

Habitat-Based PCB Environmental Quality Criteria for the Protection of Endangered Killer Whales (*Orcinus orca*)

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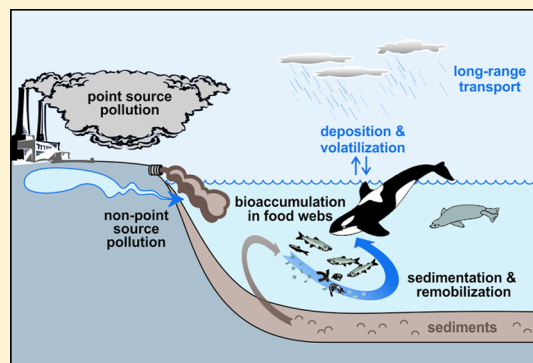
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Supporting Information

ABSTRACT: The development of an area-based polychlorinated biphenyl (PCB) food-web bioaccumulation model enabled a critical evaluation of the efficacy of sediment quality criteria and prey tissue residue guidelines in protecting fish-eating resident killer whales of British Columbia and adjacent waters. Model-predicted and observed PCB concentrations in resident killer whales and Chinook salmon were in good agreement, supporting the model's application for risk assessment and criteria development. Model application shows that PCB concentrations in the sediments from the resident killer whale's Critical Habitats and entire foraging range leads to PCB concentrations in most killer whales that exceed PCB toxicity threshold concentrations reported for marine mammals. Results further indicate that current PCB sediment quality and prey tissue residue criteria for fish-eating wildlife are not protective of killer whales and are not appropriate for assessing risks of PCB-contaminated sediments to high trophic level biota. We present a novel methodology for deriving sediment quality criteria and tissue residue guidelines that protect biota of high trophic levels under various PCB management scenarios. PCB concentrations in sediments and in prey that are deemed protective of resident killer whale health are much lower than current criteria values, underscoring the extreme vulnerability of high trophic level marine mammals to persistent and bioaccumulative contaminants.



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While the availability of Chinook salmon is considered to be a crucial driver of birth and survival rates among resident killer whales,⁶ exposure to polychlorinated biphenyls (PCBs) is also considered a major potential threat to the recovery of these populations.⁷ Killer whales from British Columbia are among the world's most PCB-contaminated marine mammals.⁷ A number of toxicological effects have been attributed to PCBs in marine mammals. They include reproductive impairment,⁸

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INTRODUCTION

Three ecotypes of killer whales (*Orcinus orca*), residents, transients, and offshores, frequent the marine waters off British Columbia (BC), Canada, and the state of Washington (WA), United States.¹ Resident killer whales are distinguished into two populations: the northern resident killer whales (NRKW), which frequent the waters between central Vancouver Island and SE Alaska, and the southern resident killer whales (SRKW), which are mostly found in the waters off southern Vancouver Island and northern Washington.^{1,2} Resident killer whales are fish-feeding whales with a strong preference for Chinook salmon (*Oncorhynchus tshawytscha*). SRKWs are listed as “Endangered” under the Canadian *Species at Risk Act* (SARA)³ and the United States *Endangered Species Act*.⁴ The NRKW population is listed as “Threatened” in Canada.⁵ Critical Habitats have been identified for both resident killer whale populations (Figure 1) under SARA, and an evaluation of the threats to these areas is currently underway.^{3,5} Less is known about the distribution of transients, and Critical Habitat

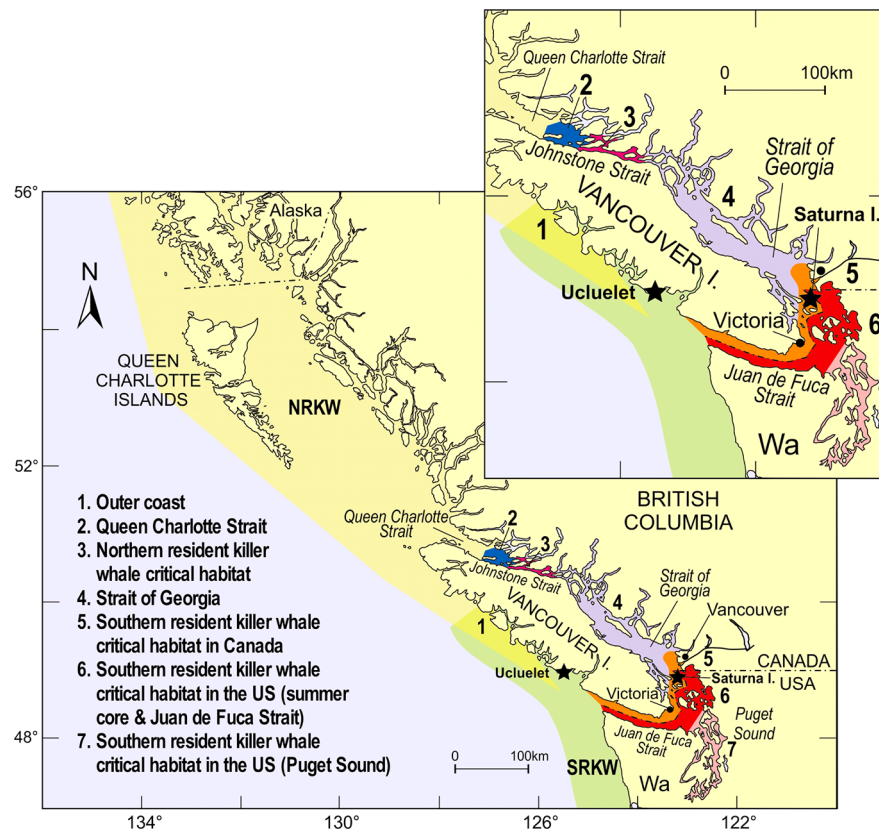


Figure 1. Map showing the seven areas of the habitat-based PCB food-web model for northern and southern resident killer whales (i.e., NRKW and SRKW, respectively). The distribution ranges for the NRKW and SRKW populations are also portrayed.

