Toward Ecosystem-Based Sediment Quality Guidelines for Polychlorinated Biphenyls (PCBs)

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ABSTRACT

To investigate whether Sediment Quality Guidelines (SQGs) for polychlorinated biphenyls (PCBs) in Canada and British Columbia achieve their objective of protecting ecosystems, we measured and compiled concentrations of PCB congeners in sediments, bivalves, crustaceans, fish, and marine mammals from 3 areas off the Pacific coast of British Columbia, Canada. The concentration data showed that whereas PCB concentrations in sediments were predominantly below the SQGs of 20 µg/kg dry weight, large fractions of the PCB concentrations in fish and shellfish species exceeded the tissue residue guideline for the consumption of fish and shellfish by wildlife (i.e., 50 µg/kg wet weight [ww]) but were below the tissue residue guideline for the consumption of fish and shellfish by human populations (i.e., 2000 µg/kg ww). Also, PCB concentrations in marine mammals exceeded toxicity reference concentrations. The concentration data were used to develop species- and location-specific Biota-Sediment Accumulation Factors (BSAF = C_{biota}/C_{sediment}), that were used to estimate PCB concentrations in wildlife species that may exist if the PCB concentration in sediments are equal to the SQGs. The results show that if the PCB concentration is equal to the SQGs, then PCB concentrations in most wildlife species can be expected to exceed the tissue residue guideline for the consumption of fish and shellfish by wildlife species and by humans, as well as toxicity reference concentrations for marine mammals. A methodology for developing SQGs for PCBs that are protective of the health of different wildlife species and human consumers of fish and shellfish from general Canadian and coastal First Nations populations was developed and applied. The proposed guidelines may provide useful guidance to establish SQGs for PCBs that can account for the ecological diversity in coastal environments and that better achieve the intent of the guidelines to protect ecosystems. The proposed methodology for guideline development may also be useful in the development of SQGs for other bioaccumulative substances. Integr Environ Assess Manag 2015;11:689–700. ©2015 SETAC

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INTRODUCTION

Sediment Quality Criteria (SQC), which in some jurisdictions are synonymous with sediment quality guidelines (SOG), are important tools in the environmental risk assessment and risk management of polychlorinated biphenyls (PCBs) and many other anthropogenic contaminants. Because of the high affinity of PCBs for sediments, bed sediments can become reservoirs of PCBs, providing exposure and possible health risks to organisms in aquatic ecosystems over long periods of time (CCME 2001). In Canada, the Canadian Council of Ministers of the Environment (CCME) derive SQG with the intention of protecting all forms of aquatic life and all aspects of their aquatic life cycles throughout an indefinite period of exposure to substances associated with bed sediments, while considering all components of the aquatic ecosystem (for which data are available) and the best available scientific knowledge (CCME 2001). The Canadian SQC for the protection of aquatic life state that "Sediment quality guidelines (SQG) provide scientific benchmarks, or reference

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points, for evaluating the potential for observing adverse biological effects in aquatic systems," and defines the objective of the SQGs to be the protection of the system rather than a particular class of organisms. It is the purpose of this research to investigate whether the SQGs meet this objective and to explore how methods for deriving SQGs can be modified to better achieve this objective.

In several jurisdictions, the derivation of SQGs involves modifications of either 1 or both of 2 methods. The first method developed by MacDonald et al. (1996) follows the empirical approach adopted by the National Oceanic Atmospheric Administration's National Status and Trends Program (NSTP) methodology (Long and Morgan 1990) and is the basis for the CCME sediment quality guideline approach. This approach applies distribution of contaminant concentrations in sediments that are associated with either "effects" or "no effects" in benthic invertebrates. A functional threshold effects level (TEL) is then calculated as the geometric mean of the 15th percentile concentration from the effects data set, and the 50th percentile concentration from the no-effects data set (MacDonald et al. 1996). The TEL is viewed to represent a concentration that would rarely cause biological effects as a result of sediment concentrations of a chemical. In Canada, the TEL is often implemented as the interim SQG (CCME 2001). A probable effects level (PEL) is also calculated as the geometric mean of the 50th percentile concentration of the

effects data and the 85th percentile concentration of the noeffects data. Chemical concentrations in sediment can be evaluated in comparison to both the TEL and PEL. The second method derives anticipated effect levels in sediment from equilibrium partitioning between water and sediments and measured effect levels in water (Di Toro et al. 1991). This method is not used by the CCME for SQG derivation but is used in other jurisdictions. In cases where SQGs do not exist or deemed not to be appropriate, a risk assessment or weight of evidence based methodology is used. Frequently used methods include the "triad" method that involves the application of sediment chemistry, laboratory toxicity tests, and benthic community health metrics to assess risks of contaminants to benthic communities (Chapman 1989), or consensus-based guidelines that can use a combination of empirical and equilibrium partitioning approaches (Swartz 1999; MacDonald et al. 2000). When selecting the method for criteria development, the management goal is critical (Wenning et al. 2005). Management involves balancing environmental, economic, and societal values. In the case of SOGs developed by the CCME's SQGs, the established goal includes the protection of upper trophic level organisms, either for inherent or cultural value or for economic value, including ensuring concentrations of contaminants in economically important fish species are safe for consumption.

