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Food Web Bioaccumulation Model for Resident Killer Whales from the Northeastern Pacific Ocean as a Tool for the Derivation of PBDE-Sediment Quality Guidelines

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Abstract Resident killer whale populations in the NE Pacific Ocean are at risk due to the accumulation of pollutants, including polybrominated diphenyl ethers (PBDEs). To assess the impact of PBDEs in water and sediments in killer whale critical habitat, we developed a food web bioaccumulation model. The model was designed to estimate PBDE concentrations in killer whales based on PBDE concentrations in sediments and the water column throughout a lifetime of exposure. Calculated and observed PBDE concentrations exceeded the only toxicity reference value available for PBDEs in marine mammals (1500 μg/kg lipid) in southern resident killer whales but not in northern resident killer whales. Temporal trends (1993–2006) for PBDEs observed in southern resident killer whales showed a doubling time of ≈5 years. If current sediment quality guidelines available in Canada for polychlorinated biphenyls are applied to PBDEs, it can be expected that PBDE concentrations in killer whales will exceed available toxicity reference values by a large margin. Model calculations suggest that a PBDE concentration in sediments of approximately 1.0 μg/kg dw produces PBDE concentrations in resident killer whales that are below the current toxicity reference value for 95 % of the population, with this value serving as a precautionary benchmark for a management-based approach to reducing PBDE health risks to killer whales. The food web bioaccumulation model may be a useful risk management tool in support of regulatory protection for killer whales.

Polybrominated diphenyl ethers (PBDEs) are emerging contaminants recently enlisted as persistent organic pollutants (POPs) by the Stockholm Convention; specifically, the tetra, penta, hexa, and hepta mixtures have been added to the list because of their persistence, toxicity, and bioaccumulative nature (de Boer 2009; UNEP 2010). Although several PBDE formulations (penta-, octa-, and deca-BDE formulations) were recently banned in North America (Birnbaum 2009; Ross et al. 2009), the ongoing contamination of the marine environment and aquatic food webs from these chemicals persists due to cycling and environmental transport (Johannessen et al. 2008; Kelly et al. 2008a, b; Ross et al. 2009).

Like the polychlorinated biphenyls (PCBs), PBDEs are ubiquitous contaminants undergoing global atmospheric transport from pollution sources (Wania and Dugani 2003; Noël et al. 2009) and can be biomagnified in food chains (Boon et al. 2002; Wolkers et al. 2004; Kelly et al. 2007, 2008a, b), causing potential health effects to apex predators. While substantial research and modeling work has been conducted to track and predict the bioaccumulation and biomagnification of PCBs in food webs (Kelly et al. 2007; Gobas and Arnot 2010; Cullon et al. 2012; Alava et al. 2012a, b; Hickie et al. 2013), our understanding on the bioaccumulation behavior and fate of PBDEs in marine food webs is limited. The only available study on dietary

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exposure to POPs by killer whales examined PCBs, dioxins, furans, and OCPs, but not PBDEs (Cullon et al. 2009).

At the top of the food web, resident killer whales from Northeastern Pacific Ocean (e.g., British Columbia, Canada, and Washington State, USA) are vulnerable to contamination by POPs. Due to their long life span, high trophic level and presence of lipid-rich tissues (e.g., blubber), killer whales can biomagnify lipophilic contaminants such as PCBs and PBDEs (Ross et al. 2000; Rayne et al. 2004; Ross 2006; Krahn et al. 2007). In British Columbia, relatively high concentrations of PBDEs were observed in male southern and northern resident killer whales, i.e., 942 and 203 μg/kg lipid, respectively (Rayne et al. 2004), as well as in male Steller sea lions (*Eumetopias jubatus*), i.e., range 336–900 μg/kg lipid (Alava et al. 2012b).

Despite having been identified as contaminants of emerging concern, there exist many gaps in our understanding of the behavior of PBDEs in the environment (Lachmuth et al. 2010). Whereas more intricate datasets have documented the rise of PBDE concentrations over time in harbor seals (*Phoca vitulina*) from Puget Sound (WA, USA) (Ross et al. 2013), it remains unclear whether longer-lived killer whales respond to environmental PBDE concentrations in a similar manner. While PCBs represent a dominant toxicological concern in killer whales (Ross 2006; Buckman et al. 2011), the increasing environmental concentrations of PBDEs highlights the growing need for new tools to understand the fate and effects of chemicals in killer whales and their habitat.

Even though some PBDE formulations have been banned or are no longer used in Canada, they are persistent and are transported atmospherically from areas that continue to use them and cycling has produced stable concentrations in the environmental compartments (Johannessen et al. 2008; Ross et al. 2009; Noël et al. 2009; Grant et al. 2011; Frouin et al. 2013). As with PCBs, PBDEs can enter killer whale habitat in a variety of ways: atmospheric deposition, urban runoff, sewage outfalls, ground water, watersheds such as the Fraser River, and smaller tributaries. For instance, local emissions of PBDEs from landfills (leachates) in British Columbia cannot be ruled out as sources of PBDEs (Li et al. 2012).

Despite recent regulations for PBDEs in Canada, there are no screening levels or sediment quality guidelines (SQGs) that provide guidance for "safe" sediment PBDE levels in coastal environments inhabited by killer whales and several other marine mammal species. While Environment Canada (EC) oversees disposal at sea activities under the terms of the Canadian Environmental Protection Act (CEPA), PBDEs are not currently examined in ocean disposal assessments. High levels of POPs have been cited as a threat to the recovery of southern resident killer whales (SRKW), which are listed as "endangered" under the terms of the Species at Risk Act in Canada (SARA; Government of Canada 2010a) and the Endangered Species Act in the United States (NOAA 2010). The northern resident killer whale (NRKW) population is listed as "Threatened" in Canada (Government of Canada 2010b).

The objective of this study was to assess the risks posed by PBDE concentrations in sediment and water to killer whales, as PBDEs in these matrices provide a basis from which to predict concentrations in the associated food web. This modeling approach is of particular value because of the inherent legal, ethical, and technical constraints to performing detailed studies of endangered species. This modeling approach also provides a means to evaluate the consequences of different PBDE management options—in the form of remediation, source control, dredging and disposal strategies, or chemical management.

Materials and Methods

Modeling Strategy

The modeling strategy included a model performance analysis, a sensitivity analysis, an uncertainty analysis, and the application of the model to suggest benchmark PBDE concentrations in sediments that are useful in characterizing risk levels. The model performance analysis involved calculating PBDE concentrations in killer whales based on observed PBDE concentrations in water and sediments of killer whale critical habitat. Calculated PBDE concentrations in killer whales were compared to observed PBDE concentrations to assess model performance. The model sensitivity analysis involved the determination of the relative importance of PBDE concentrations in water and sediments to the PBDE concentration in killer whales. The uncertainty of the model was characterized by a comparison of model calculated and observed concentrations. The model application involved the calculation of PBDE concentrations in sediments expected to result in "acceptable" PBDE concentrations in killer whales, defined here as the PBDE concentration in killer whales that is below the toxicity reference values in 95 % of the resident killer whale populations.

Study Areas and Criteria for Model Application to Resident Killer Whales

Resident killer whales are distinguished as northern residents (NRKW), which often are found in the waters off northeast Vancouver Island, BC, and southern residents (SRKW), which often are found in the waters off southeast Vancouver Island (Ford et al. 1998). In this study, the model was used to predict PBDE concentrations in

Chinook salmon and resident killer whales using empirical measurements of sediment, water, and air concentrations, and assuming 100 % time spent by each of the northern and resident killer whales in the Johnstone Strait (i.e., part of the NRKW critical habitat) and Strait of Georgia, respectively (Fig. S1, supporting information).

Critical habitat for killer whales is defined as the habitat necessary for survival or recovery of a listed wildlife species at risk, as identified in a Recovery Strategy or Action Plan. For resident killer whales, two such areas were identified largely based on their structure in funneling primary prey (Chinook salmon). Because critical habitat is so important for feeding, resident killer whales spend a considerable portion of their lives in these areas. This has implications for the disposal of potentially contaminated materials into that habitat (Lachmuth et al. 2010; Alava et al. 2012a). Under SARA, critical habitat is legally protected from degradation, and advice from science is needed to justify management decisions designed to protect all of resident killer whale habitat under the *Fisheries Act*.

PBDE Inputs to Resident Killer Whale Habitat

There are 209 theoretically possible PBDE congeners (ATSDR 2004); 13 have been detected in killer whales in BC (Rayne et al. 2004). Properties of individual congeners or homologue groups vary, causing them to have different distributions in the environment, different levels of toxicity, biotransformation rates, and half-lives (ATSDR 2004; Harju et al. 2007).

