

**DEVELOPING ECOSYSTEM BASED SEDIMENT QUALITY GUIDELINES
IN BRITISH COLUMBIA**

By

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ABSTRACT

Sediment Quality Guidelines (SQG) that do not account for biomagnification of chemicals in marine food chains, may be insufficiently protective of upper trophic level organisms. Biota-Sediment Accumulation Factors ($BSAF = C_{\text{biota}}/C_{\text{sediment}}$) quantify the relationship between concentrations in organisms and the sediment and can be applied to derive SQGs that account for biomagnification. PCB data for four sites on the B.C. coast were used to derive BSAFs. BSAF were used to assess risks to upper trophic level populations from current SQG and to derive new SQG. Bioaccumulation modeling derived BSAFs for additional species and human health risk assessment. Applying BSAFs shows that current guidelines fail to protect Orca whale, Steller sea lion and harbor seal populations or human health. SQGs back-calculated from relevant endpoints for human health, marine mammal, birds and salmon population health were all under $1 \mu\text{g}/\text{kg dw}$ – substantially lower than the current B.C. SQG of $20 \mu\text{g}/\text{kg dw}$.

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GLOSSARY

Bioaccumulation: the combined increase in chemical concentrations in organisms compared to the surrounding environment as a result of bioconcentration and biomagnification (Gobas & Morrison, 2000)

Bioaccumulation Factor (BAF): The ratio of a chemical concentration in an organism to the surrounding environment (Gobas & Morrison, 2000)

Bioconcentration: the process by which organisms' uptake chemicals through respiration and diffusion of hydrophobic chemicals from aqueous to organic media (Gobas & Morrison, 2000)

Biomagnification: The process by which chemical concentrations increase in predators relative to concentrations in diet items as a result of uptake from diet and transfer through the food web (Gobas & Morrison, 2000)

Biomagnification factor (BMF): The ratio of a chemical concentration in an organism to their diet items (Gobas & Morrison, 2000)

Biota-Sediment Accumulation Factor (BSAF): the ratio of a concentration of chemical in biota (C_B) to sediment (C_S). Often expressed in logarithmic form as $\log \text{BSAF} = \log C_B - \log C_S$ (Gobas & Morrison, 2000)

Environmental Quality Criteria (EQC): Numerical concentrations (standards, guidelines and objectives) of chemicals in a specific media that are derived to meet protection goals outlined by the responsible jurisdiction (CCME, 1999)

Octanol-water partition co-efficient (K_{OW}): the ratio of a chemical solubility in octanol to a chemical solubility in water at equilibrium. Used as a metric to describe chemical partitioning between lipid and water phases in aquatic biota. Generally expressed in logarithmic format ($\log K_{OW}$) (Mackay, 1991)

Organic carbon-water partition co-efficient (K_{OC}): the ratio of a chemical solubility in organic carbon to water. Generally estimated from K_{OW} and expressed in logarithmic format ($\log K_{OC}$) (Mackay, 1991)

Octanol-air partition co-efficient (K_{OA}): the ratio of a chemicals solubility in octanol to a chemical solubility in air. Used as a metric to describe chemical partitioning between lipids and air in terrestrial biota. Generally expressed in logarithmic format ($\log K_{OA}$) (Mackay, 1991)

Persistent organic pollutant (POP): class of chemicals defined by their persistence in the environment, tendency to bioaccumulate and toxicity (Stockholm Convention on POPs, 2004)

Probable Effects Level (PEL): The geometric mean of the 50th percentile of an effects distribution and 85th percentile of a no-effects distribution used by the CCME to indicate a level when adverse effects are expected (CCME, 1999)

Sediment Quality Guideline (SQG): a concentration of a contaminant in sediment derived to meet protection goals (CCME, 1999)

Steady state: A state where the total flux of chemical into an particular phase equals the total flux out with no net change in mass or concentration of the chemical (Gobas & Morrison, 2000)

Tissue Residue Guideline (TRG): a guideline value for whole fish tissue concentrations derived from consumption rates and TRVs to be safe for consumers of the fish (CCME, 1999)

Threshold Effect Level (TEL): The geometric mean of the 15th percentile of an effects distribution and 50th percentile of a no-effects distribution used by the CCME as interim SQGs (CCME, 1999)

Toxicity Reference Value: an exposure concentration or dose of contaminant that is not expected to cause an unacceptable level of effect to a receptor (CCME, 1999)

Trophic position: A measure of an organism's trophic status and thus level in a food web which, by providing non-integer quantities, considers the effects of omnivory, cannibalism, feeding loops, and scavenging on food web structure (Vander Zanden & Rasmussen, 1996)

1.0 INTRODUCTION

1.1 Persistent Organic Pollutants

Persistent organic pollutants, which include legacy compounds like PCBs, as well as new emerging chemicals such as polybrominated diphenyl ethers (PBDEs) and perfluorinated octanoic acids (PFOS/PFOA), remain significant management issues in many parts of Canada. As a signatory of the Stockholm Convention (2004) Canada is required to take steps toward reducing and, as much as possible, eliminating the use and production of POPs. In Canada, the Canadian Environmental Protection Act (1999) is the major piece of legislation governing environmental quality. Under Section 5 of CEPA, the procedure for the Control of Toxic Substances, all chemicals manufactured, used or imported in Canada must be evaluated for persistence, bioaccumulation and inherent toxicity. Chemicals determined to possess these three qualities are added to the Schedule 1 List of Toxic Substances, at which point the Minister of the Environment may enact regulations for a chemical to ensure human and environmental health is protected (CEPA, 1999). The Species at Risk Act (SARA) also applies to the management of contaminants by ensuring that habitats for threatened species are protected from destruction. In response to risks from chemical contaminants regulations may be enacted under CEPA or SARA requiring the management or remediation of environmental pollutants. Regulations may include restrictions on importing and exporting chemicals,

restrictions on discharges to the environment, and/or the development of environmental quality criteria.

1.2 Environmental Quality Criteria

Environmental quality criteria (EQC) refer to guidelines (EQG), standards (EQS) and objectives (EQO) set out by governmental organizations as an indication of chemical concentrations expected to be safe in a particular environmental medium. EQC act as a set of requirements that an environment should meet to be considered 'safe' from anticipated adverse effects as a result of a chemicals concentration. Contaminant concentrations below EQC, are assumed to indicate that the specified environment and species are safe from adverse effects of the chemical (CCME, 2001). EQC can be derived for any media where chemicals pose potential risks to wildlife, ecosystem or human health, including water, sediment, soil, air and tissue. In Canada, the Canadian Council of Ministers of the Environment (CCME) over sees the process of deriving EQC. The CCME is composed of Ministers of the Environment from federal and provincial governments, who determine national environmental priorities, focusing on issues that are national or international, and require intergovernmental cooperation for major changes to take place. The CCME derives Environmental Quality Guidelines, which are distinct from standards and objectives in that they are not legally binding, but provide scientific benchmarks for evaluating the potential for adverse effects to aquatic ecosystems as a result of a chemical's concentration. These guidelines may also act as goals for remediation programs, guidelines for disposal at sea programs, benchmarks for

international discussions on emission reduction and trading agreements, and in the assessment of the efficacy of regulations and monitoring programs.

For EQC to be adequately protective of the species and ecosystems in which they are embedded, the methods used to derive the guidelines must accurately describe a concentration in one medium that results in concentrations below toxicity thresholds for all biota, which requires considering environmental partitioning of chemicals, movement of chemicals through the systems, the trophic ecology of biota and potential biomagnification of chemicals through food webs. Guidelines that fail to consider these processes may result in toxic effects to organism even when environmental concentrations are perceived to be safe, resulting in unnoticed and unmanaged negative effects to the ecosystem.

Sediment Quality Guidelines are particularly important for persistent organic pollutants (POP), as the hydrophobic properties of these chemicals cause them to preferentially partition in the organic carbon of sediments in aquatic systems rather than in the water phase. Sediments may accumulate chemicals overtime, and may act as long-term reservoirs of chemicals to the aquatic environment and its organisms (CCME, 2001). Sediments also act as habitats for many invertebrate and benthic species, which are directly exposed to chemicals present. SQGs are a more practical means of environmental monitoring for POP's as concentrations may be below detectable levels in water but at measureable concentrations in sediments. SQG's are developed for total concentration of chemicals in freshwater and marine surface sediments, which correspond to the top 5cm of sediment, and provide scientific benchmarks for

evaluating the potential for adverse effects to aquatic ecosystems as a result of chemical concentrations.

The CCME derives SQGs which are numerical concentrations of a particular chemical in a sediment with the intentions of being protective of all forms of aquatic life during all life stages for an indefinite time period, while considering all components of the aquatic ecosystem for which relevant data is available and the best available scientific knowledge (CCME, 2001). While the CCME recognizes that the use of benthic invertebrates in the derivation method may result in guidelines that are under protective of upper trophic level organisms from the risks associated with biomagnifying chemicals, the overall goal of the CCME SQG is to protect all aquatic life at all times (CCME, 2001). The CCME uses a two-method approach to derive SQG: a statistical approach adapted from the USA National Status and Trends Program (NSTP), and a Spiked Sediment Toxicity Test (SSTT) approach. The NSTP method derives two guidelines, an upper and lower value that creates three ranges of chemical concentrations corresponding to levels that are rarely, occasionally and frequently associated with adverse biological effects (CCME, 2001). The first step in this methodology is to collect all relevant data from the Biological Effects Database for Sediments (BEDS), and generating an 'effect' and 'no effect' distribution of sediment concentrations. From these two distributions, a functional threshold effects level (TEL) is determined 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. Next, a probable effects level (PEL) is

derived as the geometric mean of the 50th percentile concentration of the effects data and the 85th percentile concentration of the no-effects data. The TEL indicates a concentration that is statistically dominated by no-effects data, and should represent a value that would rarely see biological effects as a result of sediment concentrations. The TEL may be implemented as the SQG, however if there is much uncertainty regarding chemical behaviour and sediment chemistry a safety factor may be applied. By establishing ranges, this method provides a practical means to assess risks from chemical concentrations in aquatic systems evaluating chemical concentration with regards to both the TEL and PEL.

The CCME also utilizes a Spiked Sediment Toxicity Test approach, where sediments are spiked with known concentrations of chemicals to establish cause and effects relationships for biological effects. Acute and chronic data developed here can be used to indicate concentrations in sediment below which are considered safe for aquatic life (Lamberson & Swartz, 1992). From this data, guidelines are derived from no-observed effect concentrations or lowest-observed effect concentrations and the application of safety factors to account for uncertainties. However, there is a lack of available data using this approach, and so it has rarely been applied. Guidelines derived using only the NSTP method are considered interim guidelines until the SSTT method can support a weight of evidence approach to create full SQG's; currently all guidelines are only interim guidelines.

The derivation method used for SQG has a direct impact on the numerical guideline and the ability of this guideline to protect the aquatic ecosystem. SQGs

are intended to be protective of all marine organisms, however the derivation process does not consider all marine organisms. The derivation methodology only uses benthic invertebrates in calculations, and does not consider toxic effect levels or anticipated concentrations in higher trophic level organisms such as fish eating birds, seals and whales. Upper trophic level organisms are particularly vulnerable to biomagnifying chemicals as these reach highest concentrations in the upper trophic levels. These organisms are often the first to experience adverse effects (Gobas & Morrison, 2000). The derivation method for SQG does not consider the biomagnification of persistent organic pollutants in the food chain, which results in chemical concentrations that are highest in top predators. Guidelines derived using toxicity data for lower food chain organisms or that fail to quantify the biomagnification of POP's may not be protective of upper trophic level organisms including marine mammals, birds and humans.

The magnitude of biomagnification is dependent on chemical properties, food chain characteristics, magnitude of exposure and an organism's ability to metabolize the chemicals. For PCB's, biomagnification can result in 10,000X to 100,000X increases in chemical concentrations up food webs. The importance of considering biomagnification in guideline development is evident in the resident Orca whale (*Orcinus orca*) population off the B.C. coast. Sediment concentrations of PCBs in the Strait of Georgia have been reported well below the Canadian Counsel of Ministers of the Environment (CCME) SQG of 21.5 µg/kg (Johannessen, 2008), however the resident Killer whales have high concentrations of PCB and increased risks of adverse health effects as a result

(Hickie et. al, 2007; Ross et. al, 2000). A clear disconnect exists between the guideline value determined to be safe and the effects on the exposed organisms. The risks to marine mammals and other top predators from PCB and newly emerging chemicals such as PDBEs is ongoing, a pressing need exists to to develop ecosystem-based approaches to derive SQG and other environmental benchmarks that accurately quantify and minimize risks to marine systems.

Here, I examine PCB concentrations in sediment and biota in the Northwest Pacific food web with the following objectives:

1.3 Objectives

The overall purpose of this research is to develop and test a better method for the derivation of sediment quality guidelines that is aimed to protect food-webs of aquatic ecosystems.

To achieve this larger objective, this research projects aims to:

1. Compile empirical biota-sediment accumulation factors (BSAF) for PCB's in marine food webs from concentrations in sediment and biota to calculate biota-sediment accumulation factors for criteria development and to investigate the main factors causing variability and uncertainty in the BSAF.
2. Estimate BSAFs using a bioaccumulation model for PCBs and evaluate the model's predictive ability.
3. Apply empirical and model predicted BSAF to assess the risk of current SQGs in British Columbia and calculate SQG that meet a variety of

protection goals including human health and the health of upper trophic level organisms.

