PBDEs, PBBs, and PCNs in Three Communities of Free-Ranging Killer Whales (*Orcinus orca*) from the Northeastern Pacific Ocean

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Polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), and polychlorinated naphthalenes (PCNs) were quantified in blubber biopsy samples collected from free-ranging male and female killer whales (*Orcinus orca*) belonging to three distinct communities (southern residents, northern residents, and transients) from the northeastern Pacific Ocean. High concentrations of ∑PBDE were observed in male southern residents (942 ± 582 ng/g lw), male and female transients (1015 ± 605 and 885 ± 706 ng/g lw, respectively), and male and female northern residents (203 ± 116 and 415 ± 676 ng/g lw, respectively). Because of large variation within sample groups, ∑PBDE levels generally did not differ statistically with the exception of male northern residents, which had lower ∑PBDE concentrations than male southern residents, male transients, and female transients, perhaps reflecting the consumption of less contaminated prey items. Male transient killer whales, which consume high trophic level prey including other cetaceans and occasionally spend time near populated areas, had ∑PBDE concentrations approximately equal to southern residents. No significant age-related relationships were observed for ∑PBDE concentrations. ∑PBDE concentrations were approximately 1−3 orders of magnitude greater than those of ∑PBB (3.0−31 ng/g lw) and ∑PCN (20−167 ng/g lw) measured in a subset of samples, suggesting that PBDEs may represent a contaminant class of concern in these marine mammals.

Introduction

Over the past several decades, the bioaccumulation of anthropogenically produced polyhalogenated aromatic compounds (PHACs) such as polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) has been raised as a concern for the health of both humans and wildlife (*1*, *2*). Through the process of bioconcentration, whereby these hydrophobic contaminants preferentially accumulate in lipid-rich tissues, these compounds are subsequently transferred via predation into higher trophic level organisms. Resulting contaminant concentrations may reach into the parts per million (mg/kg) range for top predators such as aquatic mammals, despite ambient water column concentrations in the sub-parts per trillion (ng/kg) range, with total bioconcentration factors of >7−8 orders of magnitude between the water column and organisms. Since the 1970s and 1980s, many sources of the "classic" PHACs (e.g., PCBs and DDT) have been phased out or largely eliminated in industrialized countries, resulting in general declines in environmental concentrations over the past three decades (*3*−*5*). However, new compounds have been developed or have increased in usage over this period, in some cases to replace usage of banned compounds. The levels of many of these emerging contaminants have increased during recent decades in humans and aquatic biota (*6*, *7*). These include the polybrominated diphenyl ether (PBDE) flame retardants, developed as additive flame retardants and used in quantities of up to 30 wt % in some plastics, textiles, and foams (*8*, *9*).

In the present study, we examined the congener-specific concentrations and patterns of three major PHAC classes—PBDEs, polychlorinated naphthalenes (PCNs), and polybrominated biphenyls (PBBs)—in three communities of free-ranging killer whales (*Orcinus orca*) from the moderately industrialized transboundary waters of the Puget Sound−Georgia Basin (PS−GB) in the northeastern Pacific Ocean (Figure 1). High levels of PCBs was cited as one reason for the listing in Canada of southern resident killer whales as "endangered" and the northern resident and transient communities as "threatened" (*10*). The southern resident killer whale community has declined 20% between 1996 and 2001, and a recent population viability model suggests a high risk of extinction within 150 years unless habitat improvement measures are taken (*11*). We examined PBDEs in these whales because they represent an emerging contaminant class, suspected of causing endocrine disruption and immunotoxicity (*8*, *12*), with increasing production and usage concordant with increasing levels in biota in some parts of the world (*6*, *8*). PBBs, in comparison, were manufactured in the early 1970s as flame retardants, but production was largely halted in 1974 after an accidental substitution of these compounds into cattle feed in Michigan in 1973 (*8*). We also examined the polychlorinated naphthalenes (PCNs), a compound class used primarily as dielectric fluids and insulators (*13*) but which also represents byproducts from combustion processes such as municipal solid waste incineration (*14*) and impurities in technical PCB mixtures (*15*). Total PCN production is thought to have been ca. 100 000 ton or ca. 10% that of total PCB production during the period from the early 1900s to when PCN production ceased in North America and Europe in the 1970s and 1980s (*16*−*18*). Evidence suggests that PCNs have the potential to bioaccumulate (*16*), exert "dioxin-like" toxicity (*19*−*21*) and that their toxic equivalence (TEQ) contribution in environmental compartments may also be important (*22*, *23*). As with PBDEs and PCNs, the physicochemical properties of PBBs suggest the potential for significant bioaccumulation (*8*). Hence, characterizing the extent to which these killer whale populations are exposed to new contaminants such as PBDEs, PBBs, and PCNs