In Canada, the interim sediment quality guideline for PCBs is determined by the first method described above and is 0.0215 mg/kg dry weight (dw) sediment (CCME 2001), which in British Columbia (BC) has been modified to 0.020 mg/kg dw sediment (Nagpal 1992; Fast 2006). It is generally recognized that the methodology for the development of sediment quality guidelines is limited to benthic invertebrates and does generally not consider toxicity in higher trophic level organisms such as fish, fish-eating birds, and marine mammals (Wenning et al. 2005). The lack of considering organisms in aquatic ecosystems other than benthic invertebrates is of particular concern for biomagnifying substances, such as PCBs, which achieve their highest concentrations in upper trophic level species and not in benthic invertebrates. The extent to which ecological amplification can increase concentrations of contaminants in organisms of ecosystems above those in benthic invertebrates has been documented to be in the order of a factor of 1000 to 10000 for PCBs (Kelly et al. 2007). As a result, the application of SOGs derived from information on benthic invertebrate species can put higher trophic level species in the ecosystem at substantial health risks, which runs counter to the intent of SQGs. In particular, for bioaccumulative substances that are subject to ecological amplification it is important to develop methods that can produce SQGs that are protective of all organisms in the aquatic system as well as human consumers of fish and other aquatic wildlife.

It is the objective of this study to 1) test if the CCME and BC SQGs for PCBs meet their objective of protecting the organisms of coastal marine ecosystems in British Columbia and human consumers of fish and other marine wildlife species, and 2) investigate how methods for deriving SQGs can be modified to achieve this objective. We focus on PCBs, because they exemplify a class of chemicals that biomagnify in food chains. PCBs have been well studied and much data exist on the environmental concentrations and toxicity of PCBs. This provides an opportunity to test the premise that the SQGs for PCBs, i.e., 21.5 μ g/kg (CCME) or 20 μ g/kg (BC Ministry of Environment [MOE]), based on benthic invertebrate data, meet the goal of the SQGs of adequately protecting the species within the larger aquatic system. It also provides an opportunity to investigate the methodology of sediment quality guideline development and to propose sediment quality guidelines for PCBs that do meet the intent of the SQGs process. The results of this study are likely relevant to other biomagnifying substances such as polybrominated diphenyl ethers (PBDEs), perfluorooctane sulfonates (PFOS), DDT, Hg, and others for which SQGs play an important role in environmental management.

THEORY

For SQGs to consider health risks in wildlife species and humans who consume fish and other wildlife species, it is important to recognize and quantify the relationship between the concentrations in the sediments and those in the wildlife species.

This can be achieved by the Biota-Sediment Accumulation Factors (BSAF_i), which is the ratio of the chemical concentration in biota species i ($C_{B,i}$) in units of g/kg wet weight (ww) and that in sediment (C_S) in units of g/kg dry weight (dw) sediment:

$$BSAF_i = C_{B,i}/C_S.$$
(Eqn. 1)

BSAF_i can also be expressed in terms of lipid normalized and organic carbon (C) normalized concentrations in units of kg organic C/kg lipid content, derived from the concentrations in biota lipids ($C_{L,i}$ in g/kg lipid) and sediment organic C (C_{OC} in g/kg organic carbon in sediment)

$$BSAF_{LOC,i} = C_{Li}/C_{OC}.$$
 (Eqn. 2)

The latter method accounts for the preferential partitioning of lipophilic chemicals in organic carbon of sediment and lipids of organisms and provides a simple methodology for calculating BSAF_i in sediments with different organic C content and organisms with different lipid content. The BSAF_i can be used to calculate guidelines by relating toxicity reference values in organisms to corresponding concentrations in sediments. BSAF_i can be determined empirically using measured concentration data or by using bioaccumulation models or a combination of empirical data and models.

Uncertainty and error need to be considered in the calculation and application of BSAFs. It is often advantageous to express the concentration in sediments and biota in a logarithmic format because environmental concentrations often exhibit considerable variation that often fit lognormal distributions better than normal distributions. In those cases, the $BSAF_{LOC,i}$ can be presented in a logarithmic format as log $BSAF_{LOC,i}$, which implies that a lognormal distribution of the $BSAF_{LOC,i}$ can be presented as a normal distribution of log $BSAF_{LOC,i}$ i.e.,

$$\log BSAF_{LOC,i} = \log C_{L,i} - \log C_{OC}.$$
(Eqn. 3)

Equation 3 provides a method to calculate the chemical concentration in selected biological species from the chemical concentration in the sediments and the $BSAF_{LOC,i}$ as

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$$\log C_{L,i} = \log BSAF_{LOC,i} + \log C_{OC}. \qquad (Eqn. 4)$$

and can be used in a risk assessment if a toxicity reference concentration for species i (C_{TR,i} in g/kg lipid) is available. The $BSAF_{LOC,i}$ can also be used to derive a species i specific

chemical concentration in the sediment (C_{OC,i}) that is expected to result in a $C_{TR,i}$ as

$$\log C_{OC,i} = \log C_{TR,i} - \log BSAF_{LOC,i}.$$
 (Eqn. 5)