2.0 BACKGROUND

2.1 Polychlorinated Biphenyls (PCB)

PCBs are a class of chemicals developed commercially in the 1930's for various uses in electrical equipment such as dielectric fluids, lubricants, plasticizers and sealants and many other uses (Environment Canada, 1997). PCBs consist of two benzene rings attached by a single carbon bond, containing from 2 to 10 chlorine atoms, thus have 209 possible congeners (Figure 1). The physical and chemical properties of each congener are highly reliant on the degree of chlorination.

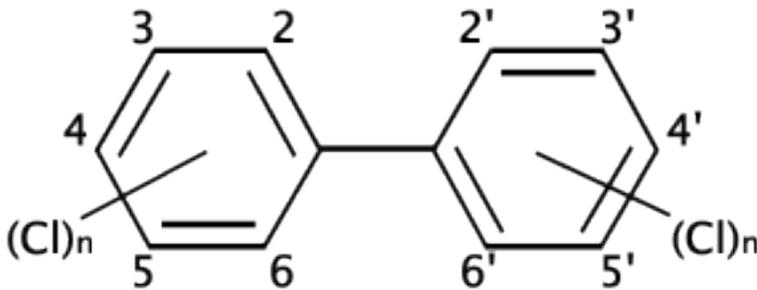


Figure 1: Structure of generic PCB molecule. The number of Cl atoms can range from 2 to 10.

Though banned in 1977, PCBs are ubiquitous in the environment as a result of their physical and chemical properties (ie: they are resistant to breakdown by heat, acids, bases and light), resulting in high persistence in the environment. PCBs are also highly lipophilic - preferentially partitioning in lipids of

organisms and binding tightly to organic carbon in dissolved, suspended or surface sediment in aquatic systems (Environment Canada, 1997).

PCBs are considered bioaccumulating chemicals - the concentration in organisms increases above external water concentrations through uptake from respiration, dermal absorption and dietary uptake. Bioaccumulation is the combined effect of bioconcentration and biomagnification. Bioconcentration refers to the increase in the chemical concentration of an organism compared to external aquatic environments from exposure to water born chemicals (Gobas & Morrison, 2000). Biomagnification refers to the uptake of chemicals through the diet, in which an organism's internal concentration then exceeds that of the diet items (Gobas & Morrison, 2000). Biomagnification can result in upper trophic level organisms reaching chemical concentrations orders of magnitude greater than the surrounding environment as chemical concentrations increase with each level of the food web. As a result of biomagnification, many upper trophic level marine mammals experience very high levels of PCBs including salmon (Cullon et. al, 2009), Harbor seals (Cullon et. al, 2005; Ross et. al, 2003), Steller sea lions (Krahn et. al, 2001) and Orca whales (Krahn et. al, 2007; Ross et. al, 2000).

PCBs exhibit toxic action through two modes of toxic action, generally referred to as 'dioxin-like' and 'non-dioxin like' toxicity. Co-planer PCBs which lack chlorine atoms in the ortho position (ie: adjacent to the carbon-carbon bond) are considered 'dioxin like' as the mode of acute toxic action is similar to that of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (Andersson *et al.*, 2000). Non-dioxin like congeners also exhibit toxic action. Neurotoxicity, neutrophil activation, increased insulin

release and activation of ryanodine-sensitive Ca^{2+} channels are reported toxic effects of non-dioxin like or non-coplanar congeners (Fisher et. al., 1998). A number of studies have reported toxic effects to marine mammals as a result of PCB exposure. These effects include reproductive impairment (Addison, 1989), immunotoxicity (Ross et. al, 1995; Ross et. al, 1996, Levin et. al, 2005), skeletal abnormalities (Ross et. al, 2000), disruption of vitamin A dynamics (Simms et. al, 1999) and endocrine disruption (Ross et. al, 1996, Ross et. al, 2000, Tabuchi et. al, 2000). PCBs are also considered probable carcinogenic substances by the International Agency for Research on Cancer and have been linked to cancer in both marine mammals (Ylitalo et. al, 2005) and humans (Bertazzi et. al, 2001).

2.2 Biota-Sediment Accumulation Factors

There are a number of measure of bioaccumulation, including bioaccumulation factors (BAF = concentration in biota / concentration in water), biomagnification factors (BMF = concentration in predator / concentration in prey), trophic magnification factors (TMF = concentration in top trophic level / concentration in one trophic level lower), or biota-sediment accumulation factors (BSAF = concentration in biota / concentration in sediment). Using bioaccumulation indicators offers a method for developing guidelines that incorporates the both the process of bioconcentration and biomagnification. Specifically, BSAF's can be used to develop SQGs that account for the bioaccumulation of chemicals, thus protecting upper trophic level organisms left vulnerable by the current approach.

The BSAF is the ratio of the chemical concentration in biota to that in sediment:

$$\text{BSAF} = C_B / C_S \quad (1)$$

where BSAF is the biota-sediment accumulation factor in kg dry weight/kg wet weight, C_B is the concentration of contaminant in fish in g/kg wet weight and C_S is the concentration in the sediment in g/kg dry weight sediment. BSAFs can also be expressed in terms of lipid normalized and organic carbon normalized concentrations in units of kg organic carbon/kg lipid content, derived from the concentration in biota in g/kg lipid and concentration in the sediment in g/kg organic carbon in sediment. The latter method accounts for the preferential partitioning of lipophilic chemicals in organic content and lipid content of sediment and fish, giving a more general measure of accumulation that is independent of the variations in organic carbon in sediments and lipid content in organisms. When calculated for upper trophic level organisms, BSAFs are indicators of the magnitude of biomagnification that occurs between sediment and a particular organism. BSAF's can then be used to calculate guidelines by relating safe concentrations in organisms to corresponding concentrations in sediments. BSAFs can be determined empirically using data from contaminated sites, or determined using bioaccumulation modeling.

Uncertainty and error need to be considered in the calculation and application of BSAFs, thus it is advantageous to express the concentration in the sediments and in biota in a logarithmic format as $\log C_B$ and $\log C_S$. The benefit of presenting the concentrations on a lognormal basis is that environmental

concentrations often exhibit considerable variation that tend to fit lognormal distributions better than normal distributions. The BSAF is then also presented in a logarithmic format as $\log \text{BSAF}$, which implies that a lognormal distribution of the BSAF can be presented as a normal distribution of $\log \text{BSAF}$. In essence, this transforms equation 1 in its logarithmic equivalent:

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

The BSAF provides a method to calculate the chemical concentration in selected biological species from the chemical concentration in the sediments as:

$$\log C_B = \log \text{BSAF} + \log C_S \quad (3)$$

This 'forward' method is used for risk assessment where a known or anticipated concentration of a chemical in sediment is used to predict concentrations in biota, which are then compared to toxicity residue values or related measures of chemical toxicity.

The BSAF can also be used to derive a chemical concentration in the sediment that is expected to result in a particular concentration C_B as:

$$\log C_S = \log C_{\text{TRV}} - \log \text{BSAF} \quad (4)$$

Where C_{TRV} is the target chemical concentration in biota determined by a toxicity reference value (TRV) or similar benchmark. This 'backward' method is useful for the development of sediment quality criteria and sediment remediation objectives as a target concentration in a particular organism is used with the BSAF to calculate a sediment concentration derived to meet the goal.

Using equation 4 generates a lognormal distribution of sediment concentrations. However if the mean of this distribution is the sediment quality criterion or sediment remediation target, then approximately 50% of the target population can be expected to exhibit concentrations in excess of the tissue residue values chosen for the calculation. In this scenario the guideline would fail to meet a protection goal of protecting 95% of a population from adverse effects. Hence, it is important to incorporate the uncertainty and/or error in the calculations.

In the forward, risk assessment approach errors and uncertainty associated with empirical data and natural variation are propagated in the estimate of $\log C_B$ and can be expressed in terms of the standard deviation of the geometric mean BSAF (SD_{BSAF}). The SD_{BSAF} can be calculated from the standard deviations of the log-normal distribution of C_S and C_B from which BSAF are calculated, as:

$$SD_{\log BSAF} = \sqrt{(SD_{\log C_S}^2 + SD_{\log C_B}^2)} \quad (5)$$

Where:

SD_{C_S} is the standard deviation of the geometric mean sediment concentration ($\log C_S$)

SD_{C_B} is the standard deviation of the geometric mean biota concentration ($\log C_B$)

In a backward calculation (with the objective to derive sediment quality criteria or sediment remediation objectives), uncertainty and error can be included to determine the geometric mean contaminant concentration in the

sediment that will cause 95% of the target population to exhibit concentrations below the TRV, i.e.

$$\log C_S = \log C_{TRV} - \log BSAF - 1.96 \log SD_{BSAF} \quad (6)$$

While equation (4) calculates sediment distribution centered on a threshold value, incorporating this uncertainty, equation (6) establishes a sediment distribution in which 95% of biota concentrations are below the threshold values chosen.

3.0 METHODOLOGY

3.1 Sediment and Biota Sampling and Analysis

Sediment and biota samples were collected from sites off the coast of British Columbia since 1997 as part of ongoing research projects at the Institute of Ocean Sciences in Sydney, B.C. The sampled media here include surface sediments, invertebrates such as Dungeness Crab (*Metacarcinus magister*), bivalves such as Blue mussels (*Mytilus trossulus*), a number of clam species, fish species including mainly English sole (*Parophrys vetulus*), but also Lingcod (*Ophiodon elongatus*), Starry flounder (*Platichthys stellatus*), and Harbor seal (*Phoca vitulina*) blubber samples as mammalian representatives.

Exact sampling coordinates are unknown, however samples were grouped into four larger sites based on the general sampling area: i.e., Vancouver harbor, Victoria harbor, the Strait of Georgia, and the Central coast (Kitimat, Prince Rupert and Queen Charlotte Strait). It was assumed that sediment samples and biota samples from each site were sampled from the same area and represent

the relationship between sediment and biota concentrations for resident organism of the area.

All samples were analyzed in the Regional Dioxin Laboratory at the Institute for Ocean Sciences in Sidney B.C. under the supervision of Dr. Michael Ikonomou using high-resolution gas chromatography and mass spectrometry (HRGC/MS). Details on sample preparation, analysis procedures and QA/QC can be found in Ikonomou et. al, 2001 and Mackintosh, 2002. Sample numbers from each site and media are shown in Table 1. Samples were analyzed for individual PCB congener concentrations and summed to represent total PCB concentrations for the samples. Congeners with less than 70% of samples above detection limits were not included and congener concentrations that were below detection limits were counted as zero concentrations. PCB concentrations for sediment and biota are reported in Appendix tables A1-A21.

Table 1: Sample size for each species sampled in each site.

Sample Size	Vancouver	Strait of Georgia	Victoria	Central Coast
Dungeness Crab	91	42	158	99
Red Rock Crab	2	10	0	0
Blue Mussels	10	19	8	3
Clams (all spp.)	0	61	0	46
English Sole	9	7	7	3
Lingcod	2	12	0	0
Starry Flounder	0	7	0	0
Harbor Seals	5	91	3	16
Sediment	17	33	30	76

3.2 Empirical BSAF Calculations

Geometric mean BSAFs were calculated for individual congeners and total PCBs using equation 2 after log-transforming sediment and biota concentrations

of PCB in pg/g. Sediment data was converted to pg PCB/g organic carbon using an average OC content of the sediments at the site (taken from literature data as OC content of sediments samples was unavailable). Organic carbon contents used can be found in Table 2. Biota concentrations were converted to pg PCB/g lipid using the lipid content of the actual samples. When lipid or moisture content of a particular sample was unavailable, the average value for samples taken from that site was used.

Variability in BSAFs was calculated using equation 5 as the geometric mean of the standard deviation of PCB concentrations in sediment and the standard deviation of PCB concentrations in biota. All statistical analysis was done in JMP 9.

Table 2: Average yearly mean air and water temperatures (°C) and organic carbon contents (%) for Vancouver Harbor, the Strait of Georgia, Victoria and Kitimat Harbors.

	Vancouver	Strait of Georgia	Victoria	Central Coast
Mean Air Temp (°C)	9.3	9.3	13.9	11.2
Mean Water Temp (°C)	9.1	9.1	8.67	8.75
Mean OC%	2.80%	4.27%	1.00%	1.4%
Source	Masson, 2007; Mackintosh, 2004	Masson, 2007; Burd et. al. 2008	Krepatevich & Pospelova, 2010	Stevenson, 2003

3.3 Bioaccumulation Modeling of BSAFs

Arnot and Gobas (2004) developed the bioaccumulation model used here for fish and invertebrates and more recently, Alava Saltos (2011) included a model for birds and marine mammals. The model incorporates multiple marine

mammals and a human health assessment following the methodology of Gobas and Arnot (2010). The objective of this model is to calculate the concentration of PCB in fish, birds and marine mammals from sediment and water concentrations and determine BSAFs accordingly. The model aims to include more species and trophic levels than empirical data are currently available for, allowing for use as management tool that can incorporate a better ecosystem perspective.

The model assumes that PCB concentrations have reached a steady-state to estimate PCB concentrations in biota, thus assuming that sufficient time has elapsed for PCBs to reach steady-state. However, equilibrium is reached more quickly in smaller organisms and often takes longer in marine mammals, thus steady state models may over estimate concentrations in biota if equilibrium has not been reached or if sediment concentrations are falling over time as a result of sedimentation (Natale, 2007). The model assumes resident organisms spend 100% of their time within the defined system – an assumption that is appropriate for species with a small habitat range but may result in an overestimation of PCB concentrations for some migratory species such as salmon or Orca whale.