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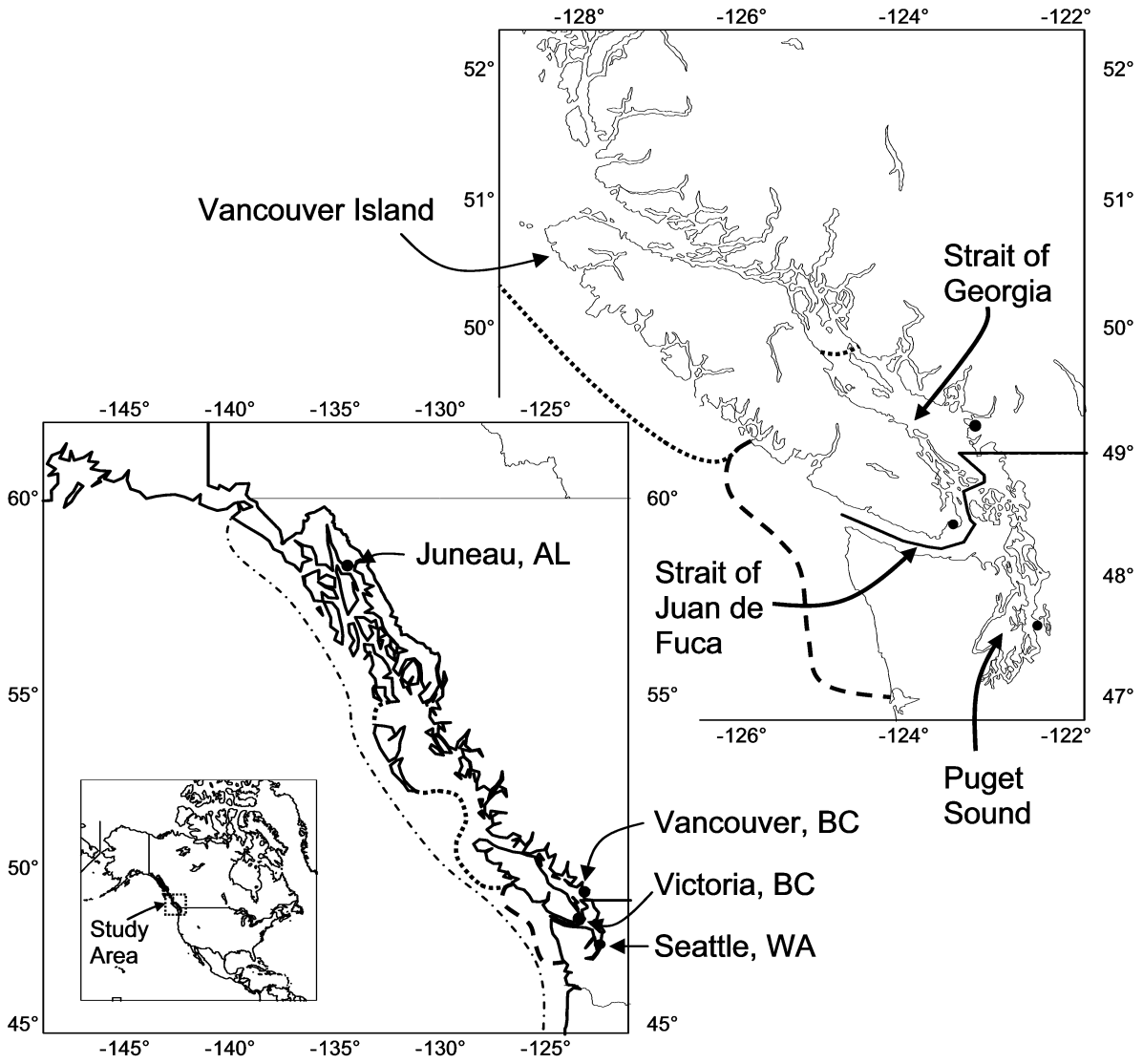

FIGURE 1. Map of the British Columbia, Washington State, and Alaskan coastlines showing core areas used during the summer feeding months (May−October) by the following three communities of killer whales: transient (dash−dot line), southern residents (dashed line), and northern residents (dotted line). Adapted from ref *25*.

represents an important background for mitigative or conservation measures.

Experimental Section

Sample Collection. Blubber biopsies from 39 killer whales inhabiting the northeastern Pacific Ocean (Figure 1) were collected from both sexes with ages ranging from 1 to 69 years between 1993 and 1996 using techniques described previously (*10*, *24*). Samples were obtained from two distinct ecotypes (residents and transients) comprising three individual communities (southern residents, northern residents, and transients). Sampling of the southern residents ($n = 5$) was limited because of high levels of vessel traffic around the animals in their summer feeding grounds in the Straits of Georgia and Juan de Fuca. Greater numbers of samples from northern residents ($n = 21$) and transients ($n = 13$) of both sexes were obtained. Biopsies consisted of skin and blubber (0.2−0.4 g). Samples were collected from small boats at a distance of approximately 5−25 m. The identity of individual whales was confirmed using a photographic catalog of residents (*25*) and transients (*26*). The blubber was stored in pesticide-grade hexane-rinsed glass vials with aluminum foil-covered caps and frozen at −20 °C until analysis.