immunotoxicity,^{9–12} skeletal abnormalities,^{7,13} endocrine disruption,^{9,14,15} and negative effects on the population growth rate.¹⁶ PCBs have also been linked to cancer in California sea lions (*Zalophus californianus*).¹⁷ While PCBs represent only one chemical class found in killer whales, they are viewed as the pre-eminent contaminant threat to high trophic level species in the northern hemisphere.^{7,18–20} In British Columbia and Washington State, a risk-based assessment of different persistent organic pollutants (POPs) in harbor seals (*Phoca vitulina*) also identified PCBs as the chemicals of greatest concern.¹⁵ Recent evidence suggests that PCBs are affecting the health of free-ranging killer whales in BC, as evidenced by upregulation of several gene targets, including the aryl hydrocarbon receptor (AhR), thyroid hormone receptor (TR α), estrogen receptor (ER α), interleukin 10 (IL-10), and metallothionein (MT1).²¹

Given the growing evidence that long-lived killer whales are exceptionally vulnerable to the accumulation of persistent environmental contaminants, scrutiny of regulations, management protocols, and permitting of activities that release or mobilize PCBs in the marine environment may help identify opportunities to reduce PCB exposure in killer whales. Sediment quality criteria (SQC) and dietary tissue residue guidelines (TRG) are two regulatory tools used to assess risks that contaminants pose to biota. In Canada, SQCs are the only broadly available criteria for the management and assessment of the contamination of aquatic environments. Three SQC for PCBs exist in Canada. These are the Canadian Council of Ministers of the Environment (CCME) Interim Sediment Quality Guideline ISQG of 21.5 $\mu\text{g}\cdot\text{kg}^{-1}$ dry weight (dw), the Canadian Environmental Protection Act (CEPA) Action Level Low for disposal at sea of 100 $\mu\text{g}\cdot\text{kg}^{-1}$ dw, and the British

Columbia's Ministry of Environment (BCMoE) sediment quality criterion of 20 $\mu\text{g}\cdot\text{kg}^{-1}$ dw. In Canada, prey tissue residue guidelines are the preferred way to assess risks associated with bioaccumulative contaminants in fish-eating wildlife. The tissue residue guideline for PCBs in Canada is 50 $\mu\text{g}\cdot\text{kg}^{-1}$ wet weight. Few studies have evaluated the degree to which these guidelines protect upper trophic level organisms most vulnerable to biomagnification in aquatic food webs.

This study (i) investigates the general origin of the PCBs found in resident killer whales and their prey by combining a newly developed area-based food-web model which incorporates time spent by highly mobile killer whales and their prey in each area; (ii) assesses PCB-related health risks to killer whales when they are exposed to PCB concentrations at current concentrations and at currently established SQCs and TRGs; and (iii) proposes PCB concentrations in sediments and prey items that are deemed to be “protective” of killer whales from harm due to PCBs.

METHODS

Modeling Approach. The PCB food-web bioaccumulation model aims to describe the relationship between PCB concentrations in sediments, the primary prey of killer whales (Chinook salmon), and northern and southern resident killer whales. The relationship between PCB concentrations in each organism i ($C_{B,i}$ in $\text{ng}\cdot\text{kg}^{-1}$ wet weight organism), its diet ($C_{D,i}$ in $\text{ng}\cdot\text{kg}^{-1}$ wet weight), and the sediment (C_S in $\text{ng}\cdot\text{kg}^{-1}$ dry weight sediment) to which it is exposed, is represented by, respectively, the biomagnification factor (BMF_i in kg wet weight diet $\cdot\text{kg}^{-1}$ wet weight) and the biota–sediment

accumulation factor (BSAF_{*i*} in kg dry weight·kg⁻¹ wet weight):²²

$$\text{BMF}_i = C_{B,i}/C_{D,i} \quad (1)$$

$$\text{BSAF}_i = C_{B,i}/C_S \quad (2)$$

The BMF_{*i*} and BSAF_{*i*} for killer whales (i.e., BMF_{KW} and BSAF_{KW} respectively) and the BSAF_{*i*} for Chinook salmon (BSAF_{SS}) are the main outputs of the model. They are complex functions which comprise elements of biological, chemical, and environmental factors including food-web structure, species' diet composition, species' body weights and lipid contents, PCB congener composition, lipid–water partition coefficients, and temperature as well as water–sediment and air–sediment PCB concentration relationships. The BMF_{*i*} and BSAF_{*i*} can be used in forward calculations, where chemical concentrations in biological species are determined from chemical concentration in diet or sediments as C_{B,*i*} = BMF_{*i*}·C_{D,*i*} or C_{B,*i*} = BSAF_{*i*}·C_S. These concentrations can then be compared to toxicological threshold concentrations (C_{TT,*i*}) for species *i* to estimate risk. The BMF_{*i*} and BSAF_{*i*} also provide methods to derive protective concentrations in sediments from toxicological threshold concentrations in biota *i* through backward calculations as C_{D,*i*} = C_{TT,*i*}/BMF_{*i*} or C_S = C_{TT,*i*}/BSAF_{*i*}. It is important to stress that while the BMF_{*i*} and BSAF_{*i*} represent exposure from, respectively, diet items or sediments, exposure of biota in the food web through other sources (i.e., water and air) are included in the calculation of the BMF_{*i*} and BSAF_{*i*}. Through parametrization of the sediment, water, and air concentration relationships, the model can represent various exposure regimes where either concentrations in water, sediment, or air are the dominant source of PCB exposure to organisms of the food web. In cases where PCB concentrations in water and sediments are not expected to maintain a constant relationship over time, such as in the case of disposal or remediation of contaminated sediments, concentrations in organism *i* (C_{B,*i*}), water (C_W), and sediment (C_S) can be expressed as follows:

$$C_{B,i} = \alpha \cdot C_W + \beta \cdot C_S \quad (3)$$

where α and β are factors describing the organism/water (in units of L/kg ww) and organism/sediment (in units of kg dw/kg ww) concentration ratios, respectively, if the PCB concentration in the sediment is zero (for α) and the PCB concentration in the water is zero (for β). Equation 3 illustrates the contributions of the PCB concentrations in water and sediment to the PCB concentration in organisms.

The model applies a steady-state solution to solve the mass balance equations. The steady state solution represents a situation where contaminant exchange has been of sufficient duration for concentrations to achieve stable concentrations. This modeling approach was chosen because of its simplicity and lack of a requirement for unavailable time dependent information. The application of the steady-state assumption is reasonable since PCB concentrations in the study area are believed to have been relatively stable over a prolonged period of time²³ and resident organisms have been exposed to PCB concentrations throughout their entire development since conception. However, in large organisms (e.g., killer whales) the time to reach steady-state is long, which can lead to changes in PCB body burden lagging behind changing environmental or biological conditions.²⁴ To reduce possible error associated with the steady-state assumption for long-lived animals, we included several age and sex categories (i.e., adult male, adult

female, and calf) to account for the effect of life stage on PCB concentrations in killer whales.