While sediment PBDE concentrations in the Strait of Georgia range from low [87 ng/kg dry weight (dw)] to extremely high (12,730 ng/kg dw) as that found in Burrard Inlet (Table S1, supporting information), freely dissolved concentration of PBDEs ranges from 1.70 to 388 pg/L (Table S2). Within this context, it is important to capture the distribution of PBDE congeners in the environment in the model. Empirical studies have found a particular set of congeners in resident killer whale habitat and biota (Ikonomou et al. 2002a; Ryane and Konomou 2002; Grant et al. 2011; Alava et al. 2012a, b; Frouin et al. 2013); however, we have restricted those included in the model to the ones with the most PBDE congeners' data in the areas of interest (Table S3). Once the model has calculated concentrations of all PBDE congeners included, a total PBDE (ΣPBDE) concentration was calculated as the sum of the concentrations of the congeners included in the model.

Physico-Chemical Properties of PBDEs

Data for PBDE congener octanol–water (Log K_{OW}) and octanol–air (Log K_{OA}) partition coefficients used in the model are summarized in Table S3. The tables contain the freshwater-based K_{OW} at the mean ambient water temperature of the areas of interest. These were used to calculate the saltwater-based K_{OW} values based on the correction factor for hydrophobic contaminants reported by Xie et al. (1997), which were used to determine the PBDE distribution between fish and water in the areas of interest. Freshwater-based K_{OW} values at 37.5 °C were used to describe partitioning between lipids and aqueous media (e.g., urine) in killer whales. Also included in Table S3 are K_{OA} values corrected to 37.5 °C, which were used in the calculation of PBDE transfer between killer whales and air, via their lungs.

Killer Whale Food Web Structure

The structure of the resident killer whale food webs, including organisms' feeding preferences and composition of prey items, was described and is available elsewhere (Lachmuth et al. 2010; Alava et al. 2012a). A schematic diagram of organisms included in the coastal food web and the representative trophic interactions considered is provided in Fig. S2. Table S4 describes the feeding preferences of the species included in the model in the coastal food web. The biological and physiological parameters used in the food web bioaccumulation model are listed in Table S5.

Field Data of PBDEs for the Food Web Model

The model was designed to focus on two specific areas that make up the major habitats, i.e., the Johnstone Strait and Strait of Georgia, of NRKW and SRKW, respectively. This was based on sampling locations as shown in Fig. S3 and the availability of PBDE sediment concentration data reported for these sites (Table S1; Grant et al. 2011). In addition, concentrations of PBDEs freely dissolved in water (Table S2) were retrieved from Frouin et al. (2013) and used as input data in the model. These concentrations were measured from dissolved XAD-column water samples collected at three stations in the Strait of Georgia: two on southern Strait of Georgia (boundary passage: 48°43N, 123°15W; Rosario Strait: 48°35N, 122°46W) and one on northern Strait of Georgia (Johnstone Strait: 50°27N, 126°01W) (Frouin et al. 2013).

A major assumption of the model is that the empirical sediment and total water PBDE concentrations used in the model are quantitatively related to the concentrations in biota included in the food web bioaccumulation model. This assumption is reasonable for several reasons. First, PBDE sediment concentrations' monitoring programs have included a significant distribution of PBDE sediment concentration hot spots throughout the Strait of Georgia (Grant et al. 2011), as illustrated in Fig. S4. A fairly large number

of independent sediment PBDE concentration measurements have been collected from the region and can provide a reasonable representation of the spatial distribution of the PBDE concentrations in the critical habitats (Figs. S3 and S4). Tables S1 and S2 indicate sites where sediment and water PBDE data were obtained and these data were used in the food web model. Second, the wildlife species included in the model are distributed over large areas of the Strait of Georgia region and most of them are year-round residents of the region, except for the oceanic stage of Chinook salmon and winter foraging areas of resident killer whales (Lachmuth et al. 2010; Alava et al. 2012a). Third, the model accounts for PBDE binding to organic carbon in the water column and sediments, which causes the PBDE to become less bioavailable. In water, PBDEs can be freely dissolved or adsorbed to particulate organic matter (POM) and dissolved organic carbon (DOC). Values for POM and DOC were obtained from the literature (Lachmuth et al. 2010). Environmental condition input variables used in the Johnstone Strait and Strait of Georgia are provided in Tables S6 and S7 (SI).

Since killer whales are warm-blooded, air-breathing organisms, in which the chemical inhalation and exhalation can be important routes for PBDE uptake and elimination, PBDE congeners' air concentrations were also incorporated in the food web models. Air concentrations of total PBDEs were obtained from the near urban Saturna Island station to represent air concentration (mean ± SE = $12.2 \times 10^{-6} \pm 6.3 \times 10^{-6}$ ng/L) in critical habitats within the Strait of Georgia, and the remote Ucluelet station for air concentration (mean ± SE = $13.7 \times 10^{-6} \pm 6.1 \times 10^{-6}$ ng/L) in offshore habitat at the west coast of Vancouver Island (Noël et al. 2009). These PBDE concentrations in air are very low and are likely an insignificant source to the killer whale.

Role of Biotransformation and Debromination of PBDEs by Biota in the Model

For the PBDE bioaccumulation modelling work, the model explicitly includes biotransformation of PBDEs (see supporting information for estimations and calibration of the biotransformation rate, k_M, in salmonid fish and killer whale, respectively). For instance, we assumed that k_M was negligible for aquatic invertebrates and most fish species, but a mean of 0.009/d was used for salmonid species (i.e., Chinook, chum and coho salmon) based on PBDE biotransformation half-lives reported for lake trout by Bhavsar et al. (2008). For killer whales, biotransformation rates estimated in a mammalian model reported by Harju et al. (2007) were calibrated to obtain a baseline data set to find plausible biotransformation rates (k_M) for PBDE congeners (Table S8) as data for metabolic transformation rate constant for each PBDE congener is scarce in marine mammals or unavailable for killer whales. These plausible k_M values were used as inputs in the model and it was assumed that debromination is represented by the production of low molecular weight BDE congeners (i.e., BDE 47, 99, 100, 153, 153) expected and calculated in the model.

PBDE Bioaccumulation Model Description

The development of the PBDE bioaccumulation model of the coastal food webs for killer whales was based on the application of a food web bioaccumulation model for PCBs developed for killer whales' critical habitats in the marine region of British Columbia, Canada (Lachmuth et al. 2010; Alava et al. 2012a), explained in detail in the supporting information. Briefly, the description of the food web bioaccumulation model expressing the net accumulation of PBDE in killer whales as function of uptake and elimination is represented by the following mass balance, steady state equation:

$$C_{\mathrm{KW},l} = \left(k_{\mathrm{A}} C_{\mathrm{AG}} + k_{\mathrm{D}} \cdot \Sigma\left(P_i \cdot C_{\mathrm{D},i}\right)\right) / \left(k_{\mathrm{O}} + k_{\mathrm{E}} + k_{\mathrm{U}} + k_{\mathrm{G}} + k_{\mathrm{P}} + k_{\mathrm{L}} + k_M\right) \quad (1)$$

where the lipid-normalized PBDE congener concentration in the killer whale is $C_{\mathrm{KW},l}$, and the net change in lipid-normalized concentration over time t (d) is $\mathrm{d}C_{\mathrm{KW},l}/\mathrm{d}t$. The gaseous aerial concentration (g/L) is C_{AG}. The inhalation rate constant (L/kg lipid/d) is k_{A}. The clearance rate constant (kg/kg lipid/d) for PBDE uptake via ingestion of food and water is k_{D}. The fraction of the diet consisting of prey item i is P_i and the concentration of the PBde congener (g/kg) in prey item i is $C_{\mathrm{D},i}$. The rate constant (d^{-1}) for PBDE exhalation via the lungs is k_{O}. The rate constant (d^{-1}) for PBDE congener elimination via excretion into feces is k_{E}. The rate constant for urinary PBDE excretion is k_{U}. The rate constant for growth dilution is k_{G}, and it accounts for net growth increases year-to-year. The rate constant for PBDE transfer into the calves is k_{P}, and it represents the lipid mass increase (equal to the calf's post-parturition lipid mass) during the gestation period. The rate constant for PBDE transfer to the calf via lactation is k_{L}, and it represents the lipid mass increase of the female whale over the year that is transferred to the calf during lactation. The rates k_{G}, k_{P}, and k_{L} (d^{-1}) are fixed annual proportional increases in body lipid weight [i.e., $\mathrm{d}W_{\mathrm{KW},1}/(\mathrm{W}_{\mathrm{KW},1} \cdot \mathrm{d}t)$] where the weight of the lipids in the killer whale is $W_{\mathrm{KW},1}$. The rate constant for metabolic PBDE congener transformation is k_M, as aforementioned.

The ultimate aim of the PBDE model is to characterize the relationship between the concentrations of PBDEs in

sediments and key biological species (i.e., Chinook salmon) in resident killer whale critical habitats for their role as a vector for biota exposure and eco-toxicological risk significance. The critical importance of Chinook salmon has been highlighted as a major driver of birth and mortality rates among resident killer whales (Ford et al. 2010), although PCBs and PBDEs could exacerbate food shortages through a variety of mechanisms (Ross et al. 2000; Ross 2006). Under this premise, the fundamental approach and output of the model is the Biota Sediment Accumulation Factor (BSAF), which characterizes the relationship between PBDE concentrations in biota (C_B; g PBDE/kg, wet weight organism) and those in sediments (C_S; g PBDE/kg, dw sediment):

$$\text{BSAF} = C_B / C_S \quad (2)$$

The model calculates BSAF values (kg dry sediment/kg wet weight organism) for selected PBDE congeners in every species included in the model. BSAF values are used to "forward" and "backward" calculate PBDE concentrations. The model application involving forward and backward calculations are applied to conduct exposure and health risk assessments and risk management, respectively (Gobas and Arnot 2010; Alava et al. 2012a). These applications are detailed in the supporting information.