Extraction Procedures and PBDE Analysis. As part of an earlier study, approximately 0.1−0.2 g of blubber was analyzed for congener-specific PCBs, PCDD/Fs, and lipid content (*10*). Briefly, blubber samples were ground with 200 g of anhydrous Na_2SO_4; spiked with a mixture of ^{13}C-labeled PCBs and PCDD/Fs; and subjected to extraction, cleanup, and carbon fiber fractionation procedures as described elsewhere (*27*). Four fractions were collected from the carbon fiber column, and those were analyzed for diortho-, monoortho-, and nonortho-PCBs and PCDD/Fs by high-resolution gas chromatography−high-resolution mass spectrometry (HRGC−HRMS). Following HRGC−HRMS analyses, the contents of the four individual fractions were combined, spiked with a suite of ^{13}C-labeled PBDE standards (method internal and performance), and analyzed for PBDEs by HRGC−HRMS. The composition of the ^{13}C-labeled PBDE standards used for quantification, the instrumental analysis conditions used, the quantification protocols, the criteria used for congener identification, and the quality assurance/quality control (QA/QC) measures undertaken for the HRGC−HRMS analysis of PBDE target analytes are described elsewhere (*6*, *27*). Because the samples were not spiked at the extraction step with labeled PBDE internal standards, percent recoveries of the PBDE method internal standards

were unknown. However, extensive method validation experiments with this matrix and others have enabled us to confirm that the extraction efficiency of the PCBs and PBDEs are similar under the experimental conditions used. Therefore, we used percent recoveries of the labeled PCB internal standards, obtained from the corresponding analyses described above, to establish the percent recoveries of the labeled PBDEs internal standards. These PCB percent recoveries were used to calculate PBDE concentrations. Of the 37 individual PBDE congeners analyzed, only the following 13 congeners (the sum of these is ∑PBDE; coeluting congeners are separated by a "/") where ≥30% of the sample values were above the method detection limit (MDL) are reported as follows: BDE15, BDEs28/33, BDE75, BDE47, BDE66, BDE100, BDE119, BDE99, BDE155, BDE154, and BDE153.

PCN and PBB Analysis. A subset of 19 males of the original 39 killer whale samples was further analyzed for PCNs and PBBs. The selection for the 19 males was based on the quality of the internal standard extraction efficiencies of the blubber extracts and the high concentrations of other contaminants known to exist in these individuals. The same extracts analyzed for PBDEs in this subset were analyzed for PCNs and PBBs using HRGC−HRMS by Axys Analytical Services (Sidney, BC, Canada). For two of the southern resident samples analyzed for PBBs, unreliable data was obtained, and these samples were omitted from the data set. The instrument used was a Micromass VG-70SE double sector HRMS equipped with a HP 5890 series II HRGC and a CTC A200S autosampler. For PCNs, a 60 m DB-5 column (0.25 mm i.d. × 0.1 μm film thickness) was used with UHP-He at 154 kPa and the following temperature program: hold at 50 °C for 1 min, 1 °C/min to 100 °C, and 7 °C/min to 300 °C. The splitless injector port, direct HRGC−HRMS interface, and the HRMS ion source were maintained at 180, 295, and 250 °C, respectively; the splitless injector purge valve was activated 2 min after sample injection. For PBBs, a 30 m DB-5HT column (0.25 mm i.d. × 0.1 μm film thickness) was used with UHP-He at 200 kPa and the following temperature program: hold at 100 °C for 3 min, 5 °C/min to 320 °C, and hold for 5 min. The splitless injector port, direct HRGC−HRMS interface, and the HRMS ion source were all maintained at 300 °C; the splitless injector purge valve was activated 2 min after sample injection.

For PCN and PBB analyses, the HRMS was operated at 8000 and 5000 resolution, respectively, under positive EI conditions (35 eV); data were acquired in the single ion monitoring (SIM) mode acquiring two chlorine or bromine cluster ions. Under SIM conditions, the two most abundant isotopes representing the parent ion were monitored for all PCN and PBB congeners. Compounds were identified only when the HRGC−HRMS data satisfied all of the following criteria: (i) peak response at least three times the background noise level; (ii) peak retention time within 6 s of that predicted from calibration runs and surrogate standard; (iii) peak maxima for the two ions coincide within 2 s; and (iv) relative ion abundance ratio for the two ions within 15% of theoretical.

Native PCN concentrations were determined against a [^{13}C]-PCB52 surrogate standard added prior to sample extraction. Mean relative response factors (RRFs) for native compounds were determined from calibration runs performed immediately before and after sample runs (maximum 12 h brackets). Surrogate recoveries determined against a [^{13}C]-1,2,3,4-TeCDD performance standard added immediately prior to instrumental analysis were monitored as general assurance of analytical quality. Of the 70 individual congeners analyzed for, only the following 23 congeners (the sum of these is ∑PCN) where ≥30% of the sample values were above the MDL are reported below: PCN21/24/14, PCN28/43, PCN29, PCN30/27/39, PCN38/40, PCN46, PCN31, PCN41, PCN52/60, PCN58, PCN50/51, PCN57, PCN66/67, and PCN64.

PBB concentrations were determined against four ^{13}C-labeled PCB surrogate standards (PCBs 37, 105, 180, and 209) added prior to sample extraction. Mean RRFs for native PBBs were determined from calibration runs performed immediately before and after sample runs (maximum 12 h brackets). Surrogate recoveries determined against ^{13}C-labeled PBB52 and PBB138 performance standards added immediately prior to instrumental analysis were monitored as general assurance of analytical quality. Of the 21 individual PBB congeners analyzed, only the following five congeners (the sum of these is ∑PBB) where ≥30% of the sample values were above the MDL are reported below: PBB26, PBB49, PBB52, PBB101, and PBB153.