Study Area. For the purpose of this study, the model focused on seven areas, including SARA defined Critical Habitats and adjacent areas, constituting the foraging range of northern and southern resident killer whales in BC and WA²⁵ (Figure 1). The habitat distribution of the NRKW includes Queen Charlotte Strait, NRKW Critical Habitat, and the Outer coast from central Vancouver Island northwards along the mainland coast into southeast Alaska, while the SRKW includes the Strait of Georgia, SRKW Critical Habitat in Canada, SRKW Critical Habitat in Juan de Fuca Strait (USA), the SRKW Critical Habitat in Puget Sound (USA), and the Outer coast from central Vancouver Island southward to Monterey Bay, California.^{1,2} The estimated times that NRKW and SRKW populations frequent these areas are detailed in Table S1 (Supporting Information) and used in the model to assess PCB exposure of killer whales in their habitat. The environmental characteristics of each area are documented in Lachmuth et al.²⁵ (see Table S2a for a list of ambient parameters)

PCB Concentrations in Study Area. Of the 209 PCB congeners, 136 have been detected in killer whales.⁷ Even though PCBs have been banned in Canada since 1977, the decline in their concentrations has been slow due to continued atmospheric delivery of PCBs from other regions of the world and ongoing cycling in aquatic environments.²³ This study was restricted to 40 PCB congeners for which concentrations in sediments are available for the areas of interest (Table S2b,c).^{25,26} The sediment sampling dates (i.e., 2002–2009) and locations are described elsewhere.^{25,26} PCB concentrations in sediments of each area were represented by log-normal distributions. Empirical PCB concentrations in water were obtained elsewhere.²⁵ Concentrations of total PCBs (ΣPCB) from a station on Saturna Island (48°47'24" N, 123°07'48" W) were used to represent air concentrations (i.e., 8.9×10^{-6} ng·L⁻¹) in the Critical Habitat of the SRKW within the Strait of Georgia.²⁷ Air concentrations (i.e., 9.3×10^{-6} ng·L⁻¹) from a station at Ucluelet (48°55'12" N, 125°32'24" W) were used to represent the offshore habitat.²⁷ Total PCB (ΣPCB) concentrations were calculated as the sum of the concentrations of the PCB congeners listed in Table S2.

Physical–Chemical Properties. The octanol–water (K_{OW}) and octanol–air (K_{OA}) partition coefficients of the PCB congener used in the model are listed in Table S2b,c. Freshwater-based K_{OW} values at 37.5 °C and the ambient temperature were used to describe PCB congener partitioning between lipids and aqueous media for warm- and cold-blooded biota, respectively. The saltwater-based K_{OW} was derived from the freshwater-based K_{OW} following Xie et al.,²⁸ and used in the model to calculate PCB uptake in biota from water. Octanol–air partition coefficients at 37.5 °C were used to calculate pulmonary PCB transfer between killer whales and air.²²

Killer Whale Food Web. The model focuses on the primary prey species identified for resident killer whales, which is dominated by salmonid species at 96% of the total diet (of which 71.5% is Chinook salmon, 24% is Chum salmon (*Oncorhynchus keta*), and other salmonids (e.g., Coho salmon, *Oncorhynchus kisutch*) comprise approximately 0.5%.^{6,29} The only non-salmonid species in killer whale diet consist of Pacific herring (*Clupea pallasii*), sablefish (*Anoplopoma fimbria*), yelloweye rockfish (*Sebastes ruberrimus*), quillback rockfish (*Sebastes maliger*), and Pacific halibut (*Hippoglossus stenolepis*). Herring and rockfish are likely not targeted as prey items by

killer whales but halibut and sablefish are directly consumed by killer whales.²⁹ Two food-web models were developed to incorporate the main difference in food-web structure between the inner- and outer-coastal areas (Figure S1) where Chinook salmon on the outer coast are thought to feed primarily on squid instead of herring on the inner coast.²⁵ Further detail and rationale for the development of the food-web structure is provided in the SI, while feeding preferences for the inner and outer coastal food webs are provided in Table S3a-c.

Model for Phytoplankton, Zooplankton, Aquatic Invertebrates, and Fish. The model for PCB uptake, elimination, and bioaccumulation in phytoplankton, zooplankton, aquatic invertebrates, and fish is described in Gobas and Arnot²² and summarized in Figure S2. The parametrization of the model for these groups of species can be found in Table S4a-c.

Killer Whales Model. The primary PCB uptake and elimination routes in killer whales are shown in Figure S3. The steady-state solution of the mass balance equation that was used to calculate the PCB concentrations in killer whales is

$$C_{KW,l} = (k_A C_{AG} + k_D \cdot \sum (P_i \cdot C_{D,i})) / (k_O + k_E + k_U + k_G + k_P + k_L + k_M) \quad (4)$$

where the lipid-normalized PCB congener concentration ($\text{ng} \cdot \text{kg}^{-1} \text{ lw}$) in the killer whale is $C_{KW,l}$ and the net change in lipid-normalized concentration over time t (d) is $dC_{KW,l}/dt$. The gaseous aerial concentration ($\text{ng} \cdot \text{L}^{-1}$) is C_{AG} . The inhalation rate constant ($\text{L} \cdot \text{kg}^{-1} \text{ lipid} \cdot \text{d}^{-1}$) is k_A . The clearance rate constant ($\text{kg} \cdot \text{kg}^{-1} \text{ lipid} \cdot \text{d}^{-1}$) for PCB 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 PCB congener ($\text{g} \cdot \text{kg}^{-1}$) in prey item i is $C_{D,i}$. The rate constant (d^{-1}) for PCB exhalation via the lungs is k_O . The rate constant (d^{-1}) for PCB congener elimination via excretion into feces is k_E . The rate constant for urinary PCB excretion is k_U . The rate constant for net somatic growth dilution is k_G . The rate constant for PCB transfer into the calves is k_P , and represents the lipid mass increase (equal to the calf's postparturition lipid mass) during the gestation period. The rate constant for PCB transfer to calves via lactation is k_L , and represents the lipid mass increase of the female whale that is transferred to the calf during lactation. The rate constant for metabolic PCB congener transformation is k_M .