The latter method is useful for the development of SQGs and sediment remediation objectives. However, because log $BSAF_{LOC,i}$ and/or log $C_{TR,i}$ are subject to error, it is important to recognize that any sediment quality criterion or sediment remediation target calculated from geometric mean values will imply that a large fraction (e.g., ~50%) of the target population can be expected to exhibit concentrations in excess of the tissue reference concentration. To include uncertainty and error in the sediment quality derivation process, Equation 5 can be modified to determine the geometric mean contaminant concentration in the sediment that will cause 95% of the target population to exhibit concentrations below the toxicity reference concentration, i.e.

$$\log C_{OC,i} = \log C_{TR,i} - \log BSAF_{LOC,i} - 165 \log SD_{BSAF},$$
(Ean. 6)

where SD_{BSAF} is the standard deviation (SD) of the geometric mean BSAF, which can be calculated from the SDs of the log normal distribution of the concentrations in biota and sediments from which the BSAF is calculated

$$SD_{\log BSAF} = \sqrt{(SD_{\log Coc^2} + SD_{\log CB^2})},$$
 (Eqn. 7)

where SD_{Coc} is the standard deviation of log C_{OC} and SD_{CB} is the SD of log C_B . The factor 1.65 applied to the SD specifies the degree to which the cumulative normal distribution of the logarithm of the concentration in the organism exceeds the logarithm of the toxicity reference concentration (Walpole 1968). A factor of 1.65 is consistent with a 5% exceedence of log $C_{B,i}$ over log $C_{TR,i}$ based on a cumulative normal distribution. A factor of 1.96 corresponds with a 2.5% exceedence of log $C_{B,i}$ based on normal distributions. Other values can be selected according to tolerance for false negatives. Finally, proposed dw-based SQGs can be derived for sediments based on organic C content by multiplying $C_{OC,i}$ by the organic C content (e.g., multiplying $C_{OC,i}$ and 0.01 for a sediment with 1% organic C).

The application of Equation 6 for multiple species of an ecosystem provides a method to derive "protective," species specific contaminant concentrations in sediments that can be expected to cause contaminant concentrations in the targeted species that are below toxicity reference concentrations in 95% of individuals of each target species. The combined set of species-specific "protective" contaminant concentrations in sediments can be used to develop SQGs with a range of objectives. For example, the goal of protecting endangered species (e.g., Southern resident killer whales in Canada) may favor the selection of the sediment concentration based on the toxicity reference concentration and BSAF for killer whales or the sediment concentration based on concentrations in Chinook salmon (i.e., the main prey of the Southern resident killer whale) aimed to protect wildlife consumer of fish and the BSAF for Chinook salmon. The goal of protecting clam beds for safe human consumption may favor the selection of sediment concentrations derived to remain below acceptable human health risk estimates for clam consumption. If the goal is the protection of the most sensitive species, then the lowest "protective" sediment concentration for the organisms of the ecosystem can be used. The combined set of protective

sediment concentrations can also be explored probabilistically (similar to an ecological risk assessment), but it may be more appropriate to identify key ecosystem functions and related protection goals. Although this approach still remains rudimentary in its ability to capture ecosystems, it presents a step beyond traditional approaches to SQG development and toward an ecosystem approach to sediment quality development.

METHODOLOGY

General

This study involves the determination of the BSAF of total PCBs from empirical PCB concentrations in sediments and biota samples from different locations in marine water of British Columbia, Canada. The BSAFs are investigated for spatial and species differences and then used to 1) assess the health risks in a range of local resident biological species and human consumers of local seafood products resulting from PCB concentrations at the sediment quality guideline, and 2) to derive target concentrations for PCBs that are protective of wildlife species and human consumers of wildlife species in the BC coastal marine system.

Sample collection and analysis

Sediment and biota samples were collected from Vancouver Harbor, Victoria Harbor, and the Strait of Georgia from 1999 to 2005. Samples were collected as part of several monitoring programs, site-specific risk assessments, and academic endeavors. The use of these samples is not ideal for BSAF development as the samples did not consist of paired sediment chemistry and biota samples, in most cases, and were collected over large spatial areas and over a long time frame. However, the large number of samples from different areas and from multiple species of different trophic levels may provide reasonably representative BSAFs. Samples included surface sediments, collected by removing the top 1 cm from a sediment sample collected with an Eckman grab sampler (n = 80), Blue Mussel (Mytilus trossulus, n = 33), various clam species including Manila clams (Venerupis philippinarum), Butter clams (Saxidomus gigantean), Horse clams (Tresus nuttallii and/or Tresus capax), Geoduck clams (Panopea generosa) from the Strait of Georgia (n = 17), Dungeness crab (*Metacarcinus* magister, hepatopancreas, n = 379), English sole (Parophrys vetulus, n = 23), Ling cod (Ophiodon elongates, n = 8), and blubber biopsies from live captured Harbor seal pups (Phoca *vitulina*, n = 101). None of the selected species are considered migratory species although some exhibit considerable mobility. All samples were analyzed for PCB concentrations in the Regional Dioxin Laboratory at the Institute for Ocean Sciences in Sidney, British Columbia, using high-resolution gas chromatography and mass spectrometry (HRGC/MS) as described in Ikonomou et al. (2001). Concentrations of all detected PCB congeners were summed to determine the total PCB (\sum PCB) concentration. Measurements of coplanar PCB concentrations were not made as part of this analysis and hence not included in \sum PCB concentrations. Lipid contents were available for 237 Dungeness crab samples, 24 English sole samples, 24 mussel samples, 8 lingcod, and 49 blubber samples (see Supplemental Data). **SPCB** Concentrations in marine mammal samples were expressed on a lipid-normalized basis based on the reported lipid content of each sample. Organic C content was not available for sediment samples. However, sediment samples were organic C normalized using reported