PBDE Health Risk Assessment

Although recent studies have found PBDEs to potentially interfere with thyroid hormones and the immune system in seals (Hall et al. 2003; Frouin et al. 2010), effects of PBDEs on the health of marine mammals are poorly understood and remain largely unknown. For instance, preliminary research on pilot whales (*Globicephala melas*) revealed a lack of correlation between total PBDEs and thyroid hormones, including free and total tri- and tetraiodothyronine (Dam et al. 2002). Thus, it is unclear if current levels of PBDEs have any toxic effect on marine mammals (Rotander et al. 2012). Therefore, with the aim to address the assessment of health risks posed by PBDEs, model calculated PBDE concentrations using the forward approach of the model were compared against the upper limit of PBDEs' threshold level (1.5 mg/kg lipid weight) associated with endocrine disruption in grey seals (*Halichoerus grypus*) (Hall et al. 2003). Furthermore, PCB-toxic effect concentration (TECs) thresholds in marine mammals were also used here as surrogates to assess health risks by PBDEs, assuming that these pollutants have similar mode of toxic action to PCBs (Alava et al. 2012a).

The rationale to use PCB-TECs is due to the lack of data for PBDE-TECs in marine mammals. Data for PCB-TECs included the revised harbor seal PCB toxicity threshold (1.3 mg/kg lipid) developed by Mos et al. (2010); the bottlenose dolphin PCB toxicity threshold (10 mg/kg lipid) reported by Hall et al. (2006); and, a previous harbor seal PCB toxicity threshold (17 mg/kg lipid) published formerly by Ross et al. (1996) (Table S9 in supporting information). Interestingly, the PBDE-TEC adopted here falls within the range of these PBC-TEC values reported for marine mammals.

In addition, the effectiveness of sediment quality criteria (SQC) for PCBs in Canada, including the Canadian Environmental Protection Act (CEPA) Action Level Low for disposal at sea of 100 μg/kg dw, the Canadian Council of Ministers of the Environment (CCME) Interim Sediment Quality Guideline (ISQG) of 21.5 μg/kg dw and the British Columbia's Ministry of Environment (BCMoE) sediment quality criterion of 20 μg/kg dw, was tested. Using the forward application, the input data for sediment was equivalent to PCB-SQC, because SQC for PBDEs are not available at the local or regional level. Under the risk management perspective, the backwards application was used to derive target PBDE concentrations for sediments with the goal to provide guidance for the estimation of preliminary PBDE-Sediment Quality Guidelines (SQGs) protective of high trophic level organisms.

Model Performance, Uncertainty, and Sensitivity Analyses

Analyses for model bias, uncertainty, and sensitivity were conducted as described elsewhere (Lachmuth et al. 2010; Alava et al. 2012a). These steps also are described in the Supporting Information.

Temporal Trends in Resident Killer Whales

With the goal to explore the temporal behaviour of PBDE levels in sentinel resident killer whales, we use PBDE concentration data reported elsewhere for the SRKW and NRKW populations (Rayne et al. 2004; Krahn et al. 2007) to predict the trend of these contaminants over time in the Strait of Georgia. Regression models were fitted using the concentration data regressed against time (year). Time series data for SRKWs were available for 1993, 1995, 2004, and 2006 (Rayne et al. 2004; Krahn et al. 2007), whereas data for NRKWs were only available for 1993 and 1994 (Rayne et al. 2004).

Results and Discussion

Predicting PBDE Concentrations and Assessing Health Risk Related to PCB-SQC

Under the hypothetical scenario where resident killer whales are confined to spending 100 % of their time in the

Strait of Georgia, observed concentrations of ∑PBDE in SRKW exceeded both the PBDEs' upper limit threshold level for endocrine disruption (1.5 mg/kg lipid) established in grey seals (Hall et al. 2003) and the recent harbor seal PCB-TEC threshold (1.3 mg/kg lipid; Mos et al. 2010), as illustrated in Fig. 1. Calculated PCB concentrations were close to this PBDE threshold and slightly above the revised PCB-TEC. In contrast, both calculated and observed ∑PBDE concentrations in NRKW where they are hypothetically constrained to Johnstone Strait fell below these thresholds.

Relative to PCB concentrations previously calculated using the same SQC values (Alava et al. 2012a), the calculated ∑PCB levels exceed calculated ∑PBDE data in all cases in which sediment quality criteria or guidelines are tested with ratios ranging from 1.4 to 2.5 (Fig. 2). The calculated ratios are higher in the more contaminated SRKW population relative to the NRKW population due to higher BSAF values found in the Strait of Georgia. This is consistent with the higher sediment PCB and PBDE concentrations in surficial sediments in parts of the industrialised Strait of Georgia (Grant et al. 2011).

Normal probability density functions and proportion of each resident killer whale population by gender exceeding TECs for each specific SQC tested are provided in Fig. S5 and Table S10. Calculated PBDE and PCB concentrations in both males and female of the SRKW population confined to the Strait of Georgia exceeded by approximately 91–100 % the grey seal PBDE-endocrine disruption threshold and revised harbor seal PCB-threshold (Table S10; Fig. 3a–c; Figs. S6a, b supporting information) when testing the three SQC.

Likewise, the proportion of males and females of the NRKW population inhabiting the Johnstone Strait exceeded these thresholds by 84–95 % and by 80–92 %, respectively (Table S10; Fig. S5a–d; Fig. S6c, d supporting information). Calculated concentrations of PCBs exceeded by 100 % all PCB-toxic effect concentrations reported for marine mammals when testing the three SQGs (provided in Table S10 for comparison purposes), as previously reported (Lachmuth et al. 2010).

Because several habitat areas can be used by the two populations of resident killer whales, the load of PBDE concentrations in killer whales should be recognized as an input from multiple areas. In this context, realistic scenarios for NRKW and SRKW may generate more realistic predictions for PBDEs as previously conducted for PCBs (Lachmuth et al. 2010; Alava et al. 2012a). Because PBDE sediment and water data for many areas (i.e., Queen Charlotte Strait, Outer Coast, and some proportions of the critical habitat of both NRKWs and SRKWs) are not available at the time of this study, we were unable to pursue these more realistic scenarios.

Deriving Target Sediment PBDE Guidelines to Protect Killer Whales

In an effort to generate proactive PBDE-Sediment Quality Guidelines that are protective of killer whales, the backward application of the BSAF model was performed. Under this premise, proposed target sediment concentrations involving the model areas to protect 95 % of resident killer whales are provided in Table 1. The mean target sediment levels ranged from 0.10 µg/kg dw when the revised harbor seal PCB-TEC (i.e., 1300 µg/kg lipid) is used to 1.70 µg/kg dw when using the previous harbor seal PCB-TEC (i.e., 17000 µg/kg lipid). We recommend an overall mean target value (i.e., SQG for PBDEs) to protect 95 % of the resident killer whale populations is 1.0 µg/kg dw.

Metabolism of PBDEs

Although killer whales have limited capacity to metabolize certain PCBs (Hickie et al. 2007; Ross et al. 2000), it is possible that they are able to biotransform some PBDE congeners, having a significant effect on the magnitude of PBDE concentrations attained in the body. BDE-47 is one of the predominant PBDE congeners in killer whales from the Northeastern Pacific Ocean (Rayne et al. 2004; Krahn et al. 2007). In fact, BDE-47 and BDE-100 dominate PBDE congeners in resident killer whales of British Columbia (Rayne et al. 2004). The importance of BDE-47 at upper trophic levels of the marine food web reflects a combination of the propensity of this congener to biomagnify and/or its generation through debromination pathways of other PBDE congeners (Sellström et al. 1993; Boon et al. 2002; Wolkers et al. 2004; Stapleton et al. 2004a; Kelly et al. 2008a, b).

BDE-209 is not usually detected in marine mammals (Rayne et al. 2004; Kelly et al. 2008a, b; Ross et al. 2013; Alava et al. 2012a, b), likely as a result of its preferential binding to the particle phase in the water column and sediments (Johannessen et al. 2008; Ross et al. 2009) and the subsequent lack of biomagnification of this high log K_{OW} congener in aquatic food webs (Wolkers et al. 2004; Kelly et al. 2008a). Some studies have demonstrated that BDE-209 is quickly debrominated to lower brominated congeners (BDE-154, -155) in fish (Stapleton et al. 2004b, 2006) and grey seals (*Halichoerus grypus*) (Thomas et al. 2005), explaining in part the lack of bioaccumulation potential in marine mammalian food webs.