A whole-organism wet weight based concentration ($\text{ng} \cdot \text{kg}^{-1} \text{ ww}$) in the killer whale C_{KW} is calculated from the whole-organism lipid content L_{KW} ($\text{kg} \text{ lw} \cdot \text{kg}^{-1} \text{ ww}$) as

$$C_{KW} = L_{KW} \cdot C_{KW,l} \quad (5)$$

The submodels for estimating uptake and elimination rates and their parametrization are detailed in the SI. The effects of calving, lactation, and somatic growth on PCB concentrations are represented in the model by annual proportional increases in body lipid. The model assumes that PCBs are homogeneously distributed among fat tissues in killer whales. This means that at the time of parturition and lactation, female animals reduce both their lipid and PCB burden to the same degree, causing no change in the PCB concentration in the lipids of the animals. However, growth in lipid mass required for offspring production and lactation, represented in the model as k_L and k_P , act to reduce the PCB concentration in the whales. Sexually mature female killer whales give birth approximately every 5 years and nurse their calves for a period of approximately 12–

24 months.³⁰ Somatic growth rate calculations are documented in the SI. The mean lifespan of killer whales is approximately 29 years for males and 50 years for females.^{30,31} Gender and age differences among whales are addressed by including separate model calculations for adult males, adult females, and calves. Biotransformation rates of the predominant PCB congeners in killer whales are considered to be very slow and negligible in this study.^{7,24} Tables S5 and S6 provide detailed descriptions of the killer whale food-web model inputs and state variables.

Model Performance. To test the model, a performance analysis was conducted where calculated PCB congener concentrations (ranging from $n = 1$ to N) in salmon and killer whales ($C_{BP,i}$) were compared to observed PCB concentrations^{7,32} ($C_{BO,i}$). This was quantitatively expressed as the mean model bias (MB_i) for each species i :

$$MB_i = 10 \left(\frac{\sum_{n=1}^N \frac{[\log(C_{BP,n}/C_{BO,n})]}{N}}{N} \right) \quad (6)$$

Model performance was also assessed for total PCBs, i.e. the sum of PCB congener concentrations (ΣPCBs), in the form of the mean model bias MB^* , where $C_{BP,i \Sigma\text{PCB}}$ and $C_{BO,i \Sigma\text{PCB}}$ are, respectively, the model calculated and observed ΣPCB concentrations in each species i for observations m ranging from $m = 1$ to the total number of concentration measurements M :

$$MB_i^* = 10 \left(\frac{\sum_{m=1}^M \frac{[\log(C_{BP,i \Sigma\text{PCB}}/C_{BO,i \Sigma\text{PCB}})]}{M}}{M} \right) \quad (7)$$

Empirical concentrations were only available for Chinook salmon and male resident killer whale from the NRKW Critical Habitat.

Model Sensitivity. The sensitivity of PCB concentrations in killer whales to variation in PCB concentrations in sediment, water, and diet was determined to explore the relative importance of PCB sources to the food web as described in the SI.

Uncertainty Analysis. Uncertainty in model inputs, represented by the standard deviation $SD_{\log C_S}$ of the mean $\log C_S$, and in the model calculations, represented by the standard deviation ($SD_{\log \text{BSAF}_i}$) of $\log \text{BSAF}_i$, are propagated in the calculation of $\log C_{B,i}$ to produce the standard deviation of the mean $\log C_{B,i}$ as $SD_{\log C_{B,i}} = \sqrt{(SD_{\log C_S}^2 + SD_{\log \text{BSAF}_i}^2)}$. In estimating PCB concentrations in killer whales from PCB concentrations in Chinook salmon, uncertainty in PCB concentrations in Chinook salmon (i.e., $\log C_{D,i}$) is represented by the standard deviation $SD_{\log C_{D,i}}$ of the mean $\log C_{D,i}$ and uncertainty in the model calculations (i.e., $\log \text{BMF}_i$) is represented by the standard deviation ($SD_{\log \text{BMF}_i}$) of $\log \text{BMF}_i$. $SD_{\log C_{B,i}}$ is calculated as $SD_{CB} = \sqrt{(SD_{\log C_{D,i}}^2 + SD_{\log \text{BMF}_i}^2)}$. Since PCB concentrations were not available for all areas and seasons, the uncertainty analysis does not fully represent geographical and temporal variations in PCB concentrations. Since empirical PCB concentrations were only available for Chinook salmon and adult male northern resident killer whales, model uncertainty determined from concentrations in the NRKW Critical Habitat was applied to all other areas. Because spatial variability in PCB concentrations in the sediments may contribute to variability in PCB concentrations in salmon and killer whales, uncertainty estimates in the BSAF and BMF are not fully independent of uncertainties in PCB concentrations in sediments and salmon. This may cause overestimation of the uncertainty in estimates of PCB concentrations in salmon and

killer whales in forward calculations. Uncertainty analysis through Monte Carlo simulation was attempted but found to be problematic and hence not applied because of interdependence of state variables and lack of data to define uncertainty distributions for several state variables.

Risk Assessment. The model was used to estimate PCB concentrations in Chinook salmon and in northern and southern resident killer whales using empirical PCB concentrations measured in sediments under three scenarios. In the first scenario, risks of current PCB concentrations in sediments in each of the seven areas of the killer whale's foraging range were determined. In a second scenario, the effect of PCB concentrations in sediments of the killer whale's entire foraging range was assessed. In a third scenario, PCB concentrations in killer whale expected as a result of PCB concentrations in sediments equal to the sediment quality criteria and PCB concentrations in Chinook salmon equal to the CCME tissue residue guideline were calculated. Each of these scenarios involved calculating the expected distribution of PCB concentrations in killer whales from PCB concentration distributions in Chinook salmon, the main diet item of killer whales, or sediment (i.e., $\log C_{B,i} = \log C_{D,i} + \log BMF_i$ or $\log C_{B,i} = \log C_S + \log BSAF_i$). The predicted PCB concentration distributions in killer whales were compared to toxicity threshold concentrations for PCBs of 17 mg·kg⁻¹ lipid weight (lw) in harbor seals,^{10,11} 10 mg·kg⁻¹ lw in bottlenose dolphins (*Tursiops truncatus*),¹⁶ and 1.3 mg·kg⁻¹ lw in harbor seals.¹⁵ Toxicity threshold concentrations for PCBs in killer whales do not exist, but the common nature of PCB toxicity in mammals provides a basis for extrapolating toxicity from other marine mammal species to killer whales in risk assessments. The distribution of PCB concentrations in salmon was also estimated from PCB concentrations in sediments (i.e., $\log C_{B,i} = \log C_S + \log BSAF_i$) and then compared to the Environment Canada TRG of 0.05 mg·kg⁻¹ wet weight (ww) to assess PCB related risks in killer whales due to salmon consumption.²³