The model requires water concentrations as an input variable. As water concentrations were unavailable, water concentrations were estimated from sediment concentrations, fraction organic carbon and K_{OC} . Organisms are more sensitive to changes in water concentrations of PCB than sediment concentrations of PCB, and the water-sediment partitioning relationship of PCB is described by K_{OC} as estimated from K_{OW} values. Werner (2010) has shown this method may over estimate water concentration which may result in an over

prediction of BSAF values if water concentrations are over estimated, if the system has not reached equilibrium or differences in sediment chemistry result in a inaccurate estimation of the water-sediment PCB relationship.

A total of 38 congeners or co-eluting congeners were chosen for inclusion in the model. PCB congeners vary in physical and chemical properties. Relevant physical chemical properties of congeners and model inputs can be found in Tables A22-A23 of the Appendix. BSAFs were calculated for each congener and as the sum of all congeners to represent total PCBs. Models were parameterized for each site, adjusting temperature and organic carbon content of sediments (Table 2). Model equations calculating the flux of PCBs were unchanged from previous versions of the model and have been well described by Gobas and Arnot (2010), Alava Saltos (2011) and Arnot and Gobas (2004).

3.4 Quantifying Uncertainty in Model Outputs

Uncertainties in model predicted BSAFs are quantified by comparing model predicted BSAFs to empirical concentrations of PCBs and calculating Model Bias: a measure of the central tendency for over-under prediction of the model. Model bias is determined for each species by comparing the predicted PCB concentrations in biota for each congener to the empirical data concentrations using:

$$MB_j = 10^{\frac{\sum \log CB_p / \log CB_o}{n}} \quad (7)$$

where:

MB_j = species specific model bias

CB_p = predicted biota concentration for congener

CB_o = observed biota concentration for congener

Model bias can also be calculated for total PCBs using the predicted and observed concentrations of the sum of all congeners in the model. Model bias indicates the models systematic over ($MB > 1$) or under ($MB < 1$) prediction of BSAFs. The standard deviation of MB (SD_{MB}) represents the variability in model bias and uncertainty in the model. Model bias was used to quantify uncertainty in model outputs as it is easily calculated when empirical data are available for comparison. MB gives a measure of the general tendency of the model accuracy allowing for inclusion of natural variation expected in PCB or individual congener concentrations within a population, which is needed for management decisions based on model results.

3.5 Coastal Food Web

The food web of the west coast marine system is complex and simplified here by choosing organisms of ecological or economic importance and grouping similar organisms as classes following the methodology in Gobas and Arnot (2004). It is assumed that organisms at similar trophic levels exhibit similar concentrations of PCBs and can thus be grouped as a trophic guild for simplification purposes - incorporating each individual species as diet items is unnecessarily complex for modeling purposes. Organisms were chosen based on importance in management decisions, importance as diet items or importance for the transfer of PCBs in marine food webs.

The general food web was assumed to be the same for all sites, but environmental parameters were adapted accordingly including water and air temperatures and organic carbon content of sediments (Table 2). The diet composition of a species influences PCB uptake from diet and in turn influences BSAF values. Alava Saltos (2011) showed PCB concentrations in Orca whales had a low sensitivity to changes in the costal food web structure, so potential inter-site differences in food web structures were considered insignificant. The diet of Orca whales was studied by Ford et. al. (2010) and used as the basis for the Orca whale food web. Similar studies on Steller sea lion diets by Olesiuk et. al. (2004) were used as the basis for the Steller sea lion component of the food web. Harbor seal diets were determined by a study from Cullon et. al. (2009). Diets of lower trophic level organisms were unchanged from previous versions of the model, mainly Gobas and Arnot (2004). A diet matrix is shown in Figure 2.

The model includes one class for phytoplankton and one for zooplankton. Eight classes of benthic invertebrates are included: two species of polychetes, amphipods, Dungeness crab, Mysis species, blue mussel, oyster and Crangon species. 14 species of fish are included: Shiner surfperch, Walleye Pollock, Northern anchovy, Pacific herring, English sole, Gonatid squid, Plainfin midshipman, Lingcod, Pacific hake, Sablefish, Halibut, Chum, Coho and Chinook salmon. Cormorants and Great Blue Heron were chosen as representative avian species. Harbor seals, Steller sea lions, and Orca whale represent marine mammals. For avian and marine mammal species male, female and juveniles are

included in the model. Scientific names and relevant species-specific input parameters are reported in Appendix tables A24-A27.

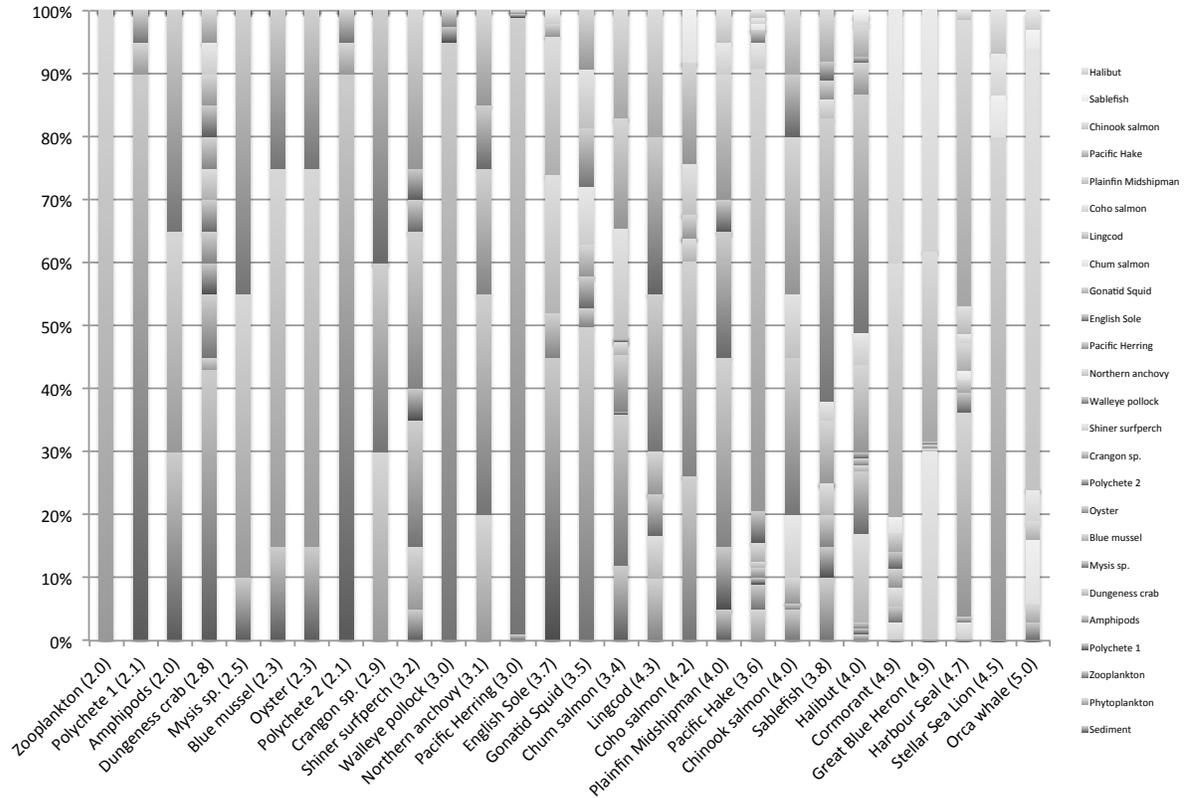


Figure 2: Diet matrix used for West Coast Ecosystem Food Web. Common names and trophic levels are reported (TL). TL reported from Alava Saltos (2011) and Condon (2007).

3.6 Ecological Risk Assessment of Current SQG for PCB

Once calculated, BSAFs were applied using Equation 3 to assess the risk from the current British Columbia sediment quality guidelines for PCBs of 0.02 µg/g (BC Water Quality Guideline Report, 2006) by assuming the concentrations of PCBs in sediments in the foraging ranges of organisms is equal to the guideline value. Predicted PCB concentrations in biota were compared to Toxicity Reference Values (TRV) for PCB in mammals (1300 µg/kg lipid- Mos, 2010), for PCB in birds (5000 µg/kg ww – Hoffman et. al, 1996) and BC Tissue

Residue Guideline (TRG) for PCB in shellfish and fish for consumption by wildlife, (0.1 µg/g ww - BC Water Quality Guideline Report, 2006), and BC TRG for shellfish and fish for human consumption (2.0µg/g ww - BC Water Quality Guideline Report, 2006). TRG's are derived to indicate chemical concentrations in prey deemed to be safe for the predators consuming them including humans. TRGs are included here to determine if SQG's meet legal obligations for protection and investigate the agreement between guidelines for varying media. Guidelines are derived for multiple medias (water, sediment, tissue). However, if environmental partitioning behavior of chemicals is not considered in the derivation process, it is possible for these guidelines to conflict with each other. For example, though sediment concentrations are below the sediment quality guideline, other media may contain concentrations above their respective guidelines. By comparing the PCB concentrations in fish and shellfish expected from PCB concentrations in sediment equal to guidelines to the TRG, the agreement or conflict of these guidelines can be assessed.

To appropriately assess the risks to aquatic organisms from PCB concentrations, it is important to quantify the uncertainty in PCB concentrations in biota a result of the uncertainty in BSAF values. For empirically derived BSAF, SD_{BSAF} was used to express this uncertainty and was calculated as the geometric mean of the standard deviations of PCB concentrations in biota and sediment using Equation 5. There is uncertainty associated with model predicted PCB concentrations as a result of uncertainty in model inputs and assumptions – this uncertainty must be quantified and expressed to apply BSAFs in an appropriate

method as well. To quantify the uncertainty related to model derived BSAF, Equation 7 is used to express the variability in MB as the SD_{MB} , which captures the uncertainty in model outputs.

3.7 Human Health Risk Assessment of Current SQG for PCB

The model also includes a human health assessment for PCBs. This assessment was included as a means to quantify how protective current sediment quality guidelines are of human health and to calculate SQG that would result in PCB concentrations in fish that are safe for human consumption. An average Canadian diet and a traditional First Nation diet were considered as the heavy reliance on fish in subsistence diets can lead to increased risks for Coastal First Nation populations. Parameters used in the HHRA can be found in Table 4 and represent EPA standard assumptions for HHRA for the typical North American diet, while First Nation average consumption values were taken from Mos et. al, 2004. The risk to human health from consumption of Chinook salmon and Dungeness crab were calculated individually and then summed to represent total risk as a hazard index for threshold toxicity and a lifetime excess human cancer risk. Hazard index (H) > 1 indicates a risk of health effects from threshold toxicity, where H < 1 is considered safe. H is calculated as:

$$H = (C_B \times CL \times FC \times ED / BW \times LT) / Rfd \quad (8)$$

Where:

C_B = concentration of PCBs in fish (mg/kg)

CL = cooking loss of PCB

FC = fish consumption (kg/day)

ED = exposure duration (years)

BW = body weight (kg)

LT = lifetime (years)

Rfd = EPA reference dose (mg PCB / kg day)

Upper bound lifetime excess cancer risk (LCR) represents the increase in cancer risk over a person's lifetime as a result of lifetime long exposure to PCB (EPA, 2011). The EPA target on lifetime excess cancer risk is 0.00001, which in essence represents 1 in 100,000 persons developing cancer as result of lifetime exposure to PCB.

$$LRC = (C_B \times CL \times FC \times ED / BW \times LT) \times q \quad (9)$$

Where:

C_B = concentration of PCBs in fish (mg/kg)

CL = cooking loss of PCB

FC = fish consumption (kg/day)

ED = exposure duration (years)

BW = body weight (kg)

LT = lifetime (years)

q = EPA developed slope factor which relates the increase in cancer risks from PCBs

Table 3: Parameters for Human Health Risk Assessment for PCBs

Parameter	Units	North American Diet	First Nation Diet
Mass of Human Consumer	(kg)	70	70
Average Daily Fish Consumption (IR)	(kg/day)	0.0076	0.029
Shellfish Daily Intake (SIR)	(kg/day)	0.00168	0.011
Exposure Duration (ED)	(years)	30	30
Lifetime (LT)	(years)	70	70
Cooking Loss Factor (CL)	Unitless	0.75	0.75
Slope factor (q)	(kg-day/mg PCB)	2	2
Reference Dose (Rfd) or Acceptable Daily Intake	(mg PCB/kg-day)	0.00002	0.00002
Target Upperbound Excess Lifetime Human Cancer Risk	Unitless	0.00001	0.00001
Target Human Health Hazard (based on Threshold Effect)	Unitless	1	1

To develop SQG protective of human health using this model, Target Tissue Concentrations for PCB in fish species were determined based on the upper-bound lifetime excess cancer risk target and the hazard index target. From these target tissue concentrations, BSAFs were used to back calculate SQG as described below.