organic C contents for Vancouver Harbor (2.8%) (Mackintosh et al. 2006), Victoria Harbor (1.0%) (Krepakevich and Pospelova 2010), and the Strait of Georgia (4.3%) (Burd et al. 2008). Concentrations below the detection limit were treated as zero concentrations. Although this method underestimates \sum PCB concentrations to some degree, the BSA- $F_{LOC,i}$ were found not to be significantly affected by this assumption because the presence of nondetected concentrations appeared to affect both organism and sediment concentrations, causing errors to cancel out. To expand the range of species in this study, we also included previously reported concentrations of PCBs in Chinook salmon (*Oncorhynchus tshawytscha*) and Northern resident (NR) and Southern resident (SR) Orca whales (*Orcinus orca*) from the Strait of Georgia (Alava et al. 2012).

BSAF calculations

Geometric mean BSAFs, in units of kg dw/kg ww and kg OC/kg lipid, were calculated for individual congeners and \sum PCBs. The geometric mean BSAFs (kg OC/kg lipid) was calculated for each species at each location. The SD of the geometric mean BSAF (SD_{BSAF}) was calculated using Equation 7.

Spatial variation of the BSAF

Statistically significant differences in $BSAF_{LOC,I}$ between sites were tested using 1-way analyses of variance (ANOVA) with Tukey Kramer post hoc tests.

Toxicity reference concentrations

Toxicity reference concentrations $(C_{TR,i})$ for PCBs in various wildlife species were compiled from several sources (Table 1). These values were used to calculate corresponding PCB target concentrations in sediments. $C_{TR,i}$'s were selected from multiple sources to represent a range of values, reflecting the uncertainty in toxicity threshold values for PCBs in mammals (Kannan et al. 2000; Levin et al. 2005; Meador et al. 2008; Mos et al. 2010; Beyer and Meador 2011).

Wildlife health risk assessment

BSAFs were used to assess \sum PCBs concentrations in BC West Coast marine species in a theoretical scenario where the

 \sum PCBs concentration in the sediments are equal to BC's sediment quality criterion for PCB of 20 µg/kg dw for sediments with a 1% organic C content, i.e., 2000 µg/kg organic C (Fast 2006) using Equation 3. Calculated \sum PCB concentrations in fish, shellfish, and crabs were then expressed on a ww basis by using the mean lipid content for each species, i.e., 0.35% (Blue Mussel), 5% (English sole), 1.1% (Ling cod), 0.55% (clams), 11% (Dungeness crab), and 14% (Chinook salmon) and compared to the Tissue Residue Guidelines (TRG) for consumption by wildlife (50 µg/kg ww) and by humans (2000 µg/kg ww) (Table 1). Calculated lipid normalized \sum PCB concentrations in marine mammals were compared directly to the toxicity reference concentrations (C_{TR i}) (Table 1).

Human health risk assessment

Following the methodology outlined in the US Environmental Protection Agency (USEPA) (USEPA 2014a) Integrated Risk Information System (IRIS), a Hazard Index (H) and Upper Bound Lifetime Excess Cancer Risk (LCR) were calculated for dietary PCB exposure in human consumers of BC West Coast marine wildlife using USEPA recommended human consumption rates of fish for risk assessment calculations (USEPA 2014a, 2014b). A consumption rate of 22 g of seafood products per day was used for an average North American diet, and a rate of 142 g per day was used for BC West Coast First Nation aboriginal people (USEPA 2014a, 2014b), who consume a diet rich in sea food products. A 70-kg human body weight was used. Calculations were conducted for each species for which empirical data were available, hence assuming that 100% of seafood consumption rate consisted of 1 species (USEPA 2011). A reference dose from the USEPA IRIS database for Arochlor 1254 of 0.02 μ g · kg⁻¹ · d⁻¹ and a slope factor (q) of 2 (kg \cdot d \cdot mg⁻¹), recommended by the USEPA IRIS database were used in the human health risk assessments (USEPA 2014a). According to Health Canada (2004), a Hazard Index greater than 1 indicates that there is a potential of adverse effects but it does not necessarily mean that adverse effects will occur. A Hazard Index less than 1.0 is considered acceptable in Canada (Health Canada 2004). According to USEPA (2000) a LCR between 10^{-4} and 10^{-6} is within the acceptable risk range.

Receptor	TRG/C _{TR}	Units	Assessment endpoint	Reference
Fish and shellfish	50	μg/kg ww	Wildlife consumption of fish and shellfish	Fast 2006
Fish and shellfish	2000	μg/kg ww	Human consumption of fish and shellfish	Fast 2006
Marine mammal	17 000	μg/kg lipid	Immunotoxicity in Harbor seals	Ross et al. 1996
Marine mammal	11 000	μg/kg lipid	Plasma retinol and thyroid hormone concentrations in Harbor seals	Kannan et al. 2000
Marine mammal	10 000	μg/kg lipid	Suppression of natural killer cell activity in harbor seals	Ross et al. 1996
Marine mammal	8600	μg/kg lipid	Plasma retinol and thyroid hormone concentrations in Harbor seals and reduction of hepatic retinol in Otter and Mink liver	Beyer and Meador 2011
Marine mammal	1300	μg/kg lipid	Biomarkers of decreased immune response and altered vitamin A concentrations in Harbor seals	Mos et al. 2010

CTR, ir Toxicity Reference Concentrations; TRG, Tissue Residue Guideline; ww, concentration based on the animal's wet weight.