Low uptake and slow excretion rates of PBDEs also may influence the bioaccumulation of PBDEs in aquatic food webs, implying that some congeners (e.g., BDE-47) might require longer time periods to reach steady state, whereas others PBDE congeners exhibit a relatively rapid rate of

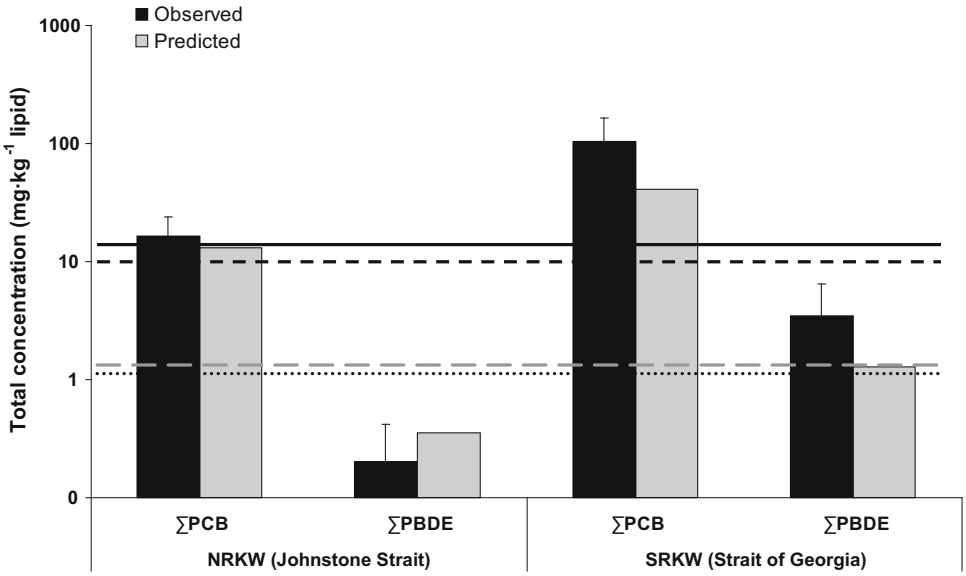

Fig. 1 Calculated and observed concentrations for ∑PBDE and ∑PCBs in resident killer whales (*NRKW* northern resident killer whales, *SRKW* southern resident killer whales) from BC. *Dotted line* represents the revised harbor seal PCB toxicity threshold (1.3 mg/kg lipid; Mos et al. 2010). *Grey, long, dashed line* is the PBDE toxicity threshold for endocrine disruption in grey seals (1.5 mg/kg lipid; Hall et al. 2003). *Black, short, dashed line* represents the bottlenose dolphin PCB toxicity threshold (10 mg/kg lipid; Hall et al. 2006). *Black solid line* represents the previous harbor seal PCB toxicity threshold (17 mg/kg lipid; Ross et al. 1996). Observed PBDE concentrations in resident killer whales were retrieved from Rayne et al. (2004), while observed PCB concentration were obtained from Ross et al. (2000). Calculated PCB data were used for comparative purposes (these data from Alava et al. 2012a)

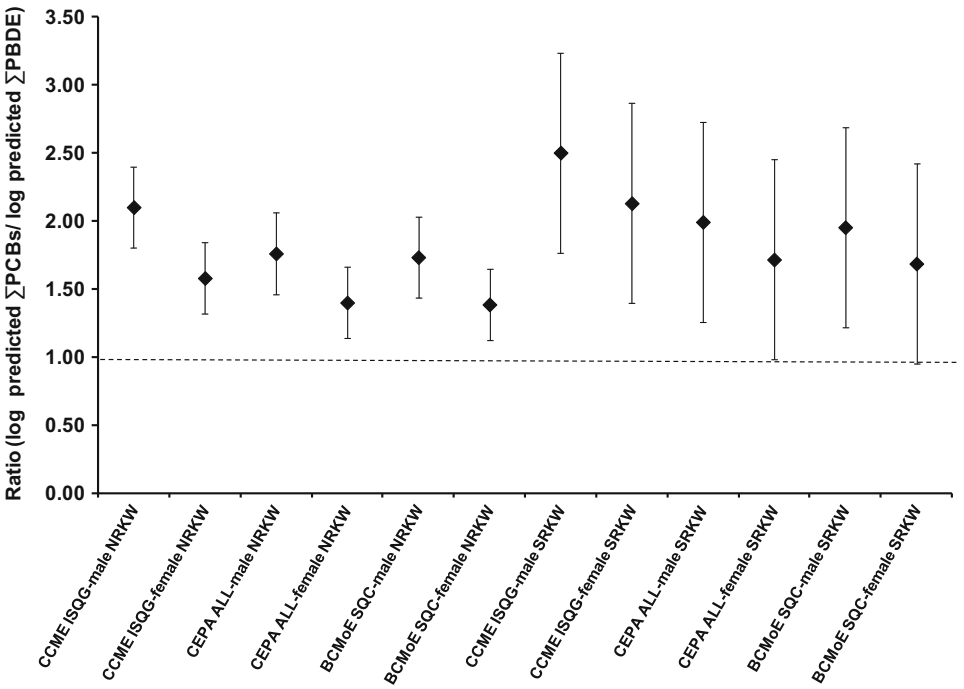

Fig. 2 Ratio of log calculated ∑PCB concentrations to log calculated ∑PBDE concentrations in NRKWs and SRKWs, including males and females, after testing the effectiveness of the PCB-CEPA Action Level Low, PCB-CCME ISQG and PCB-BCMoE SQC for PCBs, used here as proxies for PBDEs to assess SQC. *Dashed line* represents a ratio equal to 1.0, at which calculated ∑PCB concentrations are equal to calculated ∑PBDE concentrations. Ratio values above the *Dashed lines* indicated that calculated ∑PCB concentrations are higher than calculated concentrations for ∑PBDE in both NRKW and SRKW. Calculated PCB data were used here as the standard contaminant and reference for comparison purposes and was retrieved from Alava et al. (2012a). *Error bars* are the ratio of 95 % confidence intervals for each contaminant group (∑PCB/∑PBDE) calculated from the standard deviation of the model bias (SD_M)

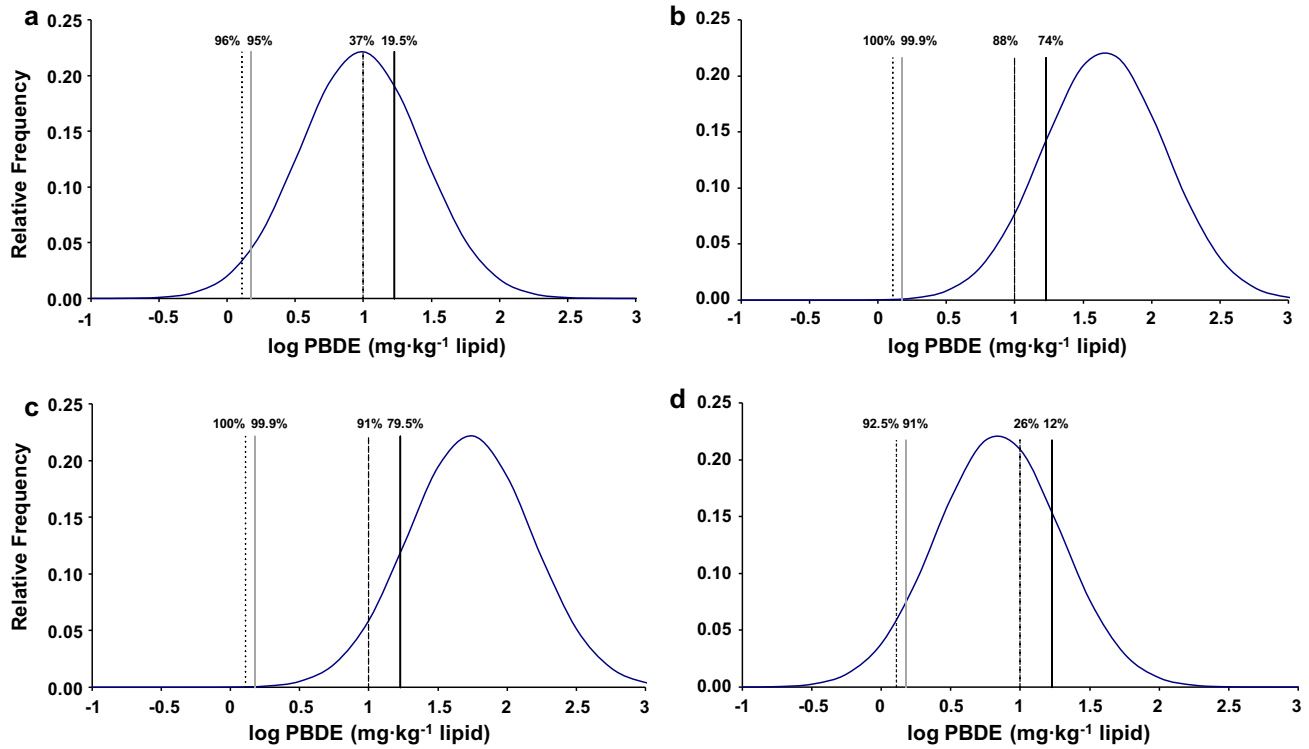

Fig. 3 Normal probability density distributions of calculated PBDE concentrations in resident killer whales spending 100 % time in the areas included in the model. **a** Testing the PCB-CCME ISQG in male SRKW. **b** Testing the PCB-CEPA Action Level Low in male SRKW. **c** Testing the PCB- BCMWLAP-SQC in male SRKW. **d** Testing the PCB-CCME ISQG in female SRKW. *Dotted line* represents the revised harbor seal PCB toxicity threshold (1.3 mg/kg lipid; Mos et al. 2010); *grey solid line* is the PBDE endocrine disruption threshold (1.5 mg/kg lipid; Hall et al. 2003); *dashed line* represents the bottlenose dolphin PCB toxicity threshold (10 mg/kg lipid; Hall et al. 2006); and *black solid line* represents the previous harbor seal PCB toxicity threshold (17 mg/kg lipid; Ross et al. 1996). Values expressed as a percentage above each line reflect the proportion of the resident killer whale population exceeding toxic effect concentrations

