from left bar to right): BDE-47, -99, -100, -153, -206, and -209. Bars represent the proportion of each contaminant relative to that present at the highest concentration within each bear sample, with actual concentrations indicated numerically for this contaminant ($\mu\text{g}/\text{kg}$). Maritime (salmon-eating) grizzly bears are represented by black bars. Interior grizzlies are represented by white bars.

Higher brominated PBDE congeners (BDE-206 to -209) had negative (albeit nonsignificant) bioaccumulation slopes, possibly indicating a preferential exposure to local sources through their consumption of vegetation.

Chemical Properties Govern Delivery of Contaminants by Salmon. Contrasting stable isotope ratio signatures in our two grizzly bear feeding groups provide a unique opportunity to quantify the relative contributions of terrestrial (i.e., vegetation) and marine (i.e., salmon) food webs to POP accumulation. By removing the contaminant proportion derived from vegetation in each maritime bear, we estimate that salmon contribute $70 \pm 34\%$ of the OC pesticides, up

to 85% of the lower brominated PBDEs and 90% of the PCBs in maritime grizzlies.

The two food webs will preferentially deliver certain individual POPs over others to the grizzly bears, reflecting the role that contaminant physicochemical properties (e.g., $\log K_{ow}$) play in regulating exchange among environmental compartments and fate in the environment. This is evidenced by an observed "peak" regression between the contaminant concentrations attributed to salmon (modified Gaussian, 4 parameter, $r^2 = 0.52$; $p < 0.0001$; Figure 3) and $\log K_{ow}$ values (26, 29). Together, the ocean and the salmon food web provide a small window ($\log K_{ow} \sim 5.9-7.5$) that strongly favors the

TABLE 3. Bioaccumulation Slopes for Individual Organochlorine (OC) Pesticides and Polybrominated Diphenyl Ether (PBDE) Congeners in Grizzly Bears Listed in Order of Highest to Lowest^a

contaminant	bioaccumulation slope	95% confidence interval (mean ± 1.96 * standard error)	r ²	p-value
oxychlordane	23057	12076 to 34038	0.68	0.003
DDE	21136	7233.9 to 35038	0.53	0.018
hexachlorobenzene (HCB)	20288	2179.8 to 38396	0.38	0.059
trans-nonachlor	10600	4778.8 to 16422	0.61	0.007
BDE ^b -47	6180.7	3417.9 to 8943.5	0.71	0.002
dieldrin	5168.0	2930.9 to 7405.2	0.72	0.002
α-chlordane	3894.1	2008.8 to 5779.3	0.67	0.004
β-hexachlorocyclohexane (β-HCH)	3623.4	1871.4 to 5375.3	0.67	0.004
DDT	2269.2	1229.7 to 3308.7	0.70	0.003
heptachlor epoxide	2158.4	1314.4 to 3002.5	0.76	0.001
α-HCH	1543.8	-868.37 to 3956.0	0.16	0.245
cis-nonachlor	1452.7	547.17 to 2358.3	0.55	0.014
BDE-99	1106.1	147.01 to 2065.2	0.39	0.054
β-endosulfan	921.18	208.96 to 1633.4	0.45	0.035
γ-chlordane	563.69	284.10 to 843.28	0.66	0.004
BDE-100	541.09	304.83 to 777.35	0.72	0.002
BDE-153	496.33	383.41 to 609.25	0.90	0.000
mirex	337.08	199.51 to 474.64	0.74	0.001
α-endosulfan	323.81	-13.918 to 661.54	0.31	0.097
BDE-28	252.82	86.387 to 419.25	0.53	0.018
BDE-154	126.20	42.708 to 209.69	0.52	0.018
2,4-DDD	97.857	-30.582 to 226.30	0.22	0.174
γ-HCH	76.401	-360.42 to 513.23	0.01	0.741
BDE-66	74.334	18.631 to 130.04	0.46	0.031
BDE-49	67.586	29.948 to 105.22	0.61	0.008
endrin	65.111	-24.183 to 154.40	0.20	0.191
endosulfan sulfate	63.659	-114.37 to 241.69	0.06	0.503
BDE-77	49.893	15.346 to 84.440	0.50	0.022
BDE-119/120	36.700	27.147 to 46.253	0.84	0.000
δHCH	36.373	14.505 to 58.241	0.57	0.016
BDE-17	30.562	16.489 to 44.635	0.69	0.003
BDE-155	22.848	14.091 to 31.605	0.77	0.001
BDE-183	21.733	-39.544 to 83.010	0.06	0.507
BDE-85	19.429	-40.710 to 79.568	0.05	0.544
BDE-140	3.1020	-2.0448 to 8.2488	0.15	0.271
BDE-138	2.1261	-21.931 to 26.183	0.00	0.867

^a Slopes were derived from the relationships between estimated proportion of meat consumed by individual grizzly bears and OC pesticide and PBDE concentrations in their tissues as a result of meat consumption. ^b BDE = brominated diphenyl ether (congener number).

delivery of POPs to bears (>85% of total concentration). This range of “enhanced accumulation” for POPs integrates processes involved in atmospheric transport to the North Pacific Ocean, deposition, subsequent uptake into marine food webs, and retention in lipids of biota. Similar patterns and peaks have been observed for bioaccumulation of legacy POPs in marine zooplankton (42) and tidal river marsh food webs (43). Consistent with our observations of a zone of enhanced accumulation, biomagnification factors (BMFs) between food and rainbow trout, *Oncorhynchus mykiss*, peaked at ~7.0 log *K_{ow}* (44) and BMFs in a freshwater food web peaked for PCBs at ~7.0 to 7.5 log *K_{ow}* (45).