3.8 Derivation of SQG

BSAF were used to derive proposed SQGs using the method outlined above and formalized in Equation 6. SQG's were designed for 95% of the population of mammals and birds to contain PCB concentrations in lipids below TRVs, and for 95% of fish and shellfish populations to contain PCB concentrations below TRGs. To ensure the 95% protection goal is met, the

variability and uncertainty in the BSAF must be accounted for. With empirical data, two standard deviations of the SD_{BSAF} is subtracted from the mean $\log C_S$ values using Equation 6. Similarly, when using model derived BSAF to back-calculate SQG from a specific endpoint the uncertainty in model predicted BSAFs must be accounted for. The SD_{MB} represents this uncertainty and is used in place of SD_{BSAF} hence equation 6 becomes:

$$\text{Log } C_S = \log(C_{TRV}) - \log(\text{BSAF}) - 1.96 \log(SD_{MB}) \quad (10)$$

As mentioned above, calculating MB and SD_{MB} requires empirical data for comparison to model predicted data. Empirical data was only available for a select number of species to determine species specific MB. However to apply BSAFs and account for uncertainties appropriately some measure of MB is needed. For species for which MB could not be calculated, a model-wide model bias was used. This overall MB was calculated as the mean MB for all species for which empirical data was available for within the site (i.e. the mean of all species-specific MB). Overall MB was used to account for uncertainties in model predicted BSAFs when empirical data was not available for a species.

4.0 RESULTS & DISCUSSION

4.1 Intra Site Variation of Empirical BSAF

A total of 118 PCB congeners were detected in sediments and biota around B.C. and \log BSAF (kg dw/kg ww) calculated for total PCBs are reported

in Tables A27-A30. BSAF (kg dw/kg ww) ranged from less than 1 kg dw/kg ww in Blue Mussels, to above 700 kg dw/kg ww in Harbor seals (Figure 3a – 3d). As PCBs are known to biomagnify, these results confirm the expectation that upper trophic levels would experience higher BSAFs.

BSAF (kg OC/kg lipid) were calculated for specific congeners in Vancouver, the Strait of Georgia, Victoria Harbor and the Central Coast. Congener specific figures are shown in Figures 1-4 of the Appendix. Congeners with a higher degree of chlorination, higher molecular weight and higher K_{OW} values were found in higher concentrations in biota than lower weight congeners.

Log BSAF normalized for organic carbon content of sediment and lipid contents of samples for both total PCBs (Figure 4a – 4d) caused an increase in log BSAF for some species (Dungeness crab in Vancouver and Victoria harbors) and lowered log BSAF in other cases (Harbor seals). This effect is dependent on the ratio of lipid content of organism to organic carbon in sediments and did not exhibit any pattern. Normalized BSAF were highest for Dungeness crabs (log BSAF = 3.09 ± 0.85 in Vancouver; log BSAF = 2.79 ± 1.23 in Victoria) followed by Harbor seals (log BSAF = 1.60 ± 0.78 in the Strait of Georgia). Lipid contents of samples are reported with the original data listed in the Appendix and OC contents are reported in Table 2.

Lipid and organic carbon normalized BSAF were used for risk assessment and SQG derivation as lipophilic chemicals such as PCBs partition in organic carbon of sediments and lipids in organism, thus variability in the fraction of these are significant factors in the variation seen for BSAFs in kg dw/kg ww.

Normalizing BSAF values aims to help reduce this variability in BSAFs within a site-specific population. However, variability was only slightly reduced. A large amount of variability remains after normalizing for OC and lipid content. Sample specific organic carbon content of sediments was unavailable and instead estimated for the whole site from literature data. Sample specific OC data would likely have reduced variability more.

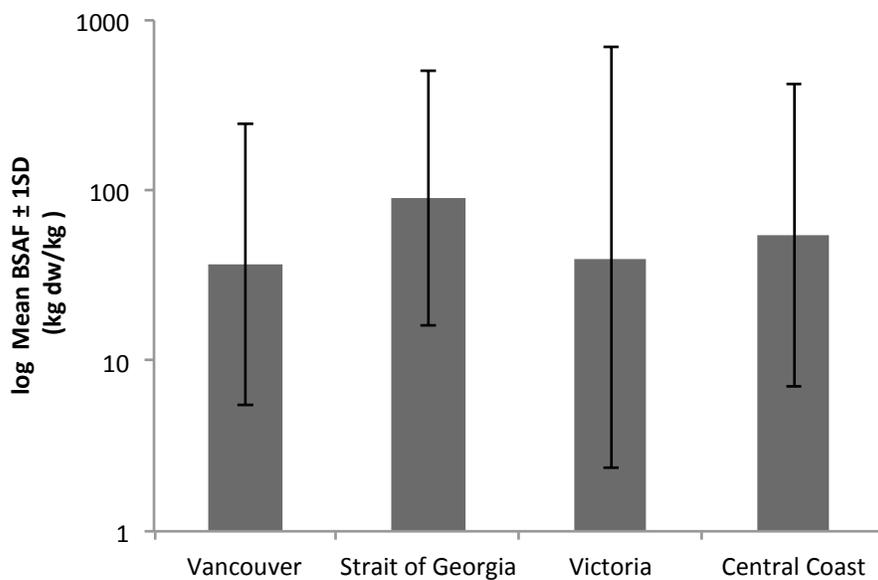


Figure 3a: Log BSAF (kg dw/kg ww) values for Total PCB in Dungeness Crab (*Metacarcinus magister*) from Vancouver Harbor, the Strait of Georgia, Victoria Harbor and the Central Coast. Error bars represent one standard deviation from the mean.

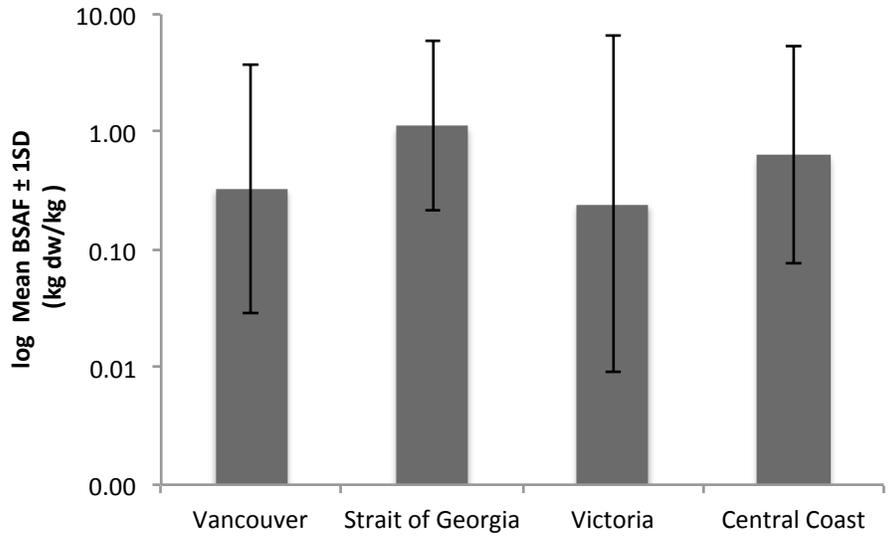


Figure 3b: Log BSAF (kg dw/kg ww) values for Total PCB in Blue Mussel (*Mytilus trossulus*) from Vancouver Harbor, the Strait of Georgia, Victoria Harbor and the Central Coast. Error bars represent one standard deviation from the mean.

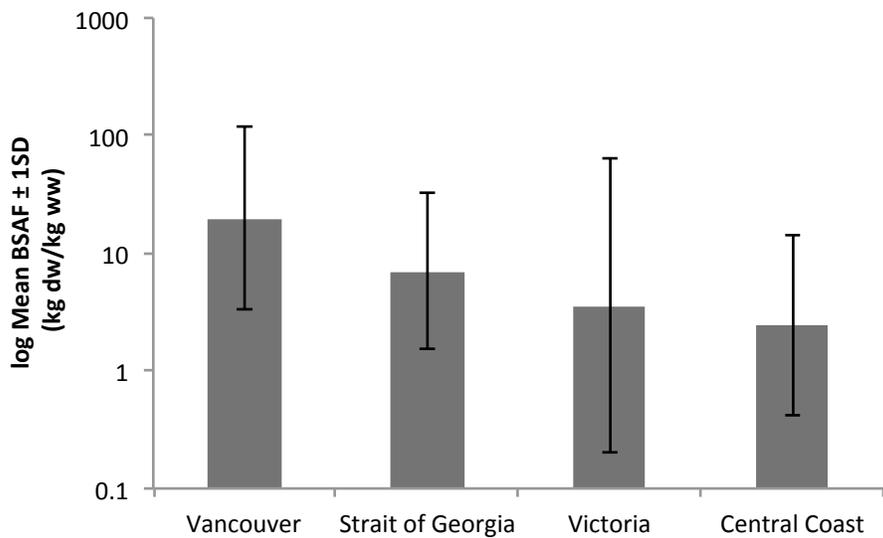


Figure 3c: Log BSAF (kg dw/kg ww) values for Total PCB in English Sole (*Parophrys vetulus*) from Vancouver Harbor, the Strait of Georgia, Victoria Harbor and the Central Coast. Error bars represent one standard deviation from the mean.

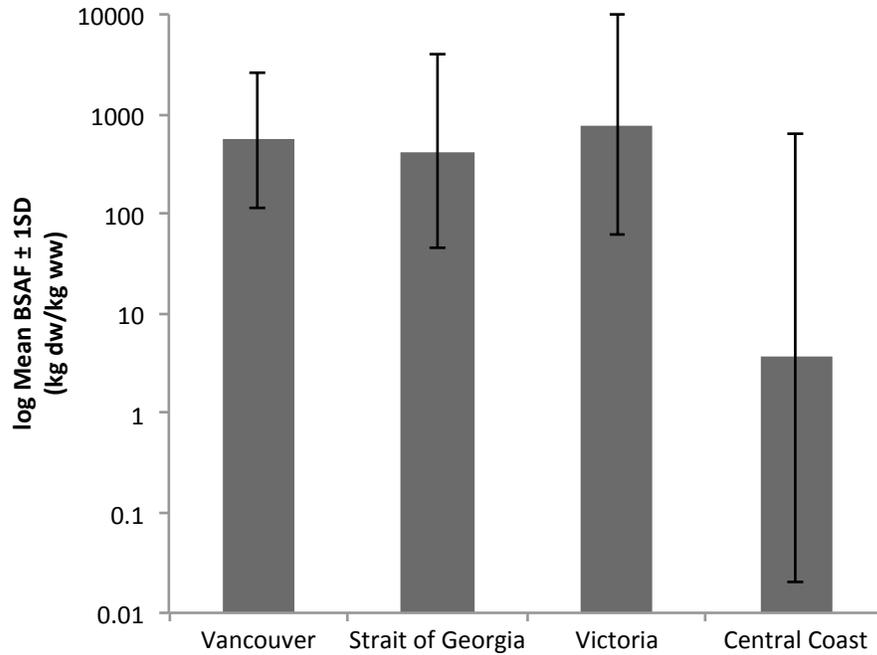


Figure 3d: Log BSAF (kg dw/kg ww) values for Total PCB in Harbor seals (*Phoca vitulina*) from Vancouver Harbor, the Strait of Georgia, Victoria Harbor and the Central Coast. Error bars represent one standard deviation from the mean.

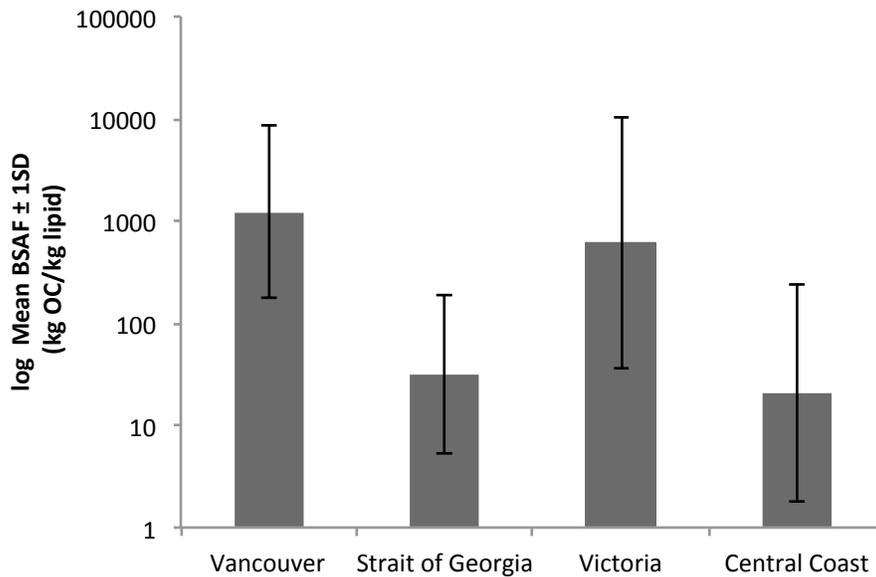


Figure 4a: Log BSAF (kg OC/kg lipid) values for Total PCB in Dungeness Crab (*Metacarcinus magister*) from Vancouver Harbor, the Strait of Georgia, Victoria Harbor and the Central Coast. Error bars represent one standard deviation from the mean.