Table 1 Derivation of target PBDE sediment quality guidelines (SQGs) to protect 95 % of the population of northern and southern resident killer whales in model areas using different effects concentrations derived in other marine mammal species

Area/population	Grey seal PBDE endocrine disruption threshold (1500 μg/kg lipid) (Hall et al. 2003)	Harbor seal PCB toxicity (17,000 μg/kg lipid) (Ross et al. 1996)	Bottlenose dolphin PCB toxicity (10,000 μg/kg lipid) (Hall et al. 2006)	Revised Harbor seal PCB toxicity (1300 μg/kg lipid) (Mos et al. 2010)
	SQG (μg/kg dw)			
Johnstone Strait				
NRKW male	0.15	1.74	1.03	0.13
NRKW female	0.06	0.65	0.38	0.05
Strait of Georgia				
SRKW male	0.28	3.15	1.85	0.24
SRKW female	0.12	1.41	0.83	0.11
*Mean ± SD	0.15 ± 0.10	1.70 ± 1.0	1.0 ± 0.60	0.10 ± 0.10

NRKW northern resident killer whale population, *SRKW* southern resident killer whale population

* Overall average to generate the target PBDE-SQG (i.e., 1.0 μg/kg dw) was calculated by averaging all SQG mean values reported in the last row

depuration likely by debromination and/or cytochrome P450 enzyme-mediated oxidative metabolism (McKinney et al. 2006; Kelly et al. 2008a, b).

It has been further shown that hydroxylated metabolites of PBDEs (OH-PBDEs) can be formed in biota. For example, formation of OH-PBDEs following BDE-47 exposure has been demonstrated in laboratory studies with fish and rats (Kierkegaard et al. 2001; Malmberg et al. 2005). OH-PBDEs have also been reported in tissues of marine wildlife, including Arctic glaucous gulls (*Larus hyperboreus*) and polar bears (*Ursus maritimus*) (Verreault et al. 2005). Measurements of PBDE metabolites (e.g., OH-PBDEs) in marine mammalian food webs corroborate these biotransformation processed illustrated here (Kelly et al. 2008b). As demonstrated with our results, it is important that food web bioaccumulation models incorporate metabolic rate constants to generate accurate predictions.

Model Performance

Although no metabolic or biotransformation rate constants are available for PBDE congeners in marine mammals, the performance of our model behaved well compared with empirical data from field studies. The ability of the model to estimate PBDE congener concentrations in biota was tested by comparing calculated concentrations in biota (i.e., Chinook salmon from the Strait of Georgia and resident killer whales from the Johnstone Strait and Strait of Georgia) to available empirical values (Harrison Lake Chinook salmon; Peter S. Ross, unpublished data); observed PBDE data for NRKW and SRKW populations were retrieved from Rayne et al. (2004).

Model calculated and empirical PBDE congeners data included are shown in Figs. S7–S10. The model bias (MB) geometric mean ± log MB (SD) was 1.76 ± 0.33 for Harrison Lake Chinook salmon, underlining overprediction as PBDE congeners' empirical data were available for a single Chinook salmon sample (Fig. S7). The model biases for male and female NRKWs were 0.6 ± 1.10 and 0.20 ± 1.26, respectively, underscoring small underprediction for males, but relatively high underprediction for females (Figs. S8 and S9). Male SRKW exhibited a MB close to one (i.e., MB ≈1.4 ± 0.45), showing little overprediction (Fig. S10). In general, for male resident killer whales under- or overprediction was small or negligible. Because observed PBDE data for female SRKW were not available (Rayne et al. 2004), we were unable to conduct comparisons and the MB for it.

These comparisons are an indication that the calculated concentrations of PBDEs are similar to or within the range of observed PBDE concentrations in male resident killer whales (i.e., calculated mean concentration values are close to the observed values). Figures S8 and S10 also illustrate that congener patterns of PBDEs in killer whales are reasonably well reproduced by the model compared to the empirical profiles found for this species. This is supported by the small uncertainty (i.e., error bias) of the model pointed out above ($SD_{MB} = 1.10$ for male NRKW; $SD_{MB} = 0.45$ for male SRKW). In general, model Bias for PBDEs (MB) and ΣPBDEs (MB*) shows fairly good agreement between calculated versus empirical data (Fig. 4).

In addition, calculated PBDE-BSAF values in Chinook salmon and male killer whales were very similar to empirical data observed in both species in northern resident killer whale critical habitat (Fig. S11, supporting information). The model, therefore, produces little systematic over- or underestimation of PCB congener concentrations.

Uncertainty Analysis

The uncertainty analysis explores the spread or deviations from the mean concentration in biota (e.g., Chinook salmon and killer whales) calculated from the standard deviation of the error model bias (BSAF) for ∑PBDEs and standard deviations of the empirical sediment data to measure the spread of the data (Lachmuth et al. 2010; Alava et al. 2012a). The empirical PBDE sediment data has a close range of values (Table S11). The mean of the log PBDE sediment concentrations (i.e., mean log C_S) ranged from −3.35 ± 0.608 mg/kg dw in the Strait of Georgia (i.e., part of the SRKW critical habitat) to −3.60 ± 0.00 mg/kg dw for the Johnstone Strait (i.e., part of the NRKW critical habitat).

However, PBDE sediment data for the Johnstone Strait was very limited with only one site sampled for sediment measurements at this area, whereas for the Strait of Georgia data were available from 40 locations. Table S11 shows that uncertainty values in the model in terms of the standard deviation SD_{CB} of log C_B (i.e., geometric mean concentration of biota) ranged from 0.42 to 0.72 for male resident killer whales (i.e., SD_{CB} of log C_B) in the Johnstone Strait and Strait of Georgia, respectively, and from 0.66 to 0.90 for female resident killer whales in the Johnstone Strait and Strait of Georgia, respectively. This suggests that spatial variation in PBDE concentrations in sediments is the dominant contributor to uncertainty in forward calculation even if the calculated mean concentration values are close to the observed values. The standard deviations can be viewed as the uncertainty in the BSAF model estimates.

Sensitivity Analysis: Evaluating the Effects of Water PBDE Concentrations on Model Outcomes

Because water represents one of the sources delivering PBDEs to the aquatic food web, a sensitivity analysis was

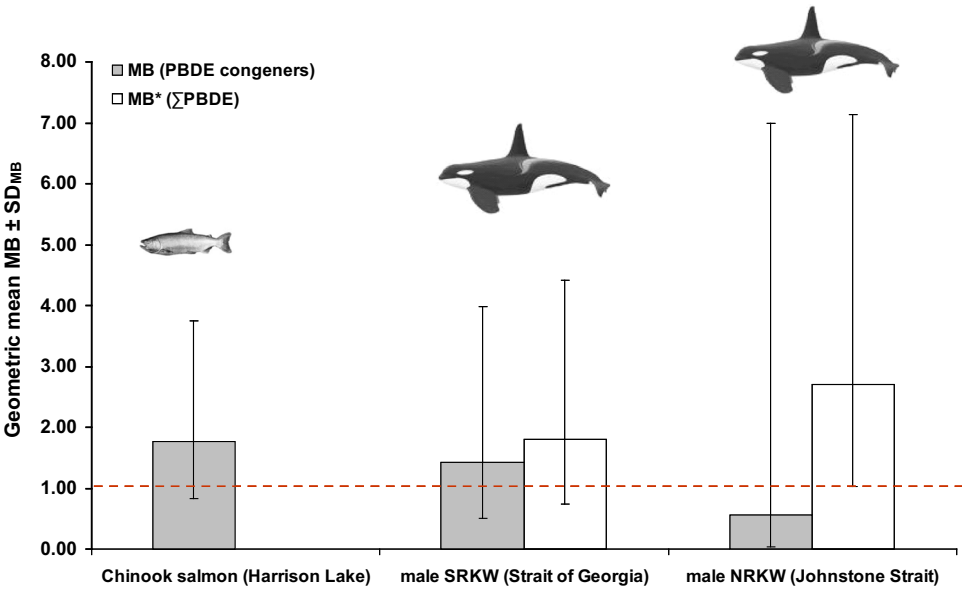

Fig. 4 Geometric means of model bias (MB) for PBDE congeners and total PBDEs (∑PBDE) in biota. *Dashed line* means MB = 1.0 (i.e., equal concentration values when comparing calculated to observed data). Due to small sample size ($n = 1$) for Harrison Lake Chinook salmon, MB for ∑PBDE was not calculated. *Error bars* are standard deviations of observed values

conducted to determine whether changes in the concentrations of PBDEs in water are associated with substantial changes in the PBDE concentration calculated in Chinook salmon and killer whales in the coastal food webs of the Johnstone Strait (NRKW critical habitat) and Strait of Georgia (SRKW critical habitat).