PCB congener concentrations in sediment and water in killer whale Critical Habitats and adjacent areas are listed in Table S7a-g (SI). PCB congener concentrations in sediment and water of the northern and southern killer whale foraging ranges were determined as average concentrations in all areas weighted by the relative time periods (see Table S1a, SI) that killer whales inhabit each area. The CCME Interim Sediment Quality Guideline³³ of 0.0215 mg·kg⁻¹ dry weight (dw); the CEPA Action Level Low³⁴ of 0.1 mg·kg⁻¹ dw; the BCMoE Sediment Quality Criteria³⁵ of 0.020 mg·kg⁻¹ dw; and the Environment Canada TRG of 0.05 mg·kg⁻¹ wet weight (ww)²³ were used in the third scenario.

Risk Management. Geometric mean \sum PCB concentrations in sediment (C_S) and in killer whale diet ($C_{D,KW}$) expected to lead to 95% of \sum PCB concentrations in killer whales being below the toxicity threshold concentrations in killer whales ($C_{TT,KW}$, see Table S8) were deemed to be protective and calculated as

$$\log C_S = \log(C_{TT,KW}) - \log BSAF_{KW} - 1.96 \cdot (SD_{\log BSAF_{KW}}) \quad (8)$$

$$\log C_{D,KW} = \log(C_{TT,KW}) - \log BMF_{KW} - 1.96 \cdot (SD_{\log BMF_{KW}}) \quad (9)$$

where $SD_{\log BSAF_{KW}}$ and $SD_{\log BMF_{KW}}$ represent model uncertainty, characterized by the standard deviation of the geometric mean model bias (MB*) for \sum PCB concentrations in killer whales. Biota sediment accumulation factors in killer whales ($BSAF_{KW}$) and biomagnification factors in Chinook salmon (BMF_{CS}) were calculated based on the current composition of sediment PCB congeners in the areas included in the study. The foraging range specific factors α and β were determined by conducting model calculations of the PCB concentrations in biota where PCB congener concentrations in sediment were set to zero (to determine α) or the PCB concentration in the water was set to zero (to determine β). The model was built in Microsoft Excel 2003–2007.

RESULTS AND DISCUSSION

Model Sensitivity. The sensitivity of modeled PCB concentrations in killer whales to measured PCB concentrations in air is low and reflects the dominance of dietary consumption in the uptake of PCBs by killer whales (Table S9). The sensitivity of PCB concentrations in killer whales to PCB concentrations in water is greater than that to PCB concentrations in sediments (Tables S9 and S10). This indicates that PCBs in the water column are the main source of PCBs for killer whales, with PCBs partitioning predominantly from water to phytoplankton and zooplankton through the pelagic food web into killer whale prey. Changing the killer whale diet composition from the "inner-coast diet" to the "outer-coast diet" had little effect on modeled PCB concentrations in killer whales for inner coastal areas (see Figure S4a,b and Table S11a,b), but did affect PCB concentrations in killer whales for the outer coastal area (see Figure S4c,d and Table S11c,d). The calculations support the idea that squid plays an important role in delivering PCBs to Chinook salmon in the outer coast area.

Model Performance. Observed and model-predicted PCB congener concentrations in salmon and killer whales show good agreement when compared against empirical data for both species^{7,32} (Figure S5). The mean model bias (MB) for PCB congeners in Chinook salmon was 1.30 with a standard deviation equivalent to a factor of 10^{0.31} or 2 (Figure S6a) and 1.23 with a standard deviation equivalent to a factor of 10^{0.36} or 2.3 for male northern resident killer whales (Figure S6b). The mean model bias (MB*) for total PCBs (\sum PCBs) was 1.24 with a standard deviation equivalent to a factor of 10^{0.18} or 1.5 for Chinook salmon and 0.94 with a standard deviation equivalent to a factor of 10^{0.33} or 2.1 for male northern resident killer whales (Figure S6). The mean model bias MB and MB* were close to 1.0 indicating no systematic over- or under-prediction of the PCB congener or \sum PCBs concentrations in salmon or killer whales. This corroborates the ability of the model to estimate concentrations of PCB congeners and \sum PCBs concentrations in the killer whale food web.

Uncertainty Analysis. The geometric mean PCB concentration in sediments ranged from 10^{-3.60±0.74} mg·kg⁻¹ dw in NRKW Critical Habitat to 10^{-1.85±1.23} mg·kg⁻¹ dw for the SRKW Critical Habitat in Puget Sound, USA (Table S12). There was considerable spatial variation in sediment PCB concentrations as revealed by the large standard deviations of the geometric mean PCB concentrations. The uncertainty in the model calculations, expressed in terms of the $SD_{\log BSAF_i}$ and estimated as the standard deviation of the geometric mean model bias (MB*) was 0.18 for Chinook salmon and 0.33 for killer whales (Table S12). The combined variability and