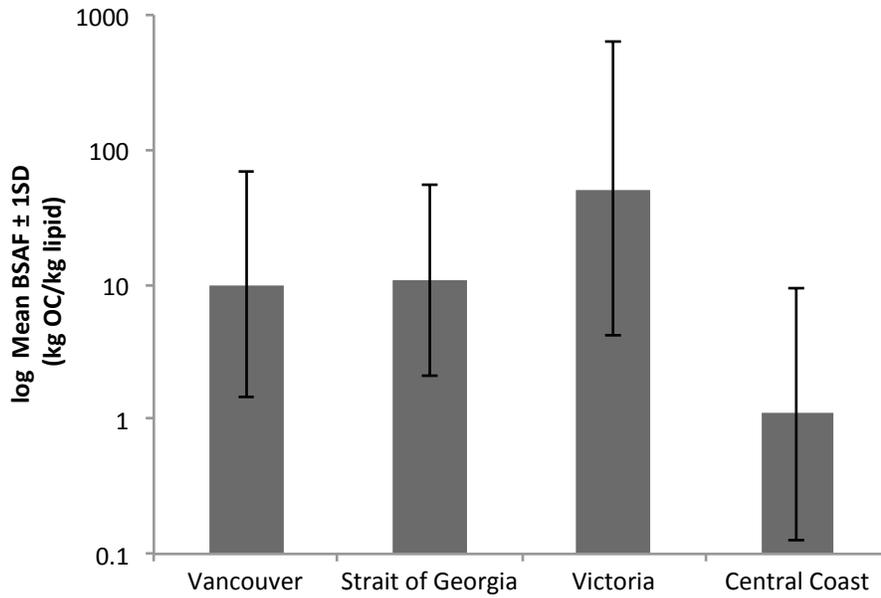


Figure 4b: Log BSAF (kg OC/kg lipid) values for Total PCB in Blue Mussel (*Mytilus trossulus*) from Vancouver Harbor, the Strait of Georgia, Victoria Harbor and the Central Coast. Error bars represent one standard deviation from the mean.

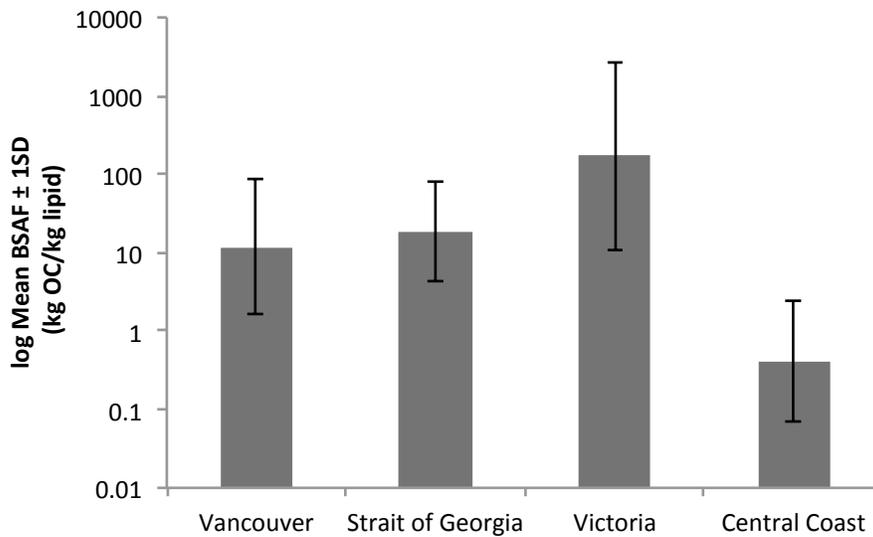


Figure 4c: Log BSAF (kg OC/kg lipid) values for Total PCB in English Sole (*Parophrys vetulus*) from Vancouver Harbor, the Strait of Georgia, Victoria Harbor and the Central Coast. Error bars represent one standard deviation from the mean.

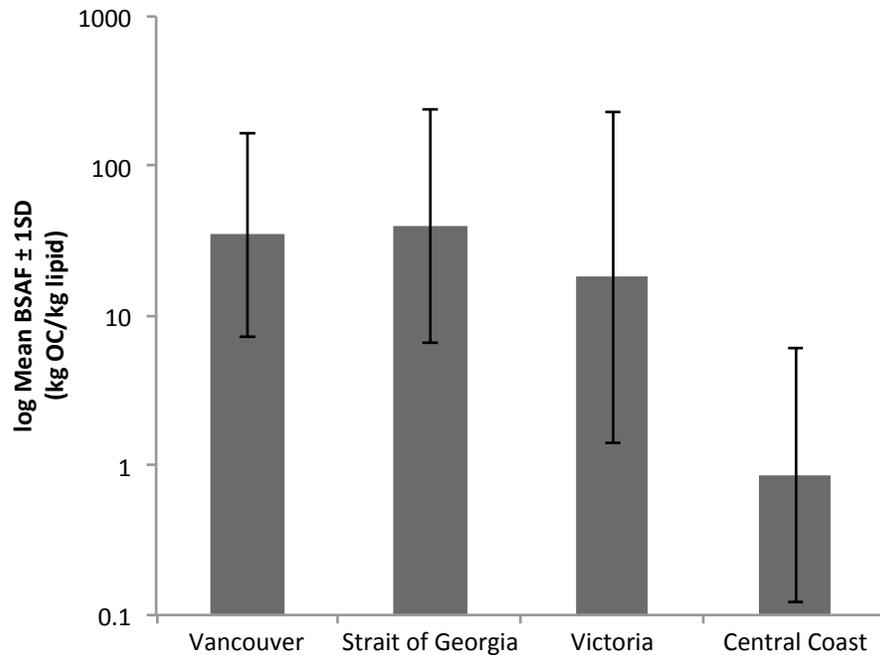


Figure 4d: Log BSAF (kg OC/kg lipid) values for Total PCB in Harbor seals (*Phoca vitulina*) from Vancouver Harbor, the Strait of Georgia, Victoria Harbor and the Central Coast. Error bars represent one standard deviation from the mean.

BSAF values showed a high degree of variation within each organism population at each site. Standard deviations of BSAFs can be found in Appendix Tables A27-A30, but generally were 2 to 3 orders of magnitude. A number of sources likely contributed to the variation seen. The spatial distribution of contaminated sediments and variability in the amount of time each sample organism is present within the contaminated range both contribute to this variability. Sampling occurred in areas with a high degree of PCB contamination. PCBs sorb to sediments in marine systems and are found in highest concentrations in sediments near point sources, which create a concentration gradient where sediments near sources have much higher concentrations than those sediments further from sources. A high concentration gradient in sediment

would increase the variability of sediment concentrations when sampling from a number of sites along the concentration gradient. Variability in BSAFs for each species within each site is increased as a result of the high variability in sediment concentrations.

The high within site variability in BSAFs seen is contributed to by the natural variation in metabolic function, diet items, and size within a population are a source of variability in chemical concentrations among a population. Here, immobile organisms sampled closer to contaminated sediments would have higher concentrations than those further away from PCB hotspots, which additionally contributes to within species variability for these organisms populations. For mobile organisms, variability in foraging range size and variability in time spent within the contaminated range also increases variability in BSAF. Individuals with larger foraging areas that range outside of areas of contaminated sediment likely have less PCB uptake as a result of consuming diet items that experience a shorter exposure to PCBs in sediments. High variability in BSAF values must be considered when using BSAFs to derive SQG as environmental quality criteria aim to protect the majority (usually 95%) of a population. A consequence of the high variability is the calculation of lower sediment quality guidelines to incorporate the desired proportion of the population.

4.2 Inter Site Variation

BSAF (kg OC/kg lipid) for Dungeness crab in Vancouver were significantly different from the Strait of Georgia and the Central Coast (ANOVA with Tukey

Kramer post hoc test, $p < 0.0001$). BSAF (kg OC/kg lipid) for Dungeness crabs from Victoria were significantly different from BSAF for Dungeness crab in the Strait of Georgia and the Central Coast (ANOVA with Tukey Kramer post hoc test, $p < 0.0001$) (Figure 4a). The differences seen between crustaceans at each site is potentially the result of variable sampling location for each site. Dungeness crabs have relatively high trophic positions for benthic invertebrates with relatively small habitat ranges and hence are good representations of PCB concentrations locally, but may not represent a spatial average for a site. Samples of crabs taken from areas of heavily contaminated sediments would be expected to have higher PCB concentrations than samples taken from less contaminated sediments. Since specific sampling locations were unavailable, the influence of sampling locations on these differences should be explored further.

BSAF (kg OC/kg lipid) for Blue Mussel (Figure 4b) from the Central Coast were significantly different from all other sites (ANOVA with Tukey Kramer post hoc test, $p < 0.0001$). English Sole (Figure 4c) showed no significant differences in lipid normalized BSAFs between any sites (ANOVA, $p = 0.068$). BSAF (kg OC/kg lipid) for Harbor seals from the Central Coast were significantly lower than BSAF for Harbor seals from Vancouver and the Strait of Georgia (ANOVA with Tukey Kramer post hoc test, $p = 0.017$).

BSAFs for all species in the Central Coast showed lower BSAFs compared to other sites, with statistically significantly lower BSAF for Crustaceans and Harbor seals. The lower BSAFs in the Central Coast for species with large foraging ranges such as Harbor seals, may suggest the

proportion of contaminated sediments within the foraging area is lower in the Central Coast compared to Vancouver harbor and the Strait of Georgia. Areas in Vancouver harbor and the Strait of Georgia have higher proportions of contaminated sediments due to long histories of industrial activities. The Central Coast has more isolated areas of contamination near industrial hotspots, but may overall offer more foraging area and prey items for seals that have lower levels of contamination.

However, the lower BSAF for Harbor seals in the Central Coast may also be a sampling artifact as sediment samples were taken near PCB hotspots as part of risk assessments for the area. The PCB concentrations in sediments used to calculate BSAFs represent a relatively high concentration for the area rather than the spatial average. As a result of large foraging ranges, PCB concentrations in fish and Harbor seals are more likely to represent an exposure more representative of the spatial average. Due to the nature of the BSAF calculation, relatively high concentrations in sediments will result in BSAFs that are artificially low.

4.3 Model Performance & Model Bias

To evaluate the accuracy of the bioaccumulation model, empirical BSAFs were used to calculate Model Bias (MB) for each species in each site (Table 4). MB=1 represents perfect agreement between model outputs and empirical data. With some notable exceptions (Harbor seals in the Central Coast, Blue Mussels in Victoria), overall MB was good.

Table 4: Geometric mean (\pm 1SD) model bias for total PCBs (Σ PCB) for each species and overall model bias for each site.

	Vancouver	Strait of Georgia	Victoria	Central Coast
Blue Mussel	14.5 \pm 0.61	0.487 \pm 3.5	148 \pm 8.05	30.77 \pm 1.21
Dungeness Crab	0.31 \pm 0.49	0.044 \pm 3.19	0.61 \pm 3.51	0.95 \pm 2.86
English Sole	0.42 \pm 0.40	0.39 \pm 2.27	40.44 \pm 3.82	16.2 \pm 1.21
Harbor Seal	1.63 \pm 0.12	1.45 \pm 1.01	63.81 \pm 1.03	204.65 \pm 2.66
Overall	0.50 4.86	0.59 0.94	6.32 5.14	2.08 7.81

In the Strait of Georgia (Figure 5), Vancouver Harbor (Figure 6) and Victoria Harbor (Figure 7) the model showed good agreement with empirically derived BSAFs. Harbor Seals in the Central Coast did have significantly lower BSAF values than predicted by the model (T-test, $p < 0.0001$) but other species showed good agreement still (Figure 8). The model under-prediction of Harbor Seals indicates that the high mobility of Harbor seals may cause the BSAF to be unrepresentative of the BSAF for the areas where PCB concentrations in the sediments were measured.

Differences in food web structure could potentially lead to lower BSAFs as the model assumes the same food web for all sites. However, Alava Saltos (2011) showed that BSAF values for marine mammals were not sensitive to changes in the food web structure. While the model is not very sensitive to certain changes in food web structure, it is highly sensitive to changes in the relationship between concentrations in sediments and concentrations in water (Alava Saltos, 2011). If water concentrations are over estimated as a result of

the system having not reached equilibrium, the methods used to estimate water concentrations or differences in sediment chemistry, the model is likely to over predict BSAF values. However, given that the model well predicts BSAFs for other species in the coast, the high model bias for Harbor seals may support that BSAF are artificially low due to sampling artifacts.

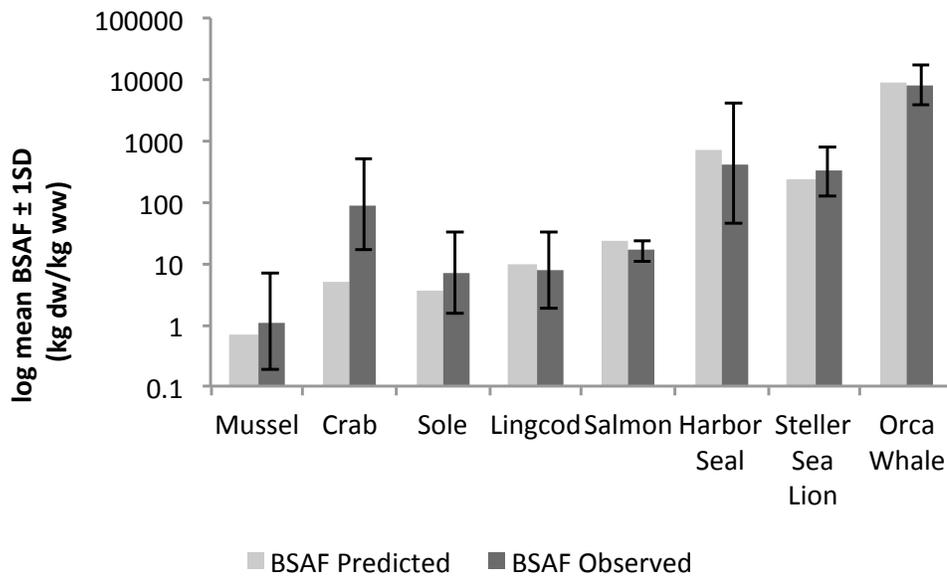


Figure 5: Predicted BSAF (kg ww/kg dw) and observed BSAF \pm 1SD (kg ww/kg dw) for various species in the Strait of Georgia.