While the mean empirical PBDE sediment:water factor was high in the Strait of Georgia (i.e., 41,848 L/kg) and Johnstone Strait (i.e., 108,690 L/kg) (based on the data reported by Grant et al. 2011 and Frouin et al. 2013), the water column concentrations of PBDEs in XAD resin (dissolved) measured in shallow water over several seasons in the Strait of Georgia were higher than those measured in deep water (Frouin et al. 2013). Similar observations were found when comparing PBDE concentrations in shallow versus deep waters measured in particle-bound (GFF) water (Frouin et al. 2013). The observation in this study illustrates that the PBDE concentration in the water does vary with depth, indicating that there is a significant PBDE concentration gradient in the water column, which may drive bioaccumulation in more shallow marine habitats or inner coast areas. This implies that all organisms, including phytoplankton, are exposed to different PBDE concentration in different habitats (i.e., coastal vs. offshore, benthic vs. pelagic) and that the thermocline and halocline do appear to have a major impact on the PBDE concentration in the water column.

The sensitivity analysis showed that a two- to tenfold increase in PBDE water concentration caused the calculated PCB concentration in biota (i.e., Chinook salmon and killer whale) to increase by the double or 10 times, respectively. Changes in PCB sediment concentrations were much less sensitive to similar increases. The results of the sensitivity analysis for tenfold increase are shown in Table S12 and indicate that PBDEs in the water column are the main source of PBDEs in killer whales in coastal marine environments. This means that the main pathway of killer whale exposure to PBDEs is through a release of PBDEs from sediments to the water column. PBDEs from contaminated sediments will enter the water column and become absorbed by phytoplankton, zooplankton, and fish directly from the water and indirectly from the water as a result of dietary exposure. PBDE concentrations in sediment dredgeate in excess of those currently existing in sediments (e.g., designated ocean disposal area) can be expected to increase PBDE concentrations in the water column and the food web.

The results of the sensitivity analysis may indicate that the bioaccumulation of PBDEs in the coastal food web for the Johnstone Strait and Strait of Georgia is likely to be driven by PBDE water concentrations. Recent studies in the Strait of Georgia showed that the net flux of PBDE appears to be from atmosphere to seawater (Noël et al. 2009) and from seawater into the sediments (Johannessen et al. 2008), implying that local atmosphere has the highest PBDE input. This supports the notion that air and water may be delivering a major portion of PBDEs to the aquatic food web, notably in more remote, oceanic areas. Within the aquatic ecosystem, the concentrations in water and sediments are related. However, these relationships are complex and dependent on the sediment diagenesis and organic carbon cycling in the system, sorption and desorption rates and the source materials (e.g., aerial particles versus water borne particles), and other processes controlling water–sediment concentration (fugacity) relationships (Gobas and Maclean 2003).

Temporal Trends of PBDEs in Resident Killer Whales

Based on the temporal data for PBDE concentrations reported in the existing literature (Rayne et al. 2004; Krahn et al. 2007), PBDEs in SRKWs from the Strait of Georgia increased exponentially from 1993 to 2006 (Fig. 5), with concentrations doubling every 4.7 years. This finding is consistent with predictions of PBDEs' accumulation during the lifespan of individuals from the SRKW population with a doubling time of 3 to 4 years, increasing over time or with age and underlying the fast emergence of PBDEs as a priority concern in these animals (Mongillo et al. 2012). Similarly, an exponential increase was detected between 1984 and 2003 in harbor seals with a double time of 3.1 years in an adjacent area in Puget Sound (WA, USA), although PBDEs levels have currently reached steady state and are showing signs of declining (Ross et al. 2013). Furthermore, exponential increases were observed from 1981 to 2000 in ringed seals (*Phoca hispida*) from the Canadian Arctic (Ikonomou et al. 2002b).

While shorter-lived harbor seals may be expected to respond more quickly to declines in environmental PBDE concentrations following regulations (Ross et al. 2013), longer lived killer whales may take more time to respond. Lack of temporal data for PBDEs after 2006 in SRKWs precludes further evaluation of this question. Yet, the calculated historical data from the 1970s to 2007 for PBDE concentrations in male SRKWs revealed an increase over time, as predicted by Mongillo et al. (2012).

Due to the lack of time series data for NRKWs, we were unable to further predict PBDE concentrations in this population, but trends in this population are likely to mirror PBDE concentrations in the SRKWs. A linear regression model showed an increasing trend between 1993 and 2004 for NRKWs (Fig. 5), but this should be interpreted with caution.

Assumptions and Limitations

As with any model, many assumptions were required for simplicity. Some of the major assumptions are discussed below. Only two geographic areas were assessed (i.e., Strait of Georgia and Johnstone Strait), assuming resident killer whales and Chinook salmon spend 100 % of their time in these areas and the model was constrained to the availability of data especially sediment and water data reported for the two areas. It was assumed that all SRKWs and NRKWs behave the same and spend the same amount of time in the two areas; however, in reality this is not the case and the output reflects an "average" rather than being specific for certain pods or individuals.

A major assumption of the model is that contaminant water–sediment partitioning is at steady-state, and this may not be the case, especially when including long-lived species, such as killer whales. However, observed and calculated PBDE concentrations in killer whales were similar with very little over- or underpredictions, so assuming steady-state conditions may not be problematic.

The food web bioaccumulation model requires sediment PBDE concentrations and organic carbon content as critical inputs to calculate PBDE concentrations in biota. These data were gathered from the literature and from unpublished data. Certain areas included in the model had plenty of sediment and water PBDE data to be used as inputs into the model (i.e., Strait of Georgia); however, other areas had very few samples (i.e., Johnstone Strait) or lacked data (i.e., outer coast, Queen Charlotte Islands). This highlights

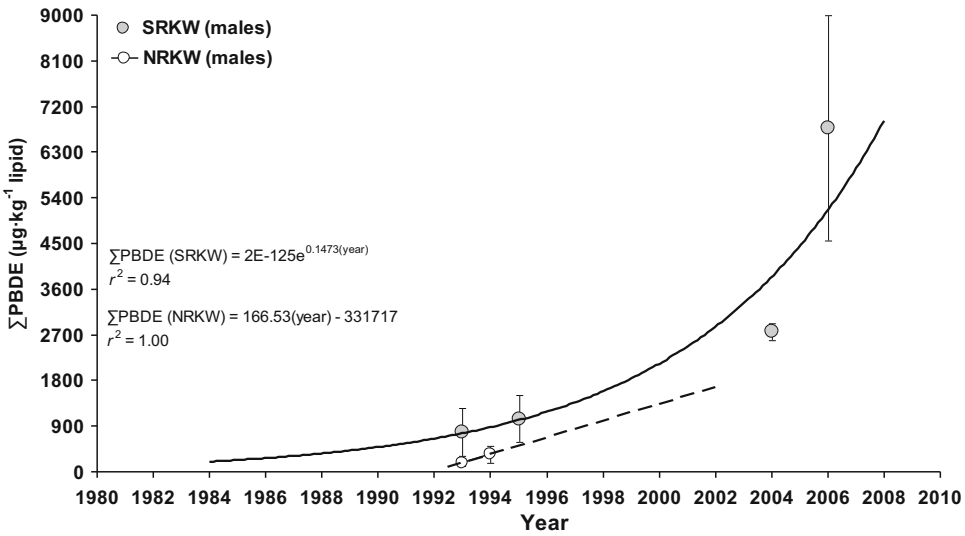

Fig. 5 Temporal trends of ∑PBDE concentrations (µg/kg lipid) for southern resident killer whales, SRKW (1993–2006), and northern resident killer whales, NRKW (1993 and 1994). An exponential increase in ∑PBDE concentrations is calculated in southern resident killer whales when the concentration data is plotted against time (years). *Error bars* are standard errors

the need for more sampling so that the accuracy of the model can be improved and realistic scenarios, including the foraging range and entire home range of resident killer whales, can be assessed. Furthermore, sediment sampling needs to occur in background areas to provide more precise PBDE distributions, because most sampling studies focus on hot spots known to be contaminated with legacy PCBs, which results in overestimations in biota. Further work is required to address resident killer whale critical habitat impacts.