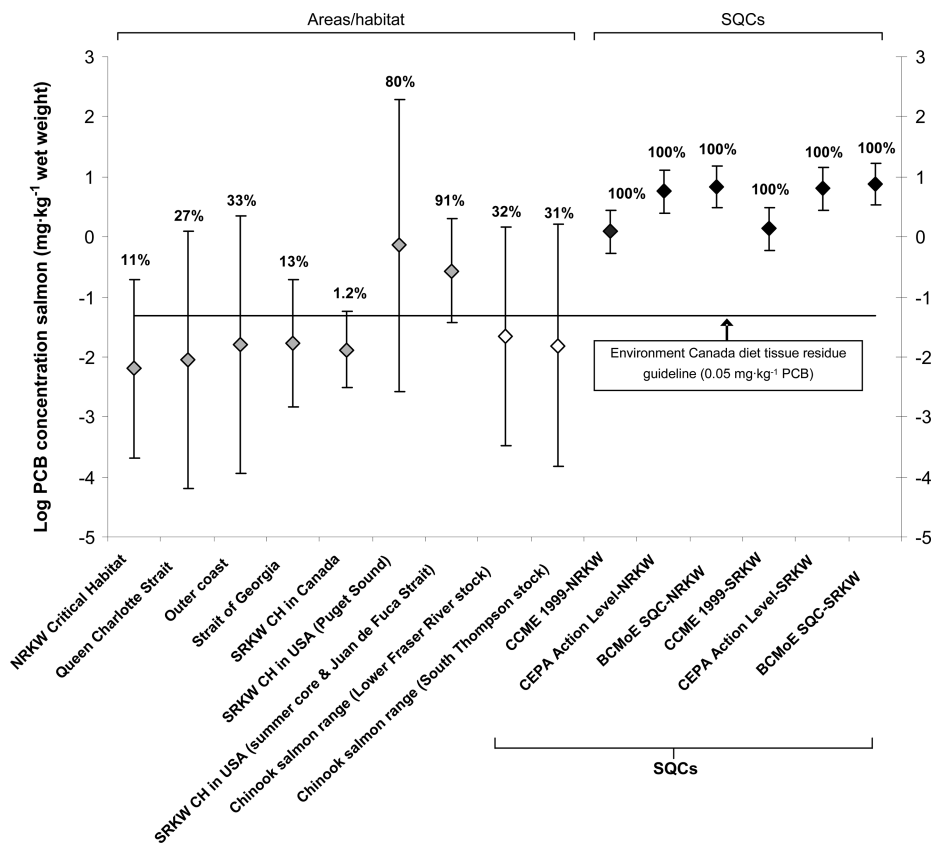


Figure 2. Expected geometric mean \sum PCB concentrations and their 95% confidence intervals in Chinook salmon ($\text{mg}\cdot\text{kg}^{-1}$ ww) resulting from \sum PCB concentrations in sediments equal to (i) those measured in each of the seven specified areas investigated (scenario 1, closed gray diamonds), assuming Chinook salmon are confined to each of the seven areas; (ii) the mean PCB concentration in sediments of the Chinook salmon foraging range of the Lower Fraser River and South Thompson subpopulations (scenario 2, open diamonds); (iii) current sediment quality criteria (SQC) values for PCBs (scenario 3, closed black diamonds). The solid line is the tissue residue guideline (TRG) for wildlife consumers of fish of $0.05 \text{ mg}\cdot\text{kg}^{-1}$ ww. Label numbers list the proportion of the Chinook salmon population exceeding the TRG. NRKW: northern resident killer whale; SRKW: southern resident killer whale; CH: Critical Habitat; CCME: Canadian Council of Ministers of the Environment; CEPA: Canadian Environmental Protection Act; BC MWLAP: British Columbia Ministry of Water, Land and Parks; SQC: Sediment Quality Criteria.

uncertainty in the PCB concentrations in the sediments is greater than the apparent uncertainty in the BMF_i and BSAF_i . This indicates that spatial variation in PCB concentrations in the sediment represents the primary source of uncertainty in the forward calculations.

Risks in Killer Whale Critical Habitats (Scenario 1).

BSAFs for \sum PCBs in Chinook salmon for each of the areas varied approximately 3.5 fold from $10^{1.40\pm 0.18} \text{ kg dw}\cdot\text{kg}^{-1}$ ww for the NRKW Critical Habitat to $10^{1.96\pm 0.18} \text{ kg dw}\cdot\text{kg}^{-1}$ ww in the U.S. portion of SRKW Critical Habitat (Table S12). BSAFs of \sum PCBs in adult male killer whales varied from $10^{3.90\pm 0.33} \text{ kg dw}\cdot\text{kg}^{-1}$ ww for the NRKW Critical Habitat to $10^{4.44\pm 0.33} \text{ kg dw}\cdot\text{kg}^{-1}$ ww in the U.S. portion of the SRKW Critical Habitat. BSAFs of \sum PCBs for adult female killer whales were lower than those for adult males and varied from $10^{3.04\pm 0.33} \text{ kg dw}\cdot\text{kg}^{-1}$ ww for the NRKW Critical Habitat to $10^{3.65\pm 0.33} \text{ kg dw}\cdot\text{kg}^{-1}$ ww of the US SRKW Critical Habitat. \sum PCB concentrations in sediments in the NRKW and SRKW Critical Habitats are sufficiently high to cause (i) \sum PCB concentrations to exceed the CCME TRG for wildlife consumers of fish in substantial portions of Chinook salmon populations (i.e., 11% the NRKW critical habitat and 80%–91% in the U.S. SRKW critical habitat; Figure 2); and (ii) \sum PCB concentrations in killer whales to exceed the $1.3 \text{ mg}\cdot\text{kg}^{-1}$ lw toxicity reference value for immunotoxicity and endocrine disruption in harbor

seals in 77%–100% of male and 41%–100% of female killer whales (Figure 3). This illustrates that current sediment PCB concentrations in Critical Habitats can lead to PCB concentrations in resident killer whales that represent a potential health concern for killer whales.

Risks in Killer Whale Foraging Range (Scenario 2).

BSAFs for \sum PCBs in Chinook salmon are approximately $10^{1.76\pm 0.18} \text{ kg dw}\cdot\text{kg}^{-1}$ ww in the NRKW and $10^{1.90\pm 0.18} \text{ kg dw}\cdot\text{kg}^{-1}$ ww in the SRKW foraging ranges (Table S12). BSAFs for \sum PCBs in adult male and female killer whales are $10^{4.22\pm 0.33}$ and $10^{3.43\pm 0.33} \text{ kg dw}\cdot\text{kg}^{-1}$ ww, respectively, in the NRKW foraging range, and $10^{4.34\pm 0.29}$ and $10^{3.55\pm 0.30} \text{ kg dw}\cdot\text{kg}^{-1}$ ww, respectively, in the SRKW foraging range. Corresponding BMFs for \sum PCBs in adult male and female NRKWs are $10^{2.46\pm 0.33}$ and $10^{1.64\pm 0.33} \text{ kg dw}\cdot\text{kg}^{-1}$ ww, respectively. \sum PCB concentrations in sediments in the NRKW and SRKW foraging ranges can be expected to lead to (i) \sum PCB concentrations in salmon that exceed the CCME TRG for wildlife consumers of fish of $0.05 \text{ mg}\cdot\text{kg}^{-1}$ ww in approximately a third of the two resident killer whale populations (Figure 2); and (ii) \sum PCB concentrations in killer whales that exceed the TRV for harbor seals¹⁵ ($1.3 \text{ mg}\cdot\text{kg}^{-1}$ lw) in 82% of NRKW males and 100% of SRKW males and in 52% of NRKW females and 86% of SRKW females (Figure 3). These results are substantiated by the