Data Analysis. Concentrations of total PBDEs, PCNs, PBBs, PCBs, and PCDD/Fs, and all congeners reported individually, are in nanogram of analyte per gram lipid weight (lw). Details on how percent lipids in each sample were determined are provided elsewhere (*6*, *28*). Error bars always indicate 95% confidence limits of the mean unless otherwise indicated. As no significant relationships were observed between age and concentrations within any sample group; data were not age-normalized. Differences between sampling groups were investigated using single-factor ANOVA.

Results and Discussion

Congener Specific Concentrations of PBDEs, PCNs, and PBBs. Concentrations of three major contaminant classes—PBDEs, PCNs, and PBBs—were determined in blubber biopsy samples collected during the period from 1993 to 1996 from killer whales, some of which spend considerable time in the PS−GB region of the northeastern Pacific Ocean (Figure 1). These samples were obtained from three communities of killer whales (southern residents, northern residents, and transients) whose feeding habits and summer distribution are reasonably well-known (*29*). Lipophilic global contaminants such as the PCBs and PCDD/Fs are known to bioaccumulate in high trophic level organisms and have been measured in these three communities of killer whales (*10*). There are distinct differences in the feeding habits of these species, and the bioaccumulative contaminants detected in their blubber are expected to be a combination of local (nonsalmonid) and global (salmonid) sources. The level of contaminant uptake from each source (local vs global) is difficult to assess as it depends on numerous and not fully understood variables. However, it is important to note that the activities of ca. 5 000 000 human residents provide a potentially considerable source of trace organic pollutants into this relatively confined marine system. The Straits of Georgia and Juan de Fuca, having a mean hydraulic residence time of approximately 100−200 d (*30*), are particularly susceptible to pollutant loadings as discharges are not readily diluted or removed from the system, and the effects of this hydrologic regime has been observed with other contaminants such as PCBs, PCDD/Fs, and organochlorine pesticides (*28*, *31*, *32*).

Concentrations of ∑PBDE in male southern residents and male and female transients sampled during the present study did not differ (942 ± 582; 1,015 ± 605; and 885 ± 706 ng/g, respectively; $p > 0.96$) but appear to be prima facie higher than in male and female northern residents, although sample size was small (203 ± 116 and 415 ± 676 ng/g; Figure 2). Because of the large variation within sample groups, these differences were not statistically significant ($p > 0.31$ for all combinations), with the exception of male northern residents, which had significantly lower ∑PBDE concentrations than male southern residents ($p < 0.002$), male transients ($p < 0.002$), and female transients ($p < 0.03$). These levels are approximately 2−10-fold greater than ∑PBDE concentrations recently reported in sperm whales from the northern Atlantic near industrialized regions of Europe (*33*) and in the range of ∑PBDE concentrations found in pilot whales from the

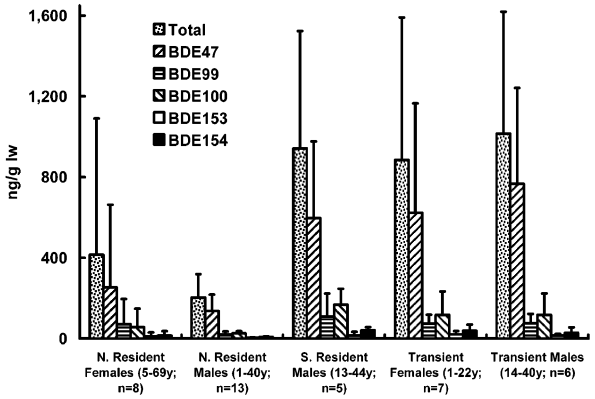

FIGURE 2. Concentrations of ∑PBDEs and the five most prevalent congeners in male and female killer whales from the three communities of killer whales. Error bars are 95% CL about the mean.

North Sea (*34*). Concentrations of ∑PBDE did not differ between male and female transients (1015 ± 605 and 885 ± 706 ng/g, respectively; $p = 0.79$) or male and female northern residents (203 ± 116 and 415 ± 676 ng/g for male and female, respectively; $p = 0.45$). This lack of a sex-based concentration difference is similar to that reported for ∑PCDD/F among these killer whales and that was attributed to metabolic removal of these compounds (*10*).

Southern residents and northern residents both have a diet that consists of fish, mainly salmonids, but southern residents spend more time in the more industrialized southern Georgia Basin and in Puget Sound (*29*). It has previously been speculated that the higher degree of PCB contamination of southern resident killer whales as compared to northern resident killer whales may reflect their consumption of more contaminated (local) prey items (*10*). Transient killer whales only appear to frequent the transboundary waters of British Columbia and Washington State on an irregular basis, and they consume marine mammals (e.g., seals and porpoises) (*29*). The high trophic level of transient killer whales likely explains their high PCB levels (*10*); the same phenomenon may explain the higher PBDE concentrations observed in transients in our study.