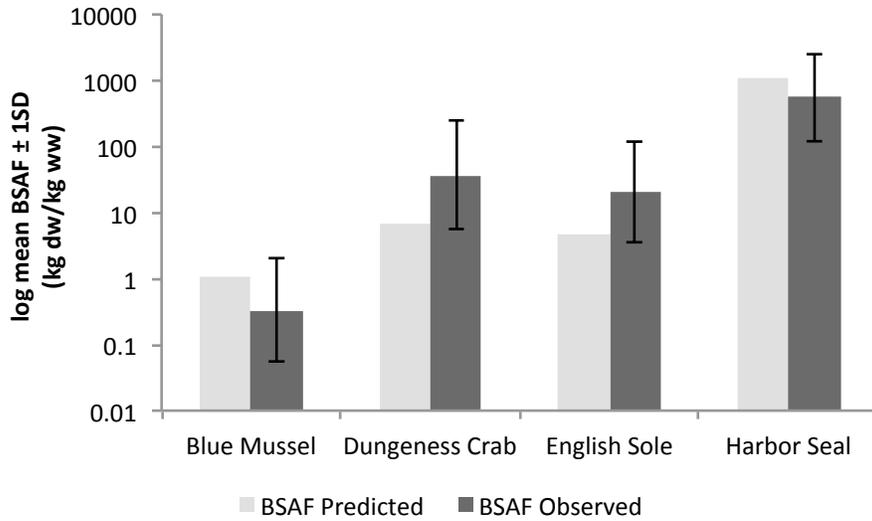


Figure 6: Predicted BSAF (kg ww/kg dw) and observed BSAF \pm 1SD (kg ww/kg dw) for various species in Vancouver.

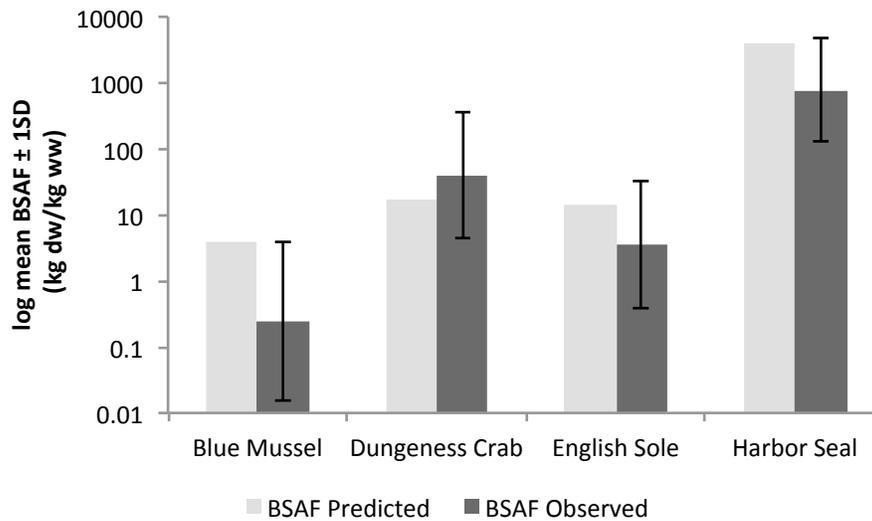


Figure 7: Predicted BSAF (kg ww/kg dw) and observed BSAF \pm 1SD (kg ww/kg dw) for various species in Victoria harbor.

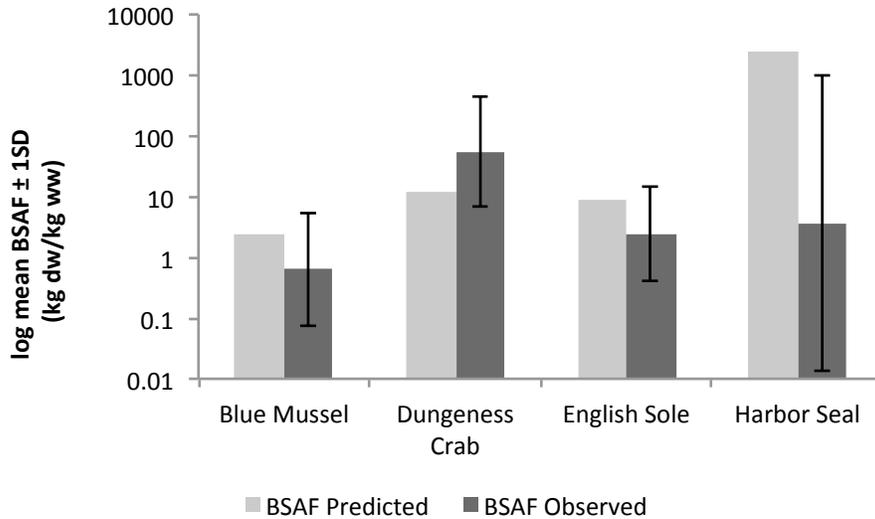


Figure 8: Predicted BSAF (kg ww/kg dw) and observed BSAF \pm 1SD (kg ww/kg dw) for various species in the Central Coast.

4.4 Sensitivity Analysis

The sensitivity of model outputs to changes in input variables has been well studied by Arnot & Gobas (2010) and Alava Saltos (2011). The effects of changes in water concentrations compared to sediment concentrations is further investigate here.

The sensitivity of Harbor seal, Steller sea lion and Orca whale PCB concentrations to changes in water and sediment concentrations was modeled and confirmed that that biota have a high sensitivity to PCB concentrations in water. Quantifying this sensitivity is important for appropriately applying BSAF values. A 10X increase in water concentration results in a 9X increase in biota concentrations for all marine mammals. A 10X increase in sediment concentrations however, result in less than 1X increase in biota concentrations. These results support that organisms are more sensitive to changes in PCB

concentration in water and that inputs of PCBs into water are driving the bioaccumulation in the food web. Recent studies suggest the flux of PCBs in the marine system move from atmosphere to water to sediments until equilibrium is established and no further net movement of PCBs occurs (Noel et. al, 2009; Johannessen et. al, 2008). Also, PCBs in the water column can concentrate in phytoplankton, zooplankton and fish to enter the food web, indicating that PCB concentrations in water drive biota concentrations. Systems in which new inputs of PCBs result in relatively high water concentrations compared to equilibrium partitioning, need to consider this high sensitivity to water concentrations. Water concentrations are often below detection limits, which makes applying water quality criteria difficult. SQG are a more appropriate management tool as concentrations are generally within measurable limits, but this relationship to water concentrations should be accounted for in guideline development to avoid under protection of upper trophic level organisms and set protective long term goals for ecosystem health.

4.5 Ecological Risk Assessment of Current SQG for PCB

BSAFs were used to predict biota concentration from a theoretical scenario where sediment concentrations are equal to the SQG's for B.C. (20 µg/kg dw assuming 1% OC or 20 µg/kg x %OC otherwise) using Equation 3. The Canadian CCME guideline (21.5 µg/kg) was also considered, but this guideline is so close in value to the B.C. SQG that differences in results were negligible from those presented here.

Predicted PCB concentrations in fish and crustacean species were compared with BC Tissue Residue Guidelines for fish and shellfish for the safe consumption by wildlife (0.1 µg/g ww) or humans (2.0 µg/g ww) to evaluate if current SQG meet the legislated protection goal set out by the TRG. At total PCB concentrations in sediment equal to the BC SQGs, greater than 50% of the Dungeness crab population would be above both TRG for consumption by wildlife and humans at each site (Figure 9 and Table 5) and not legally safe for consumption. English Sole in Vancouver and the Strait of Georgia would have large proportions of the population over TRG, with smaller proportions in Victoria and the Central Coast (Figure 10 and Table 5). Similar results were seen for Chinook Salmon (Figure 11 and Table 5). These results show that the current SQG does not ensure that PCB concentrations in fish and shellfish populations remain below the level considered safe for human or wildlife consumption, thus are legally ineligible. There is a lack of agreement between SQG and TRG as the SQG cannot ensure that tissue concentrations in fish or shellfish are below the TRG. Dungeness crab and Salmon are economically productive fisheries in British Columbia, however the SQG does not protect these fisheries either.

Table 5: Proportions of fish and shellfish populations above Tissue Residue Guidelines for wildlife (0.1 µg/g ww) and human consumption (2.0 µg/g ww) assuming PCB concentrations in sediment equal to current SQG = 20 µg/kg

	Vancouver	Strait of Georgia	Victoria	Central Coast
Proportion of Dungeness Crab population above TRG-wildlife	0.892	0.978	0.708	0.838
Proportion of English Sole population above TRG-wildlife	0.846	0.817	0.465	0.428
Proportion of Chinook Salmon population above TRG-wildlife	0.894	1.000	0.980	0.915
Proportion of Dungeness Crab population above TRG-human	0.507	0.735	0.406	0.451
Proportion of English Sole population above TRG-human	0.403	0.273	0.193	0.083
Proportion of Chinook Salmon population above TRG-human	0.357	0.010	0.670	0.554

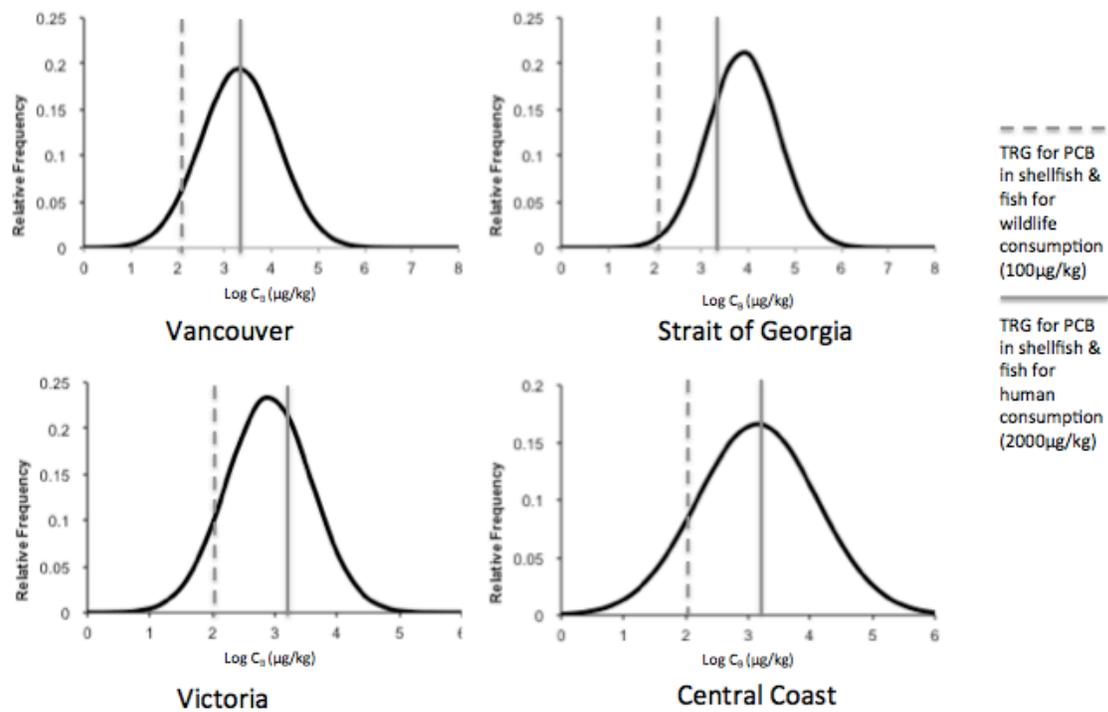


Figure 9: Assuming sediment concentrations equal to the B.C. SQG, the predicted concentrations of PCB in Dungeness crab using empirical BSAFs from each site are compared to Tissue Residue Guidelines for PCBs in fish and shellfish.