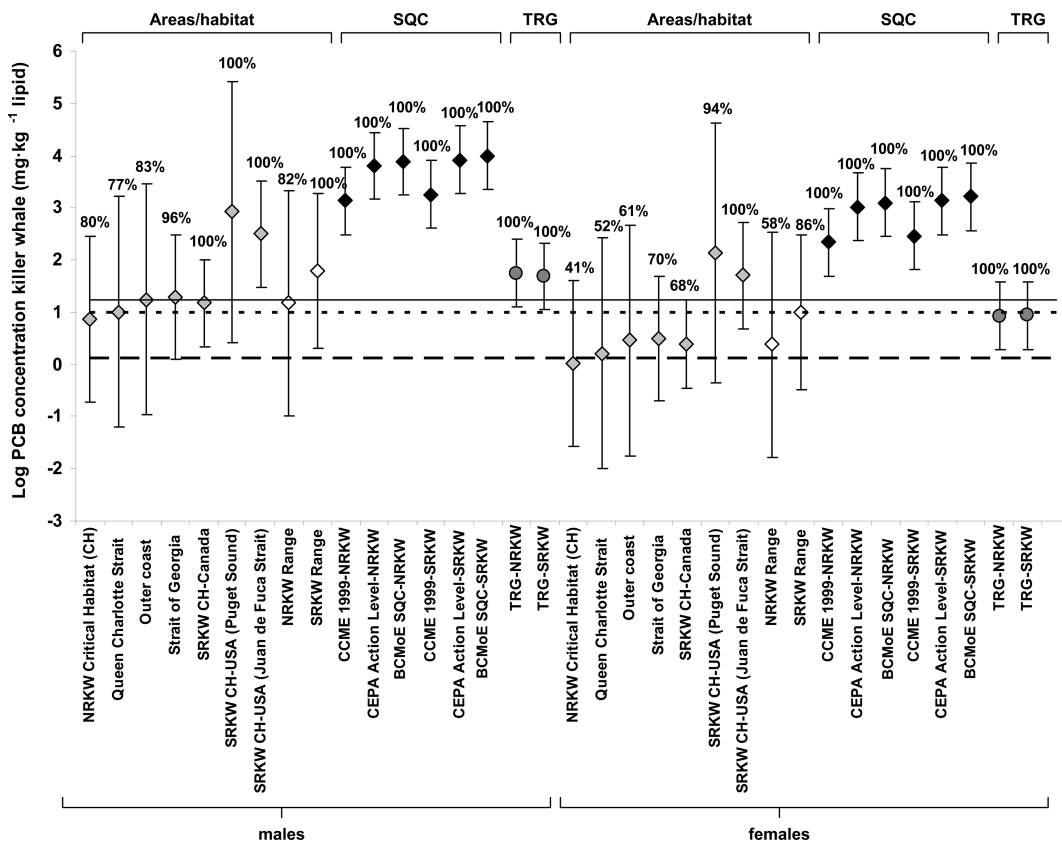


Figure 3. Expected geometric mean Σ PCB concentrations and their 95% confidence intervals in male (left) and female (right) killer whales ($\text{mg}\cdot\text{kg}^{-1}$ lipid) resulting from Σ PCB concentrations in sediments in (i) each of the seven areas investigated (scenario 1, closed gray diamonds); (ii) the entire foraging range for northern and southern resident killer whales (scenario 2, open diamonds); (iii) current sediment quality guideline (SQG) and tissue residue guideline (TRG) values for PCBs (scenario 3, closed black diamonds for SQG and gray circles for TRG). The dashed, dotted, and solid lines in ascending order are toxicity threshold concentrations of 1.3, 10, and $17 \text{ mg}\cdot\text{kg}^{-1}$ lipid, respectively. Label numbers list the proportion of the resident killer whale population exceeding the threshold concentrations of $1.3 \text{ mg}\cdot\text{kg}^{-1}$ lipid for immunotoxicity and endocrine disruption. NRKW: northern resident killer whale; SRKW: southern resident killer whale; CH: Critical Habitat; CCME: Canadian Council of Ministers of the Environment; CEPA: Canadian Environmental Protection Act; BC MWLAP: British Columbia Ministry of Water, Land and Parks; SQC: Sediment Quality Criteria.

recent evidence that PCBs are associated with an upregulation of a number of gene end points in these killer whales.²¹

Risks Related to Sediment Quality Criteria and Tissue Residue Guidelines (Scenario 3). In scenarios where Σ PCB concentrations in sediments are set to equal the three available sediment quality criteria for PCBs in Canada, predicted Σ PCB concentrations in salmon greatly exceed the CCME TRG for wildlife consumers of fish, as well as available toxicity threshold concentrations in modeled killer whales (Figures 2 and 3). In scenarios where Σ PCB concentrations in Chinook salmon were equal to the TRG for fish consuming wildlife of $0.05 \text{ mg}\cdot\text{kg}^{-1}$ ww in Canada, Σ PCB concentrations in NRKW and SRKW are also expected to exceed the toxicity threshold concentration of $1.3 \text{ mg}\cdot\text{kg}^{-1}$ lw in 100% of males and 98% of females, while toxicity threshold concentrations of $10 \text{ mg}\cdot\text{kg}^{-1}$ lw and $17 \text{ mg}\cdot\text{kg}^{-1}$ lw are exceeded in approximately 97% and 86% of males and 29% and 9% of females, respectively.

These calculations illustrate that current sediment quality criteria for PCBs, which are derived for the protection of benthic invertebrates, fail to protect higher trophic level organisms such as killer whales and do not offer meaningful guidance for the interpretation of risks of PCB-contaminated sediments in high trophic level species. The TRG for fish-eating wildlife is also inadequate in its ability to protect killer whales. These findings illustrate the importance of incorporating the

process of food-web biomagnification in the development of sediment quality criteria and tissue residue guidelines for PCBs and other bioaccumulative substances.