In contrast to previous observations of ∑PCB in killer whales (*10*), no age-related patterns were observed for ∑PBDE in any of the sample groupings. Although our sample size was small, one possible explanation for this difference between two major and similarly structured contaminant classes is that PBDE production levels are exponentially increasing (*6*), whereas ambient PCB levels in the environment have remained essentially static or declined over the past two decades (*4*). While regulations have led to diminishing levels of PCBs in aquatic food chains in North America, PBDEs continue to be used and their concentrations in killer whale prey are likely to be on the increase. However, the stability of PBDEs toward environmental or metabolic degradation is not well-established (*8*, *9*, *12*). The combined effects of increasing production levels, potentially different environmental stability as compared to PCBs, and influence of lifetime exposure to PBDEs make it difficult to readily interpret PBDE results in the context of the ages of the killer whales sampled.

Since the concentrations for PBDEs were high in these samples, we thought that other flame retardants (i.e., PBBs and PCNs) might also be readily detectable. Concentrations of these compounds were significantly lower than PBDEs within this reduced sample set (Figure 3). Northern resident killer whales had ∑PCN concentrations that were similar to southern residents (21.6 ± 6.7 and 20.4 ± 14.6 ng/g, respectively; $p > 0.87$), in contrast to that observed for ∑PBDE. Average ages for each between the northern and southern

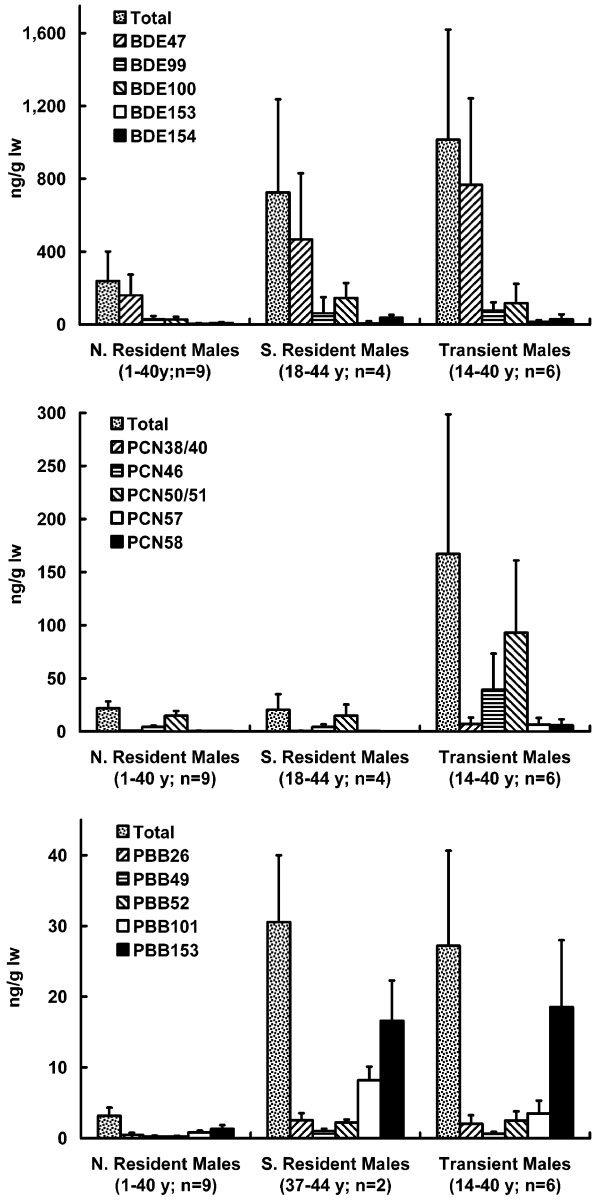

FIGURE 3. Concentrations of PBDEs, PCNs, and PBBs in selected male individuals from the three communities of killer whales. Error bars are 95% CL about the mean, except for PBBs in southern resident males, where error bars are the range about the mean.

resident contaminant groups were not different (22.8 ± 8.7 yr for PBDEs, 21.3 ± 11.2 yr for PCNs and PBBs; $p = 0.81$). All six male transients were analyzed for PBDEs, PBBs, and PCNs. Transients have much higher concentrations than the two resident killer whale communities (167 ± 131 ng/g; $p < 0.11$ and $p < 0.02$, respectively), consistent with their dietary preferences for marine mammals and other high trophic level prey. The penta-CNs 50/51 dominate the congener pattern, with the next most prevalent congener, PCN46, present at levels less than 50% that of PCNs 50/51. ΣPBB concentrations were, as with ∑PBDE, significantly higher in southern residents and transients as compared to northern residents (31.0 ± 9.4 and 27.0 ± 13.0 vs 3.1 ± 1.1 pg/g, respectively; $p = 4 \times 10^{-5}$ and 8×10^{-4}) but much lower in magnitude than ∑PBDE. No difference was noted in ∑PBB concentrations between southern residents and transients ($p > 0.80$), as was observed with ∑PBDE. These ∑PBB concentrations are up to 15-fold higher than recently reported for stranded sperm whales (ca. 2 ng/g) in the northern Atlantic near industrialized regions of Europe (*33*).