Ecosystem-based PCB SQGs

BSAFs were used to propose SQGs for PCBs using the method outlined above and formalized in Equation 6. This method produces estimates of \sum PCB concentrations in sediments that are expected to result in \sum PCB concentrations in each of the wildlife and human receptors that fall below either toxicity reference concentrations, tissue residue guide-lines for wildlife consumption and human consumption, a Hazard Index (HI) of 1 (USEPA 1997), and a life-time excess cancer risk (LCR) of 1:100000 or 10⁻⁵ (USEPA 2000) in 95% of individuals of each target receptor.

RESULTS AND DISCUSSION

Sediments

PCB concentrations were dominated by co-eluting congener groups 107/108, 116/125/117, and 153/132 (Figure S1). \sum PCB concentrations in sediments ranged between 257 ng/kg and 2.13 mg/kg and showed large intrasite variabilities, possibly reflecting the occurrence of locations with unusually high PCB concentrations (i.e., hot spots) within each of the study areas. Geometric mean total PCB concentration in sediments did show statistically significant differences (p < 0.05) among the 3 study sites. \sum PCB concentrations in sediments from the Strait of Georgia were significantly lower than those from Victoria Harbor (Figure 1). \sum PCB concentration data exceeded the B sediment quality criterion in 25% (for Vancouver Harbor), 2% (for The Strait of Georgia), and 28% (for Victoria Harbor) of the samples and in 10% of all collected samples.

Biota

Virtually all measured \sum PCB concentrations in Blue mussels, English sole, and Dungeness crabs from Vancouver Harbor and the Strait of Georgia as well as $\sum PCB$ concentrations in clams, Ling cod, and Chinook salmon from the Strait of Georgia were below the TRG for human consumption (Figure 2). Only 10% of the sampled Dungeness crabs from Victoria Harbor showed \sum PCB concentrations above the TRG for human consumption of fish and shellfish (Figure 2). Although the great majority of \sum PCB concentrations in Blue mussels, i.e., 95% to 100%, (from all locations) were below the TRG for consumption by wildlife species, significant fractions of the \sum PCB concentrations in Dungeness crabs (i.e., 60%– 85% from all locations), English sole (10%-50% from Vancouver and Victoria Harbor), and Chinook salmon (14% from the Strait of Georgia) exceeded the TRG for consumption by wildlife species (Figure 2). All measured \sum PCB concentrations in Harbor seals from Vancouver and Victoria Harbor and 50% of the Harbor seals from the Strait of Georgia as well as 95% of \sum PCB concentrations in Northern resident Orca whales exceeded the lowest available toxicity reference concentration for marine mammals of 1300 µg/kg lipid (Figure 2). The highest available toxicity reference concentration for PCBs in marine mammals was exceeded in all Harbor seal samples from Victoria Harbor and 56% of the Orca whale samples. The combined measurements of $\sum PCB$ concentrations show that whereas $\sum PCB$ concentration in sediments of Vancouver Harbor and the Strait of Georgia were generally below the SQG (Figure 1), a significant fraction of observed \sum PCB concentrations in certain fish and crab species were above the TRG for wildlife consumers. These results



Figure 1. Distribution of concentrations of \sum PCBs in sediment from (a) Vancouver Harbor, (b) the Strait of Georgia, and (c) Victoria Harbor. The red line indicated the Canadian SQG of 20 µg/kg dw for \sum PCBs in sediment.

suggest that concentrations of PCBs in sediments below the SQG cannot always be interpreted in terms of a lack of significant health risks to fish consuming wildlife. It should be stressed here that the locations of biota and sediment sampling were not always identical. The associated sampling error can contribute error in any extrapolation of sediment concentrations to wildlife health.

BSAFs

BSAFs of \sum PCB showed a high degree of variation for each species at each site (Figure 3). BSAFs typically show high variability due to variation in sediment and organism characteristics (e.g., organic C content and composition, organism size, growth rate, feeding rate, diet) and spatial variation in chemical concentration (Melwani et al. 2009; Burkhard et al. 2012). The greatest variability in the BSAF was observed for samples collected from Victoria Harbor. The smallest variability in BSAFs was observed for samples from the Strait of Georgia. Sediments within the study locations with very high PCB concentrations (i.e., hotspots) appeared to be the main source of variability in the BSAFs.



Figure 2. Distributions of \sum PCB concentrations (μ g/kg ww) in Blue mussel (mussel; n = 5 VH, n = 19 SoG, n = 9 V), Dungeness crab (crab; n-182 VH, n = 42 SoG, n = 155 V), English sole (fish; n = 9 VH, n = 7 SoG, n = 7 V), and Harbor seals (Harbor seal; n = 5 VH, n = 93 SoG, n-3 V) in Vancouver Harbor (VH), the Strait of Georgia (SoG), and Victoria Harbor (V) and in clams (n = 50), Ling Cod (Cod; n = 7), Chiook salmon (salmon) and Orca whales (Orca) in the Strait of Georgia. The solid red line indicates the tissue residue guideline (TRG) for consumption by wildlife (50 μ g/kg ww) and the dashed red line indicates the TRG for human health (2000 μ g/kg ww). The red box in the graphs for the harbor seal depicts the range of recommended toxicity reference concentrations ranging from 1300 to 17000 μ g/kg lw.