Toward Protective Sediment PCB Concentrations for Killer Whales. Σ PCB concentrations in sediments of NRKW and SRKW foraging ranges that are expected to lead to either 95% of Chinook salmon to be below the CCME TRG for wildlife consumers of fish ($0.05 \text{ mg}\cdot\text{kg}^{-1}$ ww) or 95% of killer whales exhibiting Σ PCB concentrations below the three toxicity threshold concentrations are listed in Table 1. These concentrations may be viewed as target concentrations that would, once attained, presumably protect resident killer whales from PCB-related adverse health effects. Transient killer whales may not be protected to the same degree, since they feed on marine mammals and occupy a higher trophic level than residents. These protective Σ PCB concentrations in Chinook salmon and sediments are lower than the current TRG or sediment quality criteria in Canada (Table 1).

Since these protective PCB concentrations are geometric mean concentrations of PCBs in sediments throughout the resident killer whale foraging range, the existence of areas within the foraging range of killer whales with PCB concentrations in sediments greater than the protective geometric mean concentration does not directly imply risks to killer whales. Areas within the foraging range with PCB

Table 1. Geometric Mean \sum PCBs Concentrations in Sediments ($\mu\text{g}\cdot\text{kg}^{-1}$ dw) (a) and in Chinook Salmon ($\mu\text{g}\cdot\text{kg}^{-1}$ ww) (b) of the NRKW and SRKW Foraging Ranges Required to Produce \sum PCBs Concentrations in Chinook Salmon (Diet of Killer Whales) below Canada's Tissue Residue Guideline for Wildlife Consumers of Fish of $0.05 \text{ mg}\cdot\text{kg}^{-1}$ ww or below Toxicity Threshold Concentrations of 17, 10, and $1.3 \text{ mg}\cdot\text{kg}^{-1}$ lw in 95% of Male and Female Northern and Southern Resident Killer Whales^a

	TRG = 0.05	$C_{\text{TT}} = 17$	$C_{\text{TT}} = 10$	$C_{\text{TT}} = 1.3$
a. Sediments				
NRKW male	0.39	0.058	0.034	0.0044
NRKW female	0.39	0.38	0.22	0.029
SRKW male	0.28	0.048	0.028	0.0037
SRKW female	0.28	0.270	0.16	0.021
b. Chinook Salmon				
NRKW male		3.3	2.0	0.25
NRKW female		22	13	1.7
SRKW male		3.8	2.2	0.29
SRKW female		22	13	1.6

^aThe exposure time averaged organic carbon content of the sediments is 3.1% for the NRKW and 1.9% for the SRKW foraging ranges.

concentrations in sediments below the geometric mean can compensate for areas where PCB concentrations are greater than the geometric mean. It also means that, if killer whales (or their prey) forage in an area for only a short duration, the PCB concentrations in the sediments of this areas can be in excess of the "protective" geometric mean PCB concentrations in the sediments as long as, in the remainder of the foraging range, concentrations are sufficiently low for the geometric mean not to be exceeded. Sediment quality criteria for the protection of high trophic level marine mammals with large foraging areas therefore need to consider the geographical distribution of PCB concentrations within the entire foraging range of the animals.

A second issue worth noting is that the relationship between PCB concentrations in sediment and killer whales is affected by the sediment-water concentration ratio for PCBs.³⁶ The sensitivity analysis shows that sediment-water PCB concentration ratios in the majority of the NRKW and SRKW foraging ranges are sufficiently low (likely as a result of significant current or recent atmospheric inputs of PCBs to the water column) for killer whales to receive the majority of their PCB body burden from the water via their diet. If the PCB sediment-water concentration ratios are maintained over time, the PCB concentrations in the sediments listed in Table 1 are appropriate estimates of protective concentrations.

However, if PCB sediment-water concentration ratios change, for example as a result of anthropogenic disposal or removal of PCB contaminated sediments, then protective PCB concentrations in sediments are best determined using eq 3 where α and β are, respectively, 9.5×10^8 and 410 for the NRKW foraging area and 8.7×10^8 and 390 for the SRKW foraging area. If this equation is applied in a backward calculation, protective PCB concentrations in sediments are calculated as a function of the PCB concentration in the water column (Figure 4). This illustrates that protective PCB concentrations in sediments can be substantially greater than those calculated in Table 1 as long as PCB concentrations in the water column are sufficiently low. Figure 4 also illustrates that a critical PCB concentration in the water exists that determines whether any PCB concentration in the sediments is

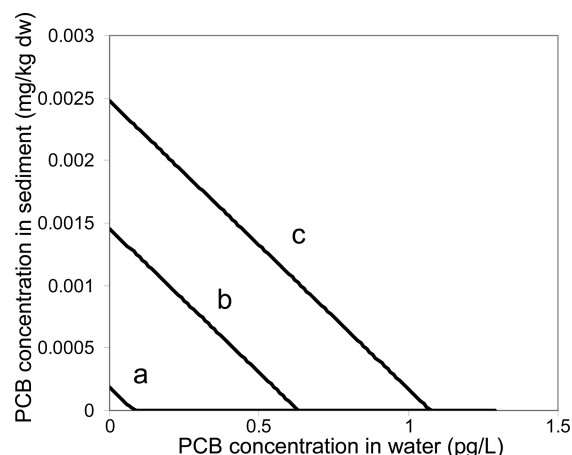


Figure 4. Geometric mean \sum PCB concentration in sediments ($\text{mg}\cdot\text{kg}^{-1}$ dw) expected to produce \sum PCB concentration in sediments in 95% of the male NRKW to be below established toxicity threshold concentrations for marine mammals of 1.3 (a), 10 (b), and $17 \text{ mg}\cdot\text{kg}^{-1}$ lipid (c) as a function of the geometric mean \sum PCB concentration in water ($\text{pg}\cdot\text{L}^{-1}$) in NRKW foraging range.

consistent with the protection goal. This critical concentration (i.e., approximately 1, 0.6, and $0.1 \text{ pg}\cdot\text{L}^{-1}$ for a C_{TT} of respectively of 17, 10, and $1.3 \text{ mg}\cdot\text{kg}^{-1}$ lw) is the PCB concentration in the water, which, without any PCB contamination in the sediment, is expected to produce the maximum concentration in the killer whale that is deemed protective. This critical concentration may be a useful tool to identify whether areas are at all suitable for disposal of PCB contaminated sediments. While this study investigated PCBs, the methodology described for deriving sediment-based criteria for PCBs may be useful to other bioaccumulative substances.

■ ASSOCIATED CONTENT

📄 Supporting Information

Tables listing model input and state variables and empirical PCB concentrations; all model equations; figures of results and rationale for food-web characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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📝 Notes

The authors declare no competing financial interest.

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