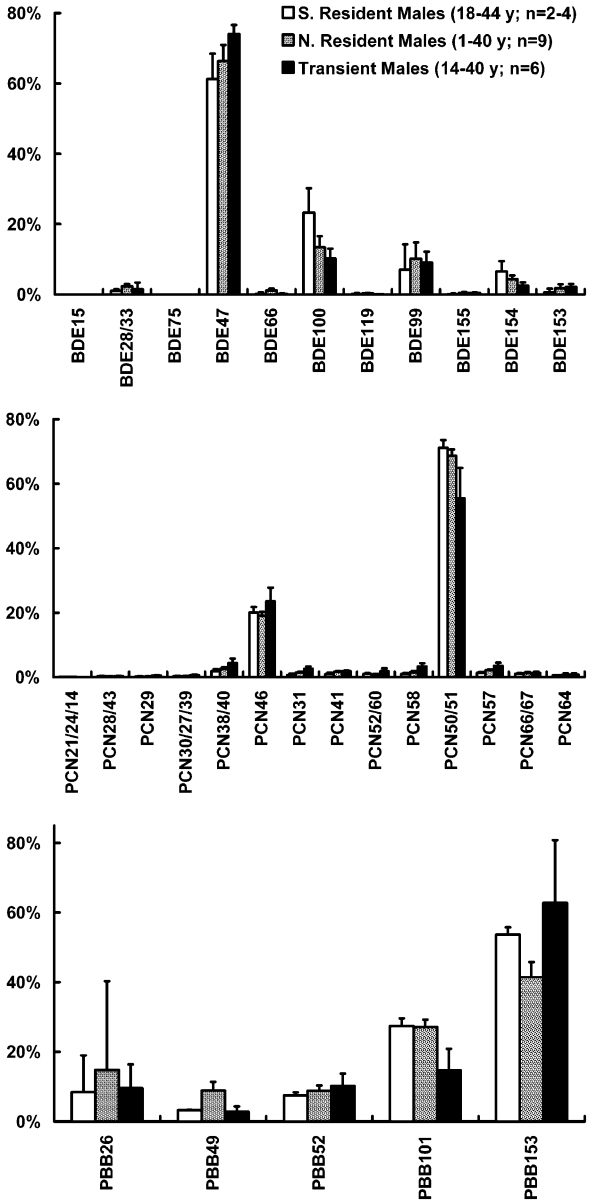

FIGURE 4. Congener patterns of PBDEs, PCNs, and PBBs in selected male individuals from the three communities of killer whales. Error bars are 95% CL about the mean, except for PBBs in southern resident males, where error bars are the range about the mean.

Congener Patterns. PBDE, PCN, and PBB congener patterns appear to differ among male individuals of different killer whale communities (Figure 4). For PBDEs, contribution to total PBDEs (as percent in ∑PBDE) increases in the order southern residents → northern residents → transients for BDE 47 (61.2 ± 7.2% → 66.3 ± 4.7% → 74.0 ± 2.6%; $p = 0.02$), while decreasing in this order for BDEs 100 (23.2 ± 7.0% → 13.4 ± 3.2% → 10.2 ± 2.8%; $p = 0.004$) and 154 (6.5 ± 3.0% → 4.3 ± 1.1% → 2.5 ± 1.0%; $p = 0.02$). There were no observable trends for the remaining congeners. That BDE47 increases in contribution from southern residents → northern residents → transients may reflect the dietary preferences of the different communities. Transients consume higher trophic level prey (i.e., marine mammals) than residents (i.e. fish) (*29*), and the higher contribution from lower brominated congeners in transients may indicate a lesser magnification of more highly brominated congeners in killer whale food chains (*35, 36*).

A similar trend was observed for PCNs, whereby transients have lower contributions of higher chlorinated congeners compared to residents, with the general order of decrease from southern residents → northern residents → transients. However, the trend in PCN congener contributions was driven by PCNs 50/51 (71.1 ± 1.9% → 68.7 ± 2.4% → 55.4 ± 9.4%; $p = 0.004$). These congeners are not the major congeners in 18 technical PCB formulations known to have PCN impurities (*15*). As shown elsewhere, these killer whales have been exposed to high levels of PCBs (*10*) via dietary intake over their lifetimes. If contaminated PCB mixtures are partially responsible for the PCNs in the northeastern Pacific Ocean, dechlorination from the more prevalent hexa- through octa-CNs in these PCB formulations (*15*) would need to have taken place. The presence of such large contributions from PCNs 50/51 remains unexplained. These congeners are not dominant in technical PCN formulations nor have they been previously reported as the dominant congeners in other soil, sediment, and biota samples (*20*, *22*, *37*, *38*). It is possible that these congeners may be preferentially formed by some industrial process (e.g., chlorination of pulp mill effluents) in this region. In general, current data suggest that congener patterns and homologue profiles of PCNs in biota are species and location specific (*22*, *37*, *38*), and rigorous comparisons of PCN patterns in killer whales to other biological samples appears to offer little insights into potential sources. For the remaining minor congeners from tri- through hexa-CNs, contributions increased in the order southern residents → northern residents → transients. With the exceptions of PCNs 28/43 ($p = 0.06$), 66/67 ($p = 0.56$), and 64 ($p = 0.36$), all these trends were statistically significant: PCNs 21/24/14 ($p = 0.04$), 29 ($p = 0.004$), 30/27/39 ($p = 0.01$), 38/40 ($p = 0.007$), 31 ($p = 0.001$), 41 ($p = 0.02$), 52/60 ($p = 0.02$), 58 ($p = 0.0004$), and 57 ($p = 0.0008$).