Conversely, more volatile POPs (log *K_{ow}* < 5.3) and heavier PBDEs (log *K_{ow}* > 7.9) are provided to grizzly bears either preferentially through terrestrial foods (where >50% of total concentration is attributable to vegetation consumption) or as a result of contaminant-induced metabolism (46). Without a more accurate picture of the composition of grizzly bear diets and their contaminant concentrations, it is not possible to adequately characterize the importance of metabolism in shaping contaminant patterns in the bears. While metabolic elimination may partly explain reduced estimates of salmon contributions for the low log *K_{ow}* contaminants, the heavier PBDEs are likely provided to the grizzlies predominantly through terrestrial vegetation. The relative abundance of heavy PBDE congeners and virtual absence of light PBDE congeners in interior bears supports the notion that metabolism is not the key factor in explaining reduced estimates of salmon contributions for the higher log *K_{ow}* contaminants.

The seasonal pulse of marine-derived nutrients associated with the influx of salmon drives the productivity and diversity

of British Columbia coastal rainforests (47, 48). While salmon sustain healthy populations of maritime grizzly bears (10), they also deliver potentially endocrine-disrupting POPs to these bears. Our results suggest that although all grizzlies share a common terrestrial food web, pre-hibernation gorging on salmon by some bears leads to an increased risk of contaminant-related health effects. Several studies on polar bears, *Ursus maritimus*, suggest that there may be potential relationships between contaminant concentrations and hormone levels, impaired immune systems, and population-level effects (49–52); however, contaminant concentrations in polar bears are much greater than those observed in our grizzlies. The TEQ values for both grizzly bear feeding groups are also well below the no-observed adverse effects level (NOAEL) for reproductive effects in mink (a mammal feeding within both aquatic and terrestrial food webs and highly sensitive to effects of PCBs) of 2000 ng/g wet weight (53).

Despite contaminant concentrations in our adult grizzly bears being lower than reported in most other species occupying high trophic positions in marine food webs (5, 54), the reproductive window may be vulnerable. PBDE concentrations (e.g., BDE-47) in the maritime grizzlies exceed those reported for women’s breast milk in Sweden (21); the latter concentrations contributed to the ban of penta- and octa-BDEs in Europe. With low reproductive rates and seasonal cycles of fasting (hibernation) (55), adult female grizzly bears may supply elevated concentrations of endocrine-disrupting chemicals to their young through transplacental and/or lactational transfer (21, 56, 57).

British Columbia grizzly bears provide two distinct signals of the fate of legacy and new POPs in the environment. While

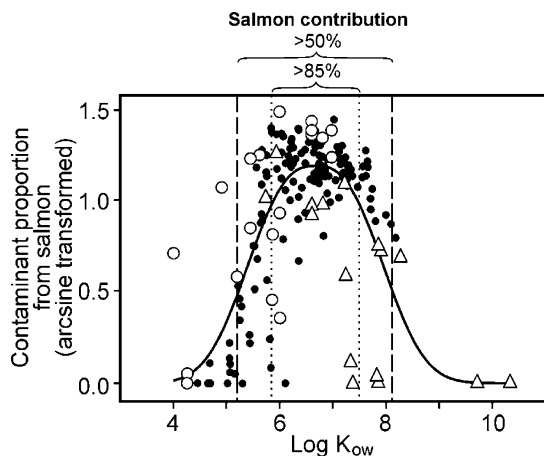


FIGURE 3. The proportion of contaminants in “maritime” grizzlies attributed to salmon correlates in a modified Gaussian (4 parameters) “peak” to log K_{ow} (solid line: $r^2 = 0.52$, $p < 0.0001$). Organochlorine (OC) pesticides (○). Polychlorinated biphenyl (PCB) congeners (●). Polybrominated diphenyl ether (PBDE) congeners (△). Area between dotted lines approximates our “range of enhanced accumulation” (5.9–7.5 log K_{ow}), where the log K_{ow} of the contaminants appears to favor ultimate partitioning into salmon and retention in bears. Salmon contributes >85% of the contaminant concentration within this area. Dashed lines represent the approximate points at which terrestrial and salmon contributions to grizzly bear contaminant concentrations are equal, although metabolism likely plays an unspecified role in elimination of lower log K_{ow} contaminants.

legacy contaminants have been largely addressed by national regulations and international treaty (e.g., Stockholm Convention), the use of PBDEs continues. Despite the ban of Penta- and Octa-BDE formulations in Europe and their potential ban in Canada and several U.S. States, the unregulated use of Deca-BDE will continue to contaminate the environment through the debromination to lighter PBDE congeners (58) and through the near-source contamination by heavier PBDE congeners. Continued exposure of both interior and maritime grizzly bears in British Columbia to PBDEs may therefore be expected over the coming decades, albeit to PBDE mixtures with contrasting profiles.

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Supporting Information Available

Table S1 demonstrates, using one of our sampled bears, how to use the theoretical calculations to obtain proportion of contaminants transported from salmon to grizzly bears. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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