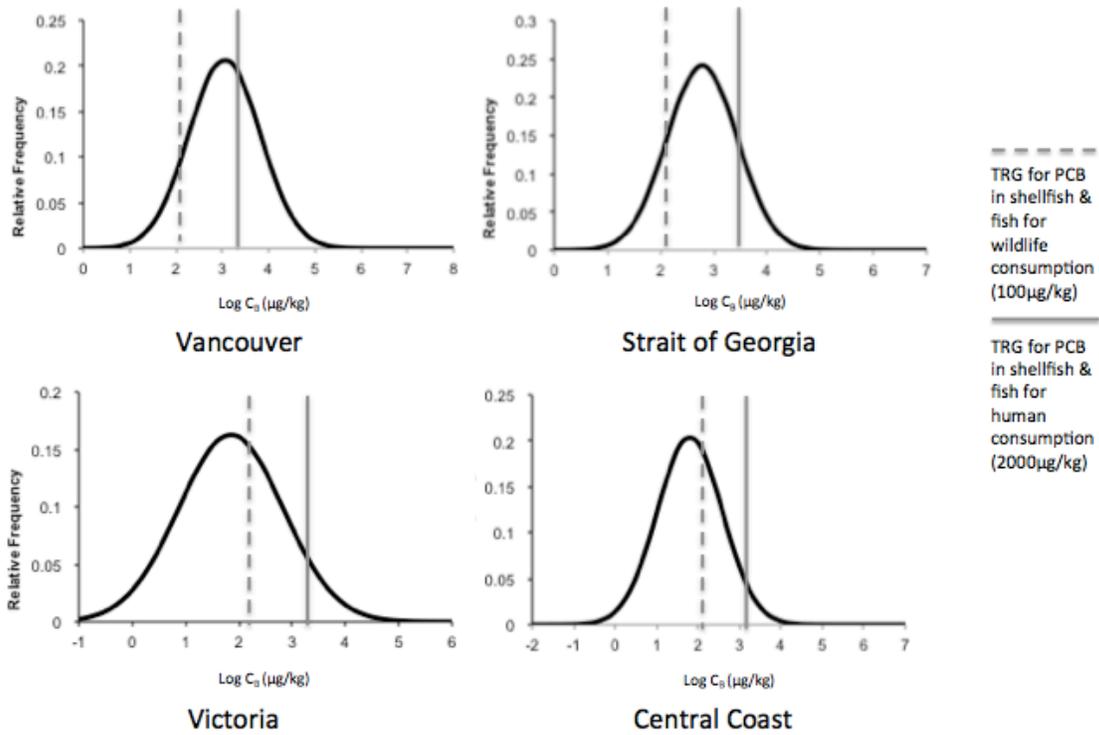


Figure 10: Assuming sediment concentrations equal to the B.C. SQG, the predicted concentrations of PCB in English sole using empirical BSAFs from each site are compared to Tissue Residue Guidelines for PCBs in fish and shellfish.

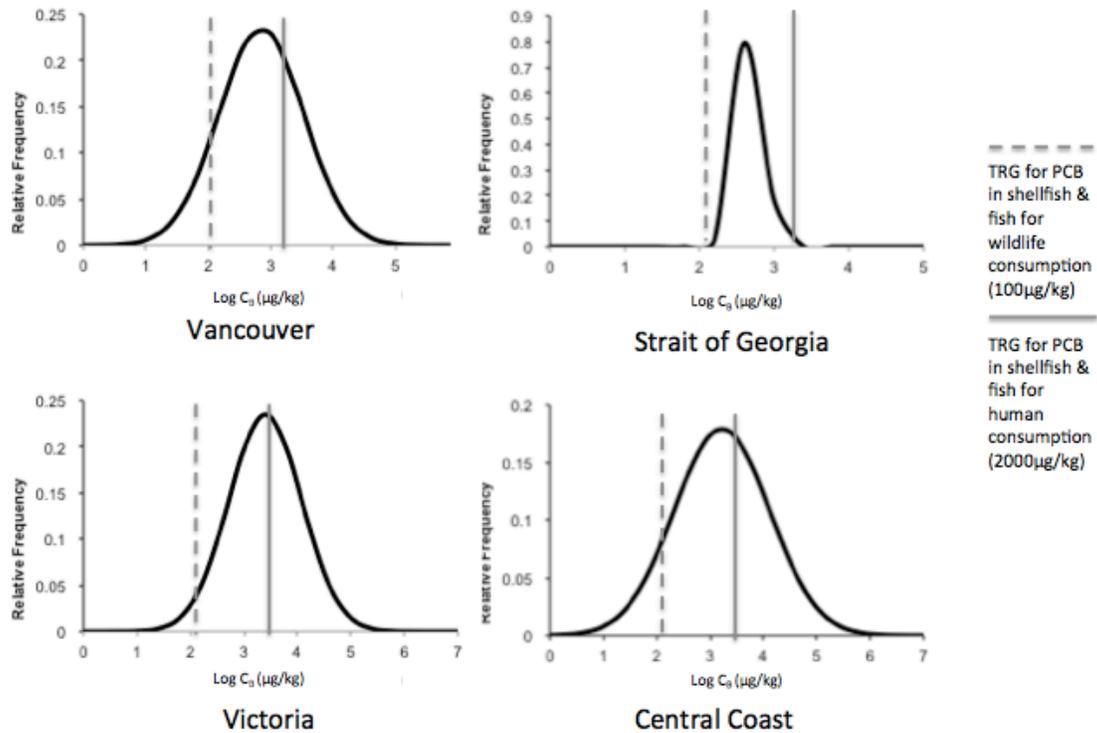


Figure 11: Assuming sediment concentrations equal to the B.C. SQG, the predicted concentrations of PCB in Chinook salmon using modeled BSAFs from each site are compared to Tissue Residue Guidelines for PCBs in fish and shellfish.

Model predicted BSAF for Cormorants and Great Blue Herons were applied to determine if current SQGs are protective of the health of piscivorous birds. Estimated PCB concentrations for approximately 50% of the population are over the TRV for birds, likely resulting in significant effects to sensitive individuals and at the population level (Figure 12 and Figure 13 and Table 6).

Table 6: Proportions of bird populations above Toxicity Reference Value for PCBs in birds assuming PCB concentrations in sediment equal to current SQG = 20 µg/kg

	Vancouver	Strait of Georgia	Victoria	Central Coast
Proportion of Cormorant population above TRV	0.506	0.420	0.868	0.657
Proportion of Blue Heron population above TRV	0.471	0.399	0.830	0.636

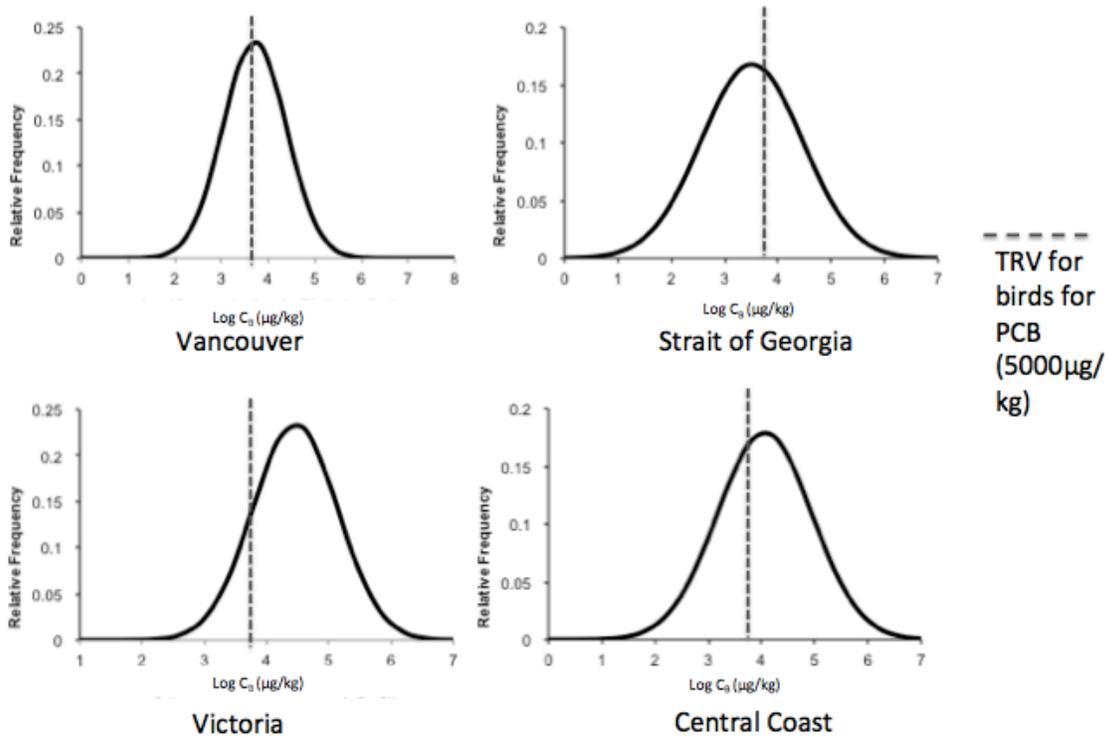


Figure 12: Assuming sediment concentrations equal to the B.C. SQG, the predicted concentrations of PCB in Cormorants using modeled BSAFs from each site are compared to Toxicity Reference Values for PCBs in birds.

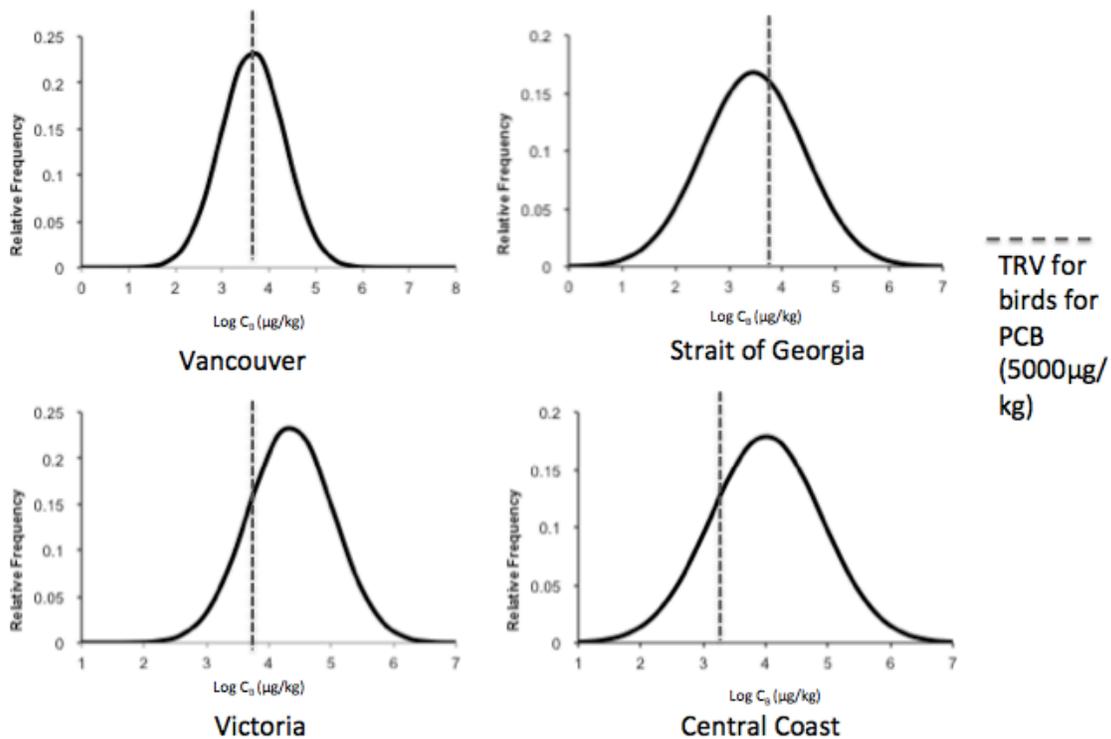


Figure 13: Assuming sediment concentrations equal to the B.C. SQG, the predicted concentrations of PCB in Great Blue Herons using modeled BSAFs from each site are compared to Toxicity Reference Values for PCBs in birds.

Harbor Seals in Vancouver Harbor, Victoria Harbor and the Strait of Georgia the majority of the population would experience wet weight body concentrations above the TRV (Figure 14 and Table 7) immunotoxicity and endocrine disruption in Mammals of 1300 μg PCB/kg ww (Mos et. al, 2010). Harbor seals in the Central Coast appear to be more protected by current guidelines, however the uncertainty in the accuracy of empirical BSAFs for the Central Coast Harbor seals discussed above indicates these results require further investigation. Populations of Steller sea lions and Orca whales are also estimated to be almost entirely above the TRV (Figures 15 and 16 and Table 7). These populations would likely experience immunotoxic effects (Levin et.al,

2004; Ross et.al, 1996), disruption of hormone function, growth and development (Simms et.al, 1999; Tabuchi et.al, 2006) as a result of PCB concentrations.

Table 7: Proportions of marine mammal populations above Toxicity Reference Value for PCBs in Harbor seals assuming PCB concentrations in sediment equal to current SQG = 20 µg/kg

	Vancouver	Strait of Georgia	Victoria	Central Coast
Proportion of Harbor seal population above TRV	0.575	0.670	0.363	0.062
Proportion of Steller sea lion population above TRV	0.460	0.277	0.764	0.628
Proportion of Orca whale population above TRV	0.995	1.000	1.000	0.991

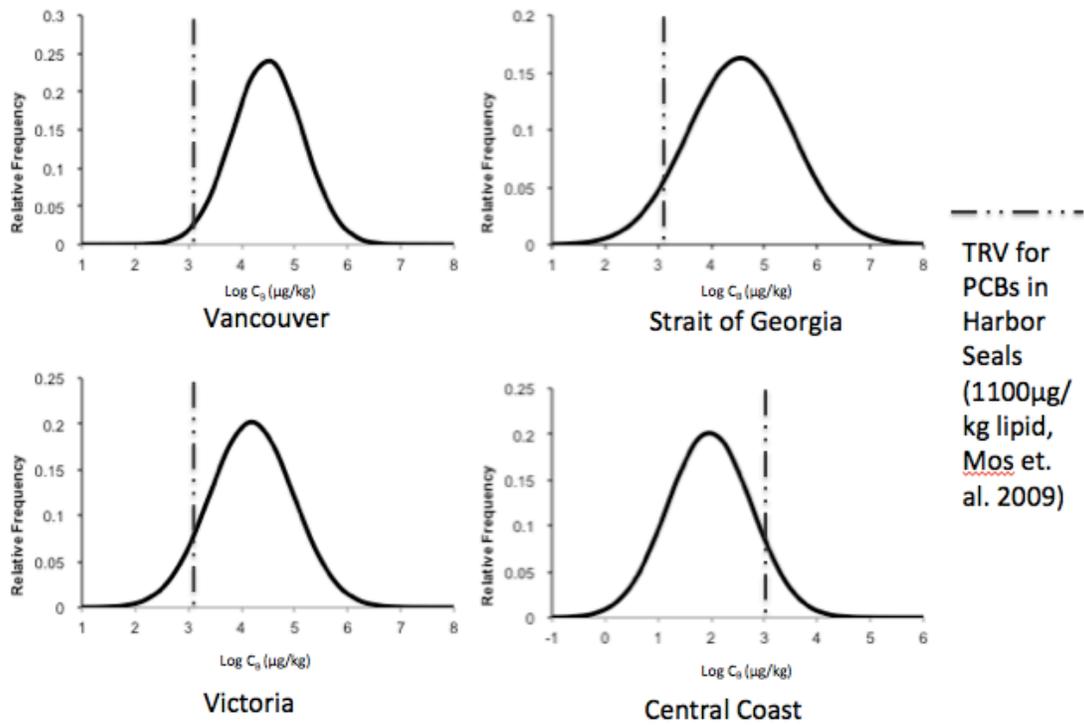


Figure 14: Assuming sediment concentrations equal to the B.C. SQG, the predicted concentrations of PCB in Harbor seals using empirical BSAFs from each site are compared to Toxicity Reference Values for PCBs in Marine mammals.