PBBs were also analyzed in male southern ($n = 2$) and northern residents ($n = 9$) and transients ($n = 6$), although the small sample size of southern residents and large variation within the transients precludes a statistical analysis of any differences among the males of these communities. PBB153 is the major congener in all samples and is a major component of the technical hexa-BB mixtures (e.g., Firemaster BP-6), although these formulations were banned in North America in the late 1970s (*8*). Thus, the large contributions of PBB153 could result from continual cycling of hexa-BB mixture in the North American environment over the past two decades. Alternatively, anaerobic debromination (*39*, *40*) of the commercial octa- and deca-BB mixtures, which are still in use worldwide (*8*), may help explain the presence of the tri- through penta-BB congeners in killer whales.

Contaminant Ratios, Correlations, and Comparisons with PCBs and PCDD/Fs. Comparisons among contaminant classes can provide insights into the relative degree of contamination of killer whales by different compounds, and may also provide some insight into potential sources of contaminants. In the present study, ratios of ∑PBDE, ∑PCN, and ∑PBB were examined among and within the male members of the three killer whale communities (Figure 5). ∑PBDE represents the dominant contaminant class measured in our study, with concentrations ranging from 10 ± 6 to 108 ± 77-fold greater than ∑PCN and ∑PBB, respectively. Ratios of ∑PBDE/∑PBB in northern residents (108 ± 77), southern residents (23 ± 11), and transients (42 ± 11) were not significantly different ($p = 0.36$) and are approximately an order of magnitude less than in sperm whales from the northern Atlantic (*33*). In comparison, southern residents have much higher PBDE/PCN ratios (83 ± 55) than either northern residents (13 ± 9; $p = 0.004$) or transients (10 ± 6; $p = 0.01$). No significant differences were observed among the PBDE/PCN ratios of northern residents and transients ($p = 0.62$). These PBDE/PCN ratios are much lower than previously reported in ringed and gray seals from Sweden (1300 and 6300, respectively) (*41*). PCNs, as with PBBs, were

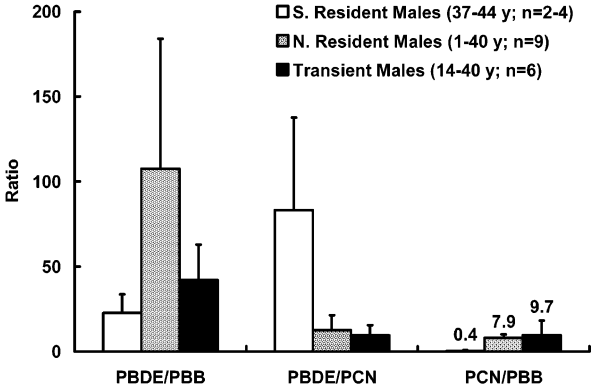

FIGURE 5. Ratios of PBDEs, PCNs, and PBDEs in selected male individuals from the three communities of killer whales. Error bars are 95% CL about the mean, except for PBDE/PBB and PCN/PBB ratios in southern resident males ($n = 2$), where error bars are the range about the mean.

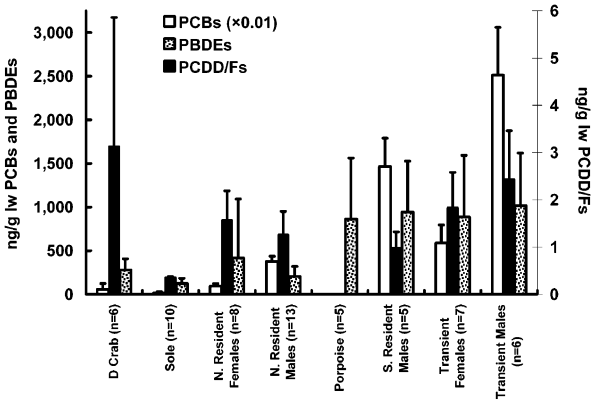

FIGURE 6. Concentrations of PCBs, PBDEs, and PCDD/Fs in marine biota from the west coast of British Columbia. PCB concentrations are multiplied by 0.01 to allow suitable representation with PBDEs on the left *y*-axis.

produced in relatively large quantities historically, but production was halted in the 1980s in the United States and Europe (*16*−*18*). Finally, southern residents have a significantly lower PCN/PBB ratio (0.4 ± 0.5) than northern residents (7.9 ± 2.3; $p = 0.02$) or transients (9.7 ± 8.6; $p = 0.28$).