The accuracy of the PBDE food web bioaccumulation model was tested by comparing the model predictions of PBDE concentrations in biota to empirical data. This was only possible for Harrison Lake Chinook salmon, northern and southern resident killer whales (except for females from the SRKW population). More sampling of other important species included in the food web is required to ensure the model makes accurate predictions at all trophic levels.

Because our understanding on metabolic capacity of PBDE congeners is limited and current biotransformation or debromination rate values for PBDEs in marine mammals and marine biota is scarce, we assumed that the biotransformation rates calibrated here account for PBDE metabolism in the model. Research on PBDE metabolism in toothed cetacean species is needed to improve further applications of the model.

Metabolic rates for specific PBDE congeners in killer whales were calibrated from a modelling study using a mammalian lab model and used in the PBDE food web bioaccumulation model. Accurate empirical measurements of lipid content for secondary prey diet items (i.e., halibut and sablefish) of resident killer whales also are needed to further improve the prediction of PBDE concentrations. However, there was a relatively good agreement between observed and calculated PBDE concentrations in male NRKWs and male SRKWs, which indicates that this component of the model worked well even though there was a limitation in regard appropriate rates of metabolism.

Contrasting the PCBs, which are no longer in use, PBDEs are still being released to the marine environment and have only recently faced regulatory scrutiny (Ross et al. 2009). Landfills and electronic waste disposal sites located around coastal cities represent likely sources of PBDEs (Li et al. 2012) to the marine environment.

There exist no current Sediment Quality Guidelines or Action Levels to guide disposal at sea practices. Toxicity testing of PBDEs in a variety of species is required. Given that they are considered to be persistent, bioaccumulative, and toxic, guideline development for PBDEs is urgently required. New data and new approaches will be required to overcome some of the constraints to their modelling, which include their reduced stability in the environment compared with PCBs, their more ready metabolism in biota compared with PCBs, and their disequilibrium among environmental matrices as a result of changing emissions histories.

Conclusions

This modelling study demonstrates that PBDEs exhibit bioaccumulation potential in resident killer whales in the NE Pacific Ocean. Calculated concentrations in endangered southern resident killer whales were higher than those calculated in threatened northern resident killer whales; this was corroborated by empirical concentrations measured in biopsies collected from individuals of both populations. The divergent PBDE concentrations between the populations may be driven by more local sources in the habitat of the southern residents. The model calculated that PBDE concentrations in southern and northern resident killer whales would exceed PBDE and PCB toxicity thresholds for marine mammals when PCB-SQC were used as data inputs for sediment concentrations. This is troubling, as observed increases in environmental PBDE concentrations, as well as in killer whales, indicate an emergent risk in terms of potential for toxicity. We used a backward calculation of the model to derive an overall target PBDE-Sediment Quality Guideline of 1.0 μg/kg dw that could provide guidance for management actions to protect killer whales and their habitat.

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References

Alava JJ, Ross PS, Lachmuth CL, Ford JKB, Hickie BE, Gobas FAPC (2012a) Habitat-based PCB environmental quality criteria for the protection of endangered killer whales (*Orcinus orca*). Environ Sci Technol 46:12655–12663

Alava JJ, Lambourn D, Olesiuk P, Lance M, Jeffries S, Gobas FAPC, Ross PS (2012b) PBDE flame retardants and PCBs in migrating Steller sea lions (*Eumetopias jubatus*) in the Strait of Georgia, British Columbia, Canada. Chemosphere 88:855–864

ATSDR (2004) Toxicological profile for polybrominated biphenyls and polybrominated diphenyl ethers. Agency for Toxic Substances and Disease Registry. U.S. Department of Health and Human Services, Public Health Service, Atlanta

Bhavsar SP, Gandhi N, Gewurtz SB, Tomy GT (2008) Fate of PBDEs in juvenile lake trout estimated using a dynamic multichemical fish model. Environ Sci Technol 42:3724–3731

Birnbaum L (2009) Effects of brominated flame retardants: health and regulations. In: 11th Annual Workshop on Brominated Flame Retardants. 19–20 June 2009, Ottawa, Ontario, Canada. p 13

Boon JP, Lewis WE, Tjoen ACMR, Allchin CR, Law RJ, De Boer J, Ten Hallers-Tjabbes CC, Zegers BN (2002) Levels of polybrominated diphenyl ether (PBDE) flame retardants in animals representing different trophic levels of the North Sea food Web. Environ Sci Technol 36:4025–4032

Buckman AH, Veldhoen N, Ellis G, Ford JKB, Helbing C, Ross PS (2011) PCB-associated changes in mRNA expression in killer whales (*Orcinus orca*) from the NE Pacific Ocean. Environ Sci Technol 45:10194–10202

Cullon DL, Yunker MB, Alleyne C, Dangerfield NJ, O'Neill S, Whiticar MJ, Ross PS (2009) Persistent organic pollutants in chinook salmon (*Oncorhynchus tshawytscha*): implications for resident killer whales of British Columbia and adjacent waters. Environ Toxicol Chem 28(1):148–161

Cullon DL, Yunker MB, Christensen JR, Macdonald RW, Whiticar MJ, Dangerfield NJ, Ross PS (2012) Biomagnification of polychlorinated biphenyls in a harbor seal (*Phoca vitulina*) food web from the strait of Georgia, British Columbia, Canada. Environ Toxicol Chem 31:2445–2455

Dam M, van Bavel B, Lindström G (2002) PBDE in Long-finned pilot whale (*Globicephala melas*) from the Faroe Islands. In: Second AMAP International Symposium on Environmental Pollution of the Arctic, Rovaniemi, Finland. 1–4 Oct 2002

de Boer J (2009) Trends in analytical and environmental chemistry of brominated flame retardants. In: 11th Annual Workshop on Brominated Flame Retardants, 19–20 June, Ottawa, Ontario, Canada. p 12

Ford JKB, Ellis GM, Barrett-Lennard LG, Morton AB, Palm RS, Balcomb KC (1998) Dietary specialization in two sympatric populations of killer whales (*Orcinus orca*) in coastal British Columbia and adjacent waters. Can J Zool 76:1456–1471

Ford JKB, Wright BM, Ellis GM, Candy JR (2010) Chinook salmon predation by resident killer whales: Seasonal and regional selectivity, stock identity of prey, and consumption rates. Pacific Biological Station, Fisheries and Oceans Canada, DFO. Can Sci Advis Sec Res Doc No. 2009/101

Frouin H, Lebeuf M, Hammill M, Masson S, Fournier M (2010) Effects of individual polybrominated diphenyl ether (PBDE) congeners on harbor seal immune cells in vitro. Mar Pollut Bull 60:291–298

Frouin H, Dangerfield N, Macdonald RW, Galbraith M, Crewe N, Shaw P, Mackas D, Ross PS (2013) Partitioning and bioaccumulation of PCBs and PBDEs in marine plankton from Strait of Georgia, British Columbia, Canada. Prog Oceanogr 115:65–75

Gobas FAPC, Arnot J (2010) Food web bioaccumulation model for polychlorinated biphenyls in San Francisco Bay, California, USA. Environ Toxicol Chem 29:1385–1395

Gobas FAPC, Maclean LG (2003) Sediment-water distribution of organic contaminants in aquatic ecosystems: the role of organic carbon mineralization. Environ Sci Technol 37:735–741

Government of Canada (2010a) Species profile: killer whale southern resident population. Species At Risk Public Registry. http://www.sararegistry.gc.ca/species/speciesDetails_e.cfm?sid=699

Government of Canada (2010b) Species profile: killer whale northern resident population. Species At Risk Public Registry. http://www.sararegistry.gc.ca/species/speciesDetails_e.cfm?sid=698

Grant PBC, Johannessen SC, Macdonald RW, Yunker M, Sanborn M, Dangerfield N, Wright C, Ross PS (2011) Environmental fractionation of PCBs and PBDEs during particle transport as recorded by sediments in coastal waters. Environ Toxicol Chem 30:1522–1532

Hall AJ, Kalantzi OI, Thomas GO (2003) Polybrominated diphenyl ethers (PBDEs) in grey seals during their first year of life-are they thyroid hormone endocrine disruptors? Environ Pollut 126:29–37

Hall AJ, Mcconnell BJ, RowlesTK Aguilar A, Borrell A, Schwacke L, Reijnders PJH, Wells RS (2006) Individual-based model framework to assess population consequences of polychlorinated biphenyl exposure in bottlenose dolphins. Environ Health Perspect 114:60–64

Harju M, Hamers T, Kamstra JH, Sonneveld E, Boon JP, Tysklind M, Andersson PL (2007) Quantitative structure-activity relationship modeling on in vitro endocrine effects and metabolic stability involving 26 selected brominated flame retardants. Environ Toxicol Chem 26:816–826

Hickie BE, Ross PS, Macdonald RW, Ford JKB (2007) Killer whales (*Orcinus orca)* face protracted health risks associated with lifetime exposure to PCBs. Environ Sci Technol 41:6613–6619