Figure 3. Log BSAF (kg OC/kg lipid) of \sum PCB for different wildlife species at 3 locations in the Pacific North west of North America, i.e., Vancouver Harbor (black), Strait of Georgia (gray), and Victoria Harbor (white). Error bars present standard deviations of the geometric mean.

Among species, geometric mean $BSAF_{LOC,i}$ of $\sum PCB$ ranged from approximately 3.5 kg OC/kg lipid in Blue mussels to approximately 2200 kg OC/kg lipid in Orca whales (Figure 3). This approximately 1000-fold range in the geometric mean BSAFs of Σ PCB among different species illustrates the large differences in the ability of different wildlife species to absorb PCBs from the ambient environment. Figure 3 indicates a general relationship between the BSAF and trophic position. Comparable relationships between the lipid normalized concentration of PCBs in biota and trophic position have been observed by several authors and illustrate the generally recognized behavior of PCBs to biomagnify in food chains (Alava et al. 2012). The BSAF_{LOC,i} of \sum PCB in Chinook salmon is in good agreement with similarly derived BSAFs of PCBs in Lake Trout (Salvelinus namaycush) from Lake Michigan (Burkhard et al. 2004).

The BSAF_{LOC,i} of \sum PCB in each of the sampled species showed no statistical significance (p > 0.05) among the 3 study sites. This may be due to similarities in ecosystem characteristics of the 3 sites, individual species at different locations feeding at similar trophic levels, and the considerable intrasite variability of BSAFs for each species. Because of the lack of statistically significant differences in the BSAFs of \sum PCB among the 3 sites, BSAFs of \sum PCB in each species were combined to derive a single geometric mean BSAF for each species with its 95% probability intervals (Table 2). The characterization of BSAFs may be improved by conducting targeted BSAF studies that include paired sediment and biota sampling over biologically significant area (e.g., a species' feeding range). Bioaccumulation modeling may offer an additional method to determine BSAFs for upper trophic level organisms. Bioaccumulation modeling is particularly useful in cases were relevant information is difficult to obtain empirically or sampling can have detrimental ecosystem effects (e.g., sampling of endangered species). A bioaccumulation model for the derivation of BSAFs was developed by Alava et al. (2012) and showed good agreement with empirical BSAFs.

Wildlife health at the SQG

At \sum PCB concentrations in sediment equal to the BC SQC of 20 µg/kg dw, \sum PCB concentrations can be expected to exceed the \sum PCB tissue residue guideline for wildlife consumption (i.e., 50 µg · kg⁻¹ ww) in Blue mussels by 44%, in clams by 80%, in English sole by 92%, in Ling cod by 98%, in Dungeness crabs by 99%, and by essentially 100% in Chinook salmon (Figure 4). If \sum PCB concentrations in sediments equal the BC SQC of 20 µg/kg dw, \sum PCB concentrations in Harbor seals and Orca whales can be expected to exceed all available toxicity reference concentrations in essentially the entire exposed population (Figure 4). Similar results were obtained by using foraging range specific bioaccumulation model predictions for Orca whale males, females, and pups (Alava et al. 2012). Harbor seal and Orca whale and possibly other

Table 2. Mean log BSAF for ∑PCB in units of kg OC/kg lipid and SDs for various species in the BC marine environment

Species	Log BSAF	SD
Blue mussel	0.86	0.91
Clams	1.37	0.66
Ling cod	1.64	0.57
English sole	0.95	0.80
Dungeness crab	1.42	0.84
Chinook salmon	1.28	0.18
Harbor seal	1.91	0.76
Orca whale (Northern residents)	3.25	0.33
Orca whale (Southern residents)	3.33	0.33

BC, British Columbia; SD, standard deviation.



Figure 4. Distributions of predicted \sum PCB concentrations (μ g/kg ww) in Blue mussel (mussel), clams, Ling cod (cod), English sole (sole), Dungeness crab (crab), Chinook salmon (salmon), Harbor seals (Harbor seals), and female and male resident Orca whales (NR orca) if \sum PCB concentrations in sediments are equal to the SQG of 20 μ g/kg dw. The solid red line indicates the TRG for consumption by wildlife (50 μ g/kg ww) and the dashed red line indicates the TRG for human health (2000 μ g/kg ww). The red box depicts the range of recommended toxicity reference concentrations ranging from 1300 to 17000 μ g/kg lw.

marine mammal populations may experience immunotoxic effects (Ross et al. 1996; Levin et al. 2004), disruption of hormone function, growth, and development (Simms et al. 2000; Tabuchi et al. 2006) if \sum PCB concentrations in the sediments are equal to the sediment quality criterion. These results suggest that the application of current SOGs cannot ensure that PCB concentrations in marine life of West Coast marine ecosystems remain below levels considered safe for wildlife consumption. These results are consistent with the findings displayed in Figure 2. Figure 2 shows that PCB concentrations in populations of wildlife species with a high degree of mobility and a capacity to "integrate" exposure concentrations over large areas are in excess of the tissue residue guideline for the wildlife consumption of fish and shellfish and certain toxicity reference concentrations even though the observed geometric mean PCB concentration in sediments in the 3 areas studied is far below the PCB sediment quality criterion of 20 µg/kg dw.