Individual PBDE congeners and ∑PBDE correlate well with each other (r = 0.99−1.00), with similar results for PBB congeners and ∑PBB (r = 0.91−0.96) and PCN congeners and ∑PCN (r = 0.86−0.92), and between individual congeners and totals for PBBs and PBDEs (r = 0.90−0.95). However, weaker correlations were found between individual congeners and totals for PCNs and PBDEs (r = 0.64−0.76) and PCNs and PBBs (r = 0.76−0.83). These results suggest that high levels of PBDEs and PBBs are not necessarily good predictors of relatively higher levels of PCNs in killer whales, which may result from potentially different sources of PCNs versus PBDEs and PBBs. Chlorinated pulp effluents in this region are a known source of PCDD/Fs to pristine areas (*31*, *42*), and the mechanisms of PCN formation from chlorination of aromatic substrates in pulp mill discharges is expected to be qualitatively similar to those producing PCDD/Fs. By comparison, PBDEs (and presumably PBBs) are not known to be formed by chlorination of pulp mill effluents but have been documented in wastewater effluents from other areas of British Columbia (*43*, *44*) and thus may arise primarily from industrialized regions (i.e., more localized sources) versus possibly more "distributed" sources of PCNs to this aquatic system (see Table 1).

Finally, we compared concentrations of ∑PBDE in the killer whales and other marine biota (*28*) from the Strait of Georgia to ∑PCB and ∑PCDD/F concentrations reported elsewhere (*10*) in these samples (Figure 6). ∑PCB concentrations range from 13 (for sole) to ca. 250 (for resident male killer whales) times higher than ∑PBDE. Note that sampling and analysis of crab, sole, and porpoise were conducted as part of a previous study, and the reader is referred elsewhere (*28*) for further details on these samples. In general, PCB/PBDE ratios are greater in killer whales (22−248, mean = 101) than in crab (20) and sole (13) from this region, and in salmon from Lake Michigan (ca. 20) (*45*). The long lifetime during which killer whales can assimilate these contaminants may partly explain these observations. However, PCBs may also be more readily bioaccumulated than PBDEs, as would be expected based on the smaller molecular size of PCBs which favors trans-membrane transport processes over that of PBDEs (*35*). Although PBDEs have higher K_{ow} values than PCBs when compared on a homologue equivalent basis (i.e., penta-BDEs vs penta-CBs) (*46*−*48*), favoring the uptake of PBDEs by lipids, the reduction in bioaccumulation potential due to the larger molecular size of PBDEs (*36*) appears to override the enhanced bioaccumulation potential of higher K_{ow} values. In comparison, ∑PBDE concentrations range from 153 to 971 (mean = 392) times that of ∑PCDD/F in killer whales, much higher than the ratio observed in crab (89), and slightly higher than that found in sole (349). The similar ratio in sole and killer whales, which are significantly greater than that in crabs, suggests PBDEs are more readily accumulated by free-swimming organisms in the water column than PCDD/Fs in comparison to the reverse observation in benthic organisms such as crabs. The presence of lower PBDE to PCDD/F ratios in crabs may arise from their exposure to contaminated sediments and/or reduced metabolic capacity to degrade and excrete PCDD/Fs versus PBDEs. In support of these observations, we also note the ratio of contaminant concentrations between killer whale and English sole trophic levels is higher for ∑PCB (6−192 depending on killer whale sample group) than for ∑PBDE (1.7−8.2) or ∑PCDD/F (2.7−6.9).

In conclusion, these results show that with concentrations only 1−2.5 orders of magnitude less than ∑PCB and 1−3 orders of magnitude greater than ∑PBB, ∑PCN, and ∑PCDD/F in three communities of free ranging killer whales from the

TABLE 1. Average Correlation Coefficients among Concentrations of PBDEs, PCNs, and PBBs in Selected Northern Resident Killer Whales ($n = 9$)[a]

	$PB_{4-6}DEs$	∑PBDE	$PC_{3-6}Ns$	∑PCN	$PB_{3-6}Bs$
$PB_{4-6}DEs$	0.99(0.98−1.00)				
∑PBDE	0.99(0.99−1.00)				
$PC_{3-6}Ns$	0.66(0.48−0.83)	0.64(0.49−0.79)	0.86(0.79−0.95)		
∑PCN	0.76(0.73−0.78)	0.74	0.92(0.83−0.99)		
$PB_{3-6}Bs$	0.91(0.79−0.98)	0.90(0.80−0.95)	0.76(0.60−0.95)	0.84(0.83−0.93)	0.91(0.76−1.00)
∑PBB	0.95(0.92−0.96)	0.93	0.76(0.66−0.89)	0.83	0.96(0.81−1.00)

[a] Subscripts represent number of halogen substituents. Values in parentheses are range of correlation coefficients for the congeners of interest. Correlations among total contaminant concentrations (i.e., ∑PBDE vs ∑PCN) have only one value, thus no range is reported.

northeastern Pacific Ocean, PBDEs must be considered as one of the potentially dominant organohalogen contaminants in aquatic biota. Our findings provide additional evidence toward the hypothesis that high trophic level marine mammals are particularly vulnerable to accumulating high concentrations of persistent and bioaccumulative compounds, raising concerns about adverse health effects (*49*). While little is known about health effects of these flame retardants, some evidence suggest that PBDEs and related compounds may present a health risk to biota (*50*).

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Supporting Information Available

Concentrations of PBDEs, PBBs, and PCNs on a wet weight basis and percent lipid values for individual killer whale samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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