Hickie BE, Cadieux MA, Riehl KN, Bossart GD, Alava JJ, Fair PA (2013) Modeling PCB-bioaccumulation in the bottlenose dolphin (*Tursiops truncatus*): estimating a dietary threshold concentration. Environ Sci Technol 47(21):12314–12324

Ikonomou MG, Rayne S, Fischer M, Fernandez MP, Cretney W (2002a) Occurrence and congener profiles of polybrominated diphenyl ethers (PBDEs) in environmental samples from coastal British Columbia, Canada. Chemosphere 46:649–663

Ikonomou MG, Rayne S, Addison RF (2002b) Exponential increases of the brominated flame retardants, polybrominated diphenyl ethers, in the Canadian Arctic from 1981 to 2000. Environ Sci Technol 36:1886–1892

Johannessen SC, Macdonald RW, Wright CA, Burd B, Shaw DP, van Roodselaar A (2008) Joined by geochemistry, divided by history: PCBs and PBDEs in Strait of Georgia sediments. Mar Environ Res 66:S112–S120

Kelly BC, Ikonomou MG, Blair JD, Morin AE, Gobas FAPC (2007) Food web specific biomagnification of persistent organic pollutants. Science 317:236–239

Kelly BC, Ikonomou MG, Blair JD, Gobas FAPC (2008a) Bioaccumulation behaviour of polybrominated diphenyl ethers (PBDEs) in a Canadian Arctic marine food web. Sci Total Environ 40:60–72

Kelly BC, Ikonomou MG, Blair JD, Gobas FAPC (2008b) Hydroxylated and methoxylated polybrominated diphenyl ethers in a Canadian arctic marine food web. Environ Sci Technol 42:7069–7077

Kierkegaard A, Burreau S, Marsh G, Klasson Wehler E, de Wit C, Asplund L (2001) Metabolism and distribution of 2,2′,4,4′ tetrabromo 14C diphenyl ether in pike (Esox lucius) after dietary exposure. Organohalogen Compd 52:58–61

Krahn MM, Hanson MB, Baird RW, Boyer RH, Burrows DG, Emmons CK, Ford JKB, Jones LL, Noren DP, Ross PS, Schorr GS, Collier TK (2007) Persistent organic pollutants and stable isotopes in biopsy samples (2004/2006) from southern resident killer whales. Mar Pollut Bull 54:1903–1911

Lachmuth CL, Alava JJ, Hickie BE, Johannessen SC, Macdonald RW, Ford JKB, Ellis GM, Gobas FAPC, Ross PS (2010) Ocean disposal in resident killer whale (*Orcinus orca*) critical habitat: science in support of risk management. DFO, Can Sci Advis Sec Res Doc 2010/116

Li B, Danon-Schaffer M, Li LY, Ikonomou MG, Grace JR (2012) Occurrence of PFCs and PBDEs in landfill leachates from across Canada. Water Air Soil Pollut 223(6):3365–3372

Malmberg T, Athanasiadou M, Marsh G, Brandt I, Bergman A (2005) Identification of hydroxylated polybrominated diphenyl ether metabolites in blood plasma from polybrominated diphenyl ether exposed rats. Environ Sci Technol 39:5342–5348

McKinney MA, Cesh LS, Elliott JE, Williams TD, Garcelon DK, Letcher RJ (2006) Novel brominated and chlorinated contaminants and hydroxylated analogues among North American west coast populations of bald eagles (*Haliaetus leucocephalus*). Environ Sci Technol 40:6275–6281

Mongillo TM, Holmes EE, Noren DP, Van Blaricom GR, Punt AE, O'Neill SM, Ylitalo GM, Hanson MB, Ross PS (2012) Predicted polybrominated diphenyl ether (PBDE) and polychlorinated biphenyl (PCB) accumulation in southern resident killer whales. Mar Ecol Prog Ser 453:263–277

Mos L, Cameron M, Jeffries SJ, Koop BF, Ross PS (2010) Risk-based analysis of PCB toxicity in harbor seals. Integr Environ Assess Manag 6:631–640

NOAA (2010) Endangered Species Act Status of Puget Sound Killer Whales. National Oceanic and Atmospheric Administration, Northwest Regional Office, National Marine Fisheries Service. http://www.nwr.noaa.gov/Marine-Mammals/Whales-Dolphins-Porpoise/Killer-Whales/ESA-Status/Index.cfm

Noël M, Dangerfield N, Hourston RAS, Belzer W, Shaw P, Yunker MB, Ross PS (2009) Do trans-Pacific air masses deliver PBDEs to coastal British Columbia, Canada? Environ Pollut 157:3404–3412

Rayne S, Ikonomou MG (2002) Reconstructing source PBDE congener profiles from SPMDs in the Fraser River, British Columbia, Canada: comparison to commercial mixtures. Environ Toxicol Chem 21:2292–2300

Rayne S, Ikonomou MG, Ross PS, Ellis GM, Barrett-Lennard LG (2004) PBDEs, PBBs, and PCNs in three communities of free-ranging killer whales (*Orcinus orca*) from the Northeastern Pacific Ocean. Environ Sci Technol 38:4293–4299

Ross PS (2006) Fireproof killer whales: flame-retardant chemicals and the conservation imperative in the charismatic icon of British Columbia. Can J Fish Aquat Sci 63:224–234

Ross PS, De Swart RL, Van Loveren H, Osterhaus ADME, Vos JG (1996) The immunotoxicity of environmental contaminants to marine wildlife: a review. Ann Rev Fish Dis 6:151–165

Ross PS, Ellis GM, Ikonomou MG, Barrett-Lennard LG, Addison RF (2000) High PCB concentrations in free-ranging Pacific killer whales, *Orcinus orca*: effects of age, sex and dietary preference. Mar Pollut Bull 40:504–515

Ross PS, Couillard CM, Ikonomou MG, Johannessen SC, Lebeuf M, Macdonald RW, Tomy GT (2009) Large and growing environmental reservoirs of Deca-BDE present an emerging health risk for fish and marine mammals. Mar Pollut Bull 58:7–10

Ross PS, Noël M, Lambourn D, Dangerfield N, Calambokidis J, Jeffries S (2013) Declining concentrations of persistent PCBs, PBDEs, PCDEs, and PCNs in harbor seals from the Salish Sea. Prog Oceanogr 115:160–170

Rotander A, van BaveL B, Polder A, Rigét F, Auðunsson GA, Gabrielsen GW, Víkingsson G, Bloch D, Dam M (2012) Polybrominated diphenyl ethers (PBDEs) in marine mammals from Arctic and North Atlantic regions, 1986–2009. Environ Int 40:102–109

Sellström U, Jansson B, Kierkegaard A, de Wit CA, Odsjö T, Olsson M (1993) Polybrominated diphenyl ethers (PBDE) in biological samples from the Swedish environment. Chemosphere 26:1703–1718

Stapleton HM, Letcher RJ, Baker JE (2004a) Debromination of polybrominated diphenyl ether congeners BDE 99 and BDE 183 in the intestinal tract of the common carp (*Cyprinus carpio*). Environ Sci Technol 38:1054–1061

Stapleton HM, Alaee M, Letcher RJ, Baker JE (2004b) Debromination of the flame retardant decabromodiphenyl ether by juvenile carp (*Cyprinus carpio*) following dietary exposure. Environ Sci Technol 38:112–119

Stapleton HM, Brazil B, Holbrook RD, Mitchelmore CL, Benedict R, Konstantinov A, Potter D (2006) *In vivo* and *In vitro* debromination of decabromodiphenyl ether (BDE 209) by juvenile rainbow trout and common carp. Environ Sci Technol 40:4653–4658

Thomas GO, Moss SEW, Asplund L, Hall AJ (2005) Absorption of decabromodiphenyl ether and other organohalogen chemicals by grey seals (*Halichoerus grypus*). Environ Pollut 133:581–586

UNEP (2010) The Nine New POPs: an introduction to the nine chemicals added to the Stockholm Convention by the Conference of the Parties at its fourth meeting. United Nations Environment Program Secretariat of the Stockholm Convention on Persistent Organic Pollutants. http://chm.pops.int/Programmes/NewPOPs/Publications/tabid/695/language/en-US/Default.aspx

Verreault J, Gabrielsen GW, Chu S, Muir DC, Andersen M, Hamaed A et al (2005) Flame retardants and methoxylated and hydroxylated polybrominated diphenyl ethers in two Norwegian Arctic top predators: glaucous gulls and polar bears. Environ Sci Technol 39:6021–6028

Wania F, Dugani C (2003) Assessing the long-range transport potential of polybrominated diphenyl ethers: a comparisons of four multimedia models. Environ Toxicol Chem 22:1252–1261

Wolkers H, Van Bavel B, Derocher AE, Wiig O, Kovacs KM, Lydersen C, Lindstrom G (2004) Congener specific accumulation and food chain transfer of polybrominated diphenyl ethers in two Arctic food chains. Environ Sci Technol 38:1667–1674

Xie WH, Shiu WY, Mackay D (1997) A review of the effect of salts on the solubility of organic compounds in seawater. Mar Environ Res 44:429–444