The results further illustrate that there is a lack of consistency between the SQG and the tissue residue guideline for wildlife consumption because \sum PCB concentrations at the SQC can be expected to produce \sum PCB concentrations in many marine species that are well above the tissue residue guideline. Although \sum PCB concentrations in sediments, water, and biota are related, these relationships are not

reflected in the environmental quality guidelines available for risk assessment and management.

The main reason for the inability of current SQGs to protect higher trophic level organisms is that the sediment quality guidelines are based on toxicity data for small benthic invertebrates. The SQG therefore considers the direct relationship between concentrations in sediments and benthic organisms but does not consider the trophic relationships that can elevate concentrations in organisms of the food web by orders magnitude over those in small benthic invertebrates. These findings illustrate the importance of incorporating the process of food web biomagnification in the development of sediment quality guidelines and tissue residue guidelines for PCBs and other bioaccumulative substances.

Human health

Figure 4 illustrates that in a scenario where $\sum PCB$ concentrations in sediments are equal to the BC SQG of 20 µg/kg dw, $\sum PCB$ concentrations can be expected to exceed the $\sum PCB$ tissue residue guidelines for human consumption of fish and shellfish of 2000 µg · kg⁻¹ ww in Blue mussels by 3%, in clams by 6%, in English sole by 28%, in Ling cod by 22%, in Dungeness crabs by 67%, in Chinook salmon by 97%, and in Harbor seals by 100%. A more

detailed human health risk assessment involving the calculation of a hazard index and lifetime cancer risks from the consumption of seafood products exposed to \sum PCB concentrations in sediment equal to the BC SQG of 20 µg/kg dw indicates that the mean Hazard Index (H) can be expected to exceed 1 for coastal First Nation consumers of any of the diet items that were investigated (Figure 5). The greatest hazard indices were calculated for the consumption of Chinook salmon (H = 545) and Harbor seal meat (H = 7155) assuming a consumption rate of Harbor seal equal to that of fish. Figure 5 further illustrates that if PCB concentrations are at the SQG, consumption of all investigated sea foods except Blue mussels at a typical North American consumption rate is associated with a Hazard Index greater than 1. A Hazard Index greater than 1 indicates the possibility of adverse effects resulting from a life time consumption of these fish and shellfish species.

PCBs have been classified as a probable human carcinogen by the Agency for Research on Cancer and the USEPA (1996). Figure 6 illustrates that if \sum PCB concentrations in sediments are at the SQG, the geometric mean excess lifetime cancer risk of 1:100 000 (often considered to be acceptable for environmental exposures) is exceeded for standard North American or coastal First Nation's consumers of all evaluated sea foods. A geometric mean excess lifetime cancer risk of approximately 2:100 or 2% is estimated for a First Nation's seafood consumption rate of Dungeness crabs or Chinook salmon and 29% for a similar rate of consumption of Harbor seal meat for the hypothetical case where the \sum PCB concentration in sediment is at the SQG. If an acceptable geometric mean excess lifetime cancer risk of 1:1 00 000 is selected as a goal for environmental quality to be represented by the SQG, then the current SQG can be expected to fail the protection of typical North American and coastal First Nation's consumers from PCBs in many different types of seafood products. If a geometric mean Hazard Index greater than 1 is selected as a criterion for environmental quality to be represented by the SQG, then the current SQG also fails to protect North

American and coastal First Nation's consumers of most seafood products (Blue mussels being the exception).

Sediment quality guidelines

If empirical BSAFs (kg dw/kg ww) are used to calculate a \sum PCB concentration in sediments that meets protection goals for wildlife and human health, then \sum PCB concentrations in sediments are found that are in most cases far below the current SQG (Figure 7). \sum PCB concentrations in sediments (for sediment with a 1% organic C content) that are expected to meet the various protection goals for wildlife consumers of seafood products with a 95% probability, range from 0.002 µg/ kg dw or 0.2 µg/kg organic C for the protection of Orca whales (using a $C_{TR,i}$ of 1300 µg/kg lipid) to 0.62 µg/kg dw for sediments with 1% organic C) or 62 µg/kg organic C for the protection of wildlife consumers of Blue mussels (using the TRG for wildlife consumers of 50 μ g/kg ww). \sum PCB concentrations in sediments with a 1% organic C content that are expected to meet human health related protection goals (i.e., H = 1 and $R = 10^{-5}$) with a 95% probability range from 0.005 µg/kg dw or 0.5 µg/kg organic C for First Nation's consumers of Chinook salmon (and even lower for consumers of Harbor seals) to 25 µg/kg dw for Blue mussel consumers at standard North American dietary consumption rates. The current BC and CCME SQGs of 20 µg/kg dw (assuming 1% organic C in sediments) and 21.5 µg/kg dw, respectively, are too high to protect most wildlife species and human consumers of seafood products. The low values for the \sum PCB concentrations in sediments that meet the various protection goals for wildlife and human health are partly caused by including the variability in observed BSAFs. Supplemental Data figure S2 illustrates that even when ignoring the variability in the BSAF, the current BC and CCME SQGs still fail to meet protection goals for most wildlife species and human consumers of seafood products. It can also be argued that the scenario of a uniform spatial distribution of PCB concentrations in the sediments at the guideline value is extreme and unrealistic for species with a large area of geographical distribution such as



Figure 5. Calculated hazard index (H) resulting from the consumption of Blue Mussel, clams, Ling cod, English sole, Dungeness crab, Chinook salmon, and Harbor seals at consumption rates typical for general North Americans (NA Diet) and coastal First Nation's people (FN Diet) if the \sum PCB concentration in the sediments equals the SQG of 20 μ g/kg dw. A Hazard Index greater than 1 indicates a level of concern. Error bars represent the standard deviation of the mean.



Figure 6. Calculated geometric mean excess human life time cancer risk resulting from the consumption Blue mussel, clams, Ling cod, English sole, Dungeness crab, Chinook salmon, and Harbor seals at consumption rates typical for general North Americans (NA Diet) and coastal First Nation's people (FN Diet) if the \sum PCB concentration in the sediments equals the SQG of 20 μ g/kg dw. An excess human life time cancer risk of 0.00001 indicates a level of concern. Error bars represent the standard deviation of the mean.



Figure 7. \sum PCB concentrations in sediments with an organic carbon content of 1% (in units of μ g/kg dw) that are expected to meet with a 95% probability the 1) PCB tissue residue guidelines (TRG) of 50 μ g/kg ww in fish and shellfish for the protection of wildlife consumers and PCB toxicity reference concentrations (C_{TR,i}) for marine mammals recommended by several authors (**top**); and 2) PCB tissue residue guidelines (TRG) of 2000 μ g/kg ww in fish and shellfish for the protection of human consumers, a hazard index H of 1 and upper bound excess life time cancer risk of 10⁻⁵ for human consumers of the various species at general North American (NA) and coastal First Nations (FN) seafood consumption rates (**bottom**).

Chinook salmon and Orca whales. However, even if only 10% of the foraging range contains PCB concentrations in sediment and the other 90% contains no PCBs, \sum PCB concentrations in sediments (for sediment with a 1% organic C content) expected to protect resident Orca whales range from 0.27 to 0.02 or 0.2 μ g/kg dw depending on the selection of the C_{TR}. Similarly, if only 10% of the Chinook salmon foraging range includes PCB contaminated sediments, then 1) a \sum PCB concentration in the sediments of 1.2 and 0.18 μ g/kg dw can be expected to produce a Hazard Index less than 1 in 95% of Chinook salmon consumers at standard North American and First Nations seafood consumption rates respectively, and 2) Σ PCB concentration in the sediments of 0.30 and 0.045 µg/kg dw can be expected to produce an excess life time cancer risk less than 10^{-5} in 95% of Chinook salmon consumers at standard North American and coastal First Nations seafood consumption rates, respectively. These concentrations are still considerably lower than the current PCB SQG of 20 µg/kg dw.

Figure 7 illustrates how BSAFs, either derived from empirical data (as done in this study) or by using food web bioaccumulation models (Alava et al. 2012), could inform the development of sediment quality guidelines. Figure 7 shows that different protection goals are associated with different guideline values. PCB concentrations expected to protect wildlife species differ among species and also differ from those that aim to avoid or reduce human health risks. Hence, the selection of the protection goals is critical in the development of SQGs. Current BC SQGs were derived to protect benthic invertebrates. The approach presented in this article may support an approach where SQGs are derived for a range of ecosystem and human health-related objectives. Examples of such objectives may be the regulation disposal of PCB contaminated sediments at sea, the remediation of contaminated sites, the protection of specific endangered species, the protection of human health, or the preservation of ecosystem integrity. The approach described in this study may not fully address all ecosystem functions but may provide a step toward a more ecosystem-oriented approach to the development of sediment quality guidelines.

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SUPPLEMENTAL DATA

Figure S1. a) Congener profiles of PCBs in Vancouver Harbor sediments. Error bars represent 1 SD of the mean. b) Congener profiles of PCBs in Strait of Georgia sediments. Error bars represent 1 SD of the mean. c) Congener profiles of PCBs in Victoria Harbor sediments. Error bars represent 1 SD of the mean.

Figure S2. \sum PCB concentrations in sediments with an organic C content of 1% (in units of µg/kg dw) that are expected to meet with a 95% probability (i) PCB tissue residue guidelines (TRG) of 50 µg/kg ww in fish and shell fish for the protection of wildlife consumers and PCB toxicity reference concentrations (CTR) for marine mammals recommended by several authors (Top Panel); and (ii) PCB tissue residue guidelines (TRG) of 2000 µg/kg ww in fish and shell fish for the protection of human consumers, a hazard index H of 1 and upper bound excess life time cancer risk of 10-5 for human consumers of each species at general North American (NA) and Fist Nations (FN) seafood consumption rates

(Bottom Panel). The presented values are derived following equation 6 and assuming that there is no uncertainty in the $BSAF_{LOC,I}$, $SD_{BSAF} = 0$.

File S1. An excel spreadsheet with all previously unpublished "raw" data on measured PCB congener concentrations and lipid contents of individual samples.

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