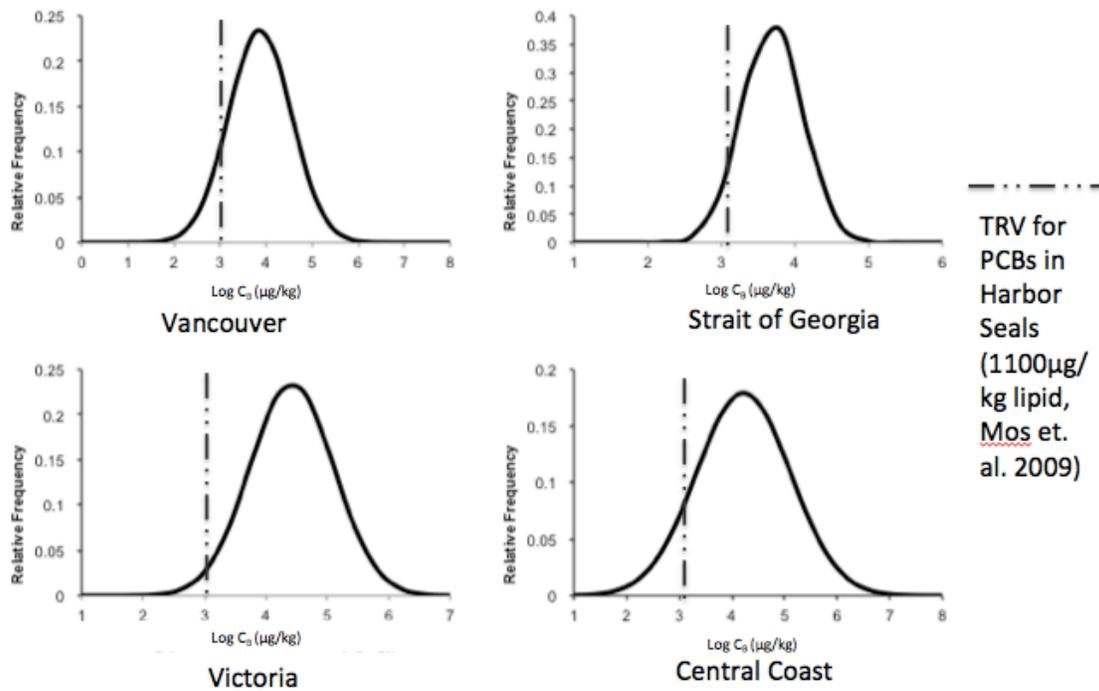


Figure 15: Assuming sediment concentrations equal to the B.C. SQG, the predicted concentrations of PCB in Steller sea lions using modeled BSAFs from each site are compared to Toxicity Reference Values for PCBs in Marine mammals.

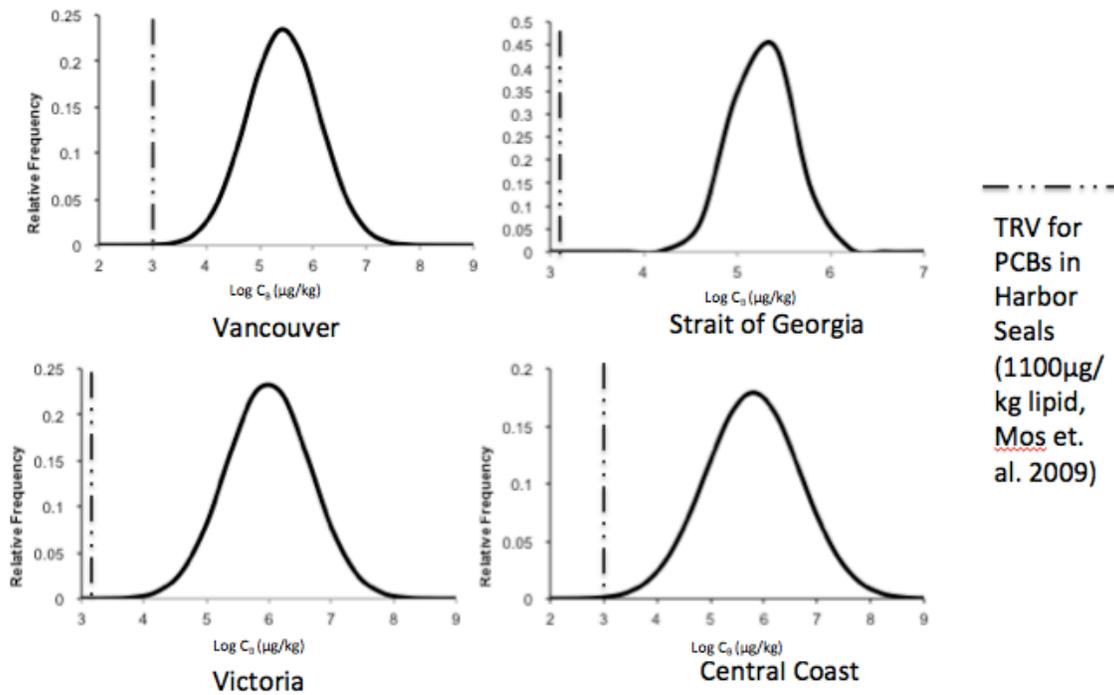


Figure 16: Assuming sediment concentrations equal to the B.C. SQG, the predicted concentrations of PCB in Orca whales using modeled BSAFs from each site are compared to Toxicity Reference Values for PCBs in Marine mammals.

The protection goal for SQG in Canada is to protect all aquatic life at all life stages (CCME, 2001), however, this assessment of current SQG using BSAFs has shown that the current guideline is failing to meet the protection goal for every species considered. The current SQG does not ensure that fisheries are protected and products are safe for consumption by humans or wildlife, as the majority of these populations would be over the TRG for PCB in fish and shellfish. Consumers of fish and shellfish, including birds and multiple marine mammal species are not protected by the current SQG as this risk assessment shows anticipated adverse effects to a high fraction of the populations given PCB concentrations in sediments equal to the current SQG. Similar results were found at all sites, indicating the failure of SQG to meet protection goals is a result of the derivation process not accounting for biomagnification and not site or species specific anomaly.

4.6 Human Health Risk Assessment of Current SQG for PCB

A human health risk assessment for both the threshold and lifetime excess cancer risk of PCB exposure was used to evaluate if current SQGs effectively protect human health from exposure to PCB acquired through eating salmon and Dungeness crab over a lifetime. The Hazard Index calculated for threshold effects and the Lifetime Excess Cancer Risk for both populations is shown in Table 8. With the exception of the Strait of Georgia for a typical diet, all sites are above target levels for human health ($H = 1$; $LCR = 1:100,000$), indicating an unacceptable risk to human health for both a typical diet and a traditional First

Nation diet. In the case of a traditional First Nation diet in B.C., which is more reliant on marine food sources, there is an exceptionally high LCR indicating up to 0.7% of the population would be expected to develop cancer from lifetime exposure to PCB from diet items – a value that is unacceptably high. Current SQGs are not protective of human health and put communities with a heavy reliance on fish and shellfish at particularly high risk of both acute toxicity and carcinogenic effects of PCBs.

Table 8: Hazard Index and Lifetime Cancer Risk from PCBs in fish and shellfish assuming a sediment concentration equal to the B.C. SQG.

Site	Average North American Diet		Traditional First Nation Diet	
	Hazard Index	Lifetime Human Cancer Risk	Hazard Index	Lifetime Human Cancer Risk
Vancouver	1.30	52: 100,000	5.09	203: 100,000
Strait of Georgia	0.89	35:100,000	3.46	138: 100,000
Victoria	4.55	182: 100,000	17.9	699: 100,000
Central Coast	2.97	119: 100,000	11.5	461: 100,000

4.7 Derivation of Sediment Quality Guidelines

Empirical and model predicted BSAFs were used to calculate SQG's to meet relevant protection goals including TRG for fish and shellfish, TRV for avian species and marine mammals and human health endpoints. Clearly, SQG derived using this method are orders of magnitude below the current guideline,

regardless of the specific endpoint used to derive them. These guidelines, as well as the current B.C. SQG, CCME SQG and Disposal at Sea SQG are shown in Figure 17. Current SQG only meet protection goals for low trophic level benthic invertebrates, represented here by Oysters. SQG derived to meet any of the outlined protection goals for human health or the health of upper trophic level organisms would require a SQG less than $1\mu\text{g}/\text{kg}$ dw sediment. Current B.C. and CCME SQG are $20\mu\text{g}/\text{kg}$ dw (assuming 1% OC in sediments) and $21.5\mu\text{g}/\text{kg}$ dw respectively - these guidelines over estimate the allowable PCB concentrations in sediments required to protect upper trophic level organisms by a factor of 20X. The Environment Canada Disposal at Sea guideline dictates at what PCB concentration in harbor sediments are considered clean enough to be dredged and disposed of at designated marine sites – some of which are in areas considered critical Orca whale habitat (Lachmuth, et. al. 2010). The sediments dredged and disposed of in these habitats may contain PCB concentrations up to 100X the concentrations determined here to be safe for Orca whales.

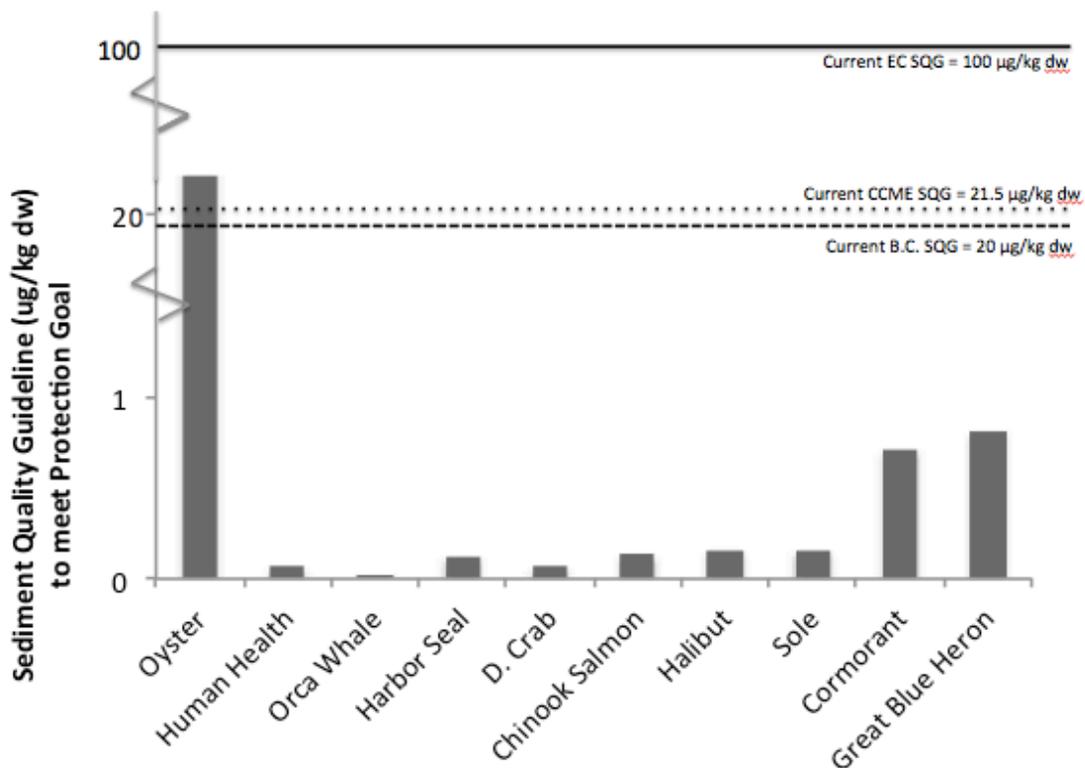


Figure 17: Sediment Quality Guidelines derived using BSAFs to meet human and environmental health protection goals for each species in relation to current Canadian sediment quality guidelines.

5.0 Conclusions

Biota-sediment accumulation factors can be used as an effective tool for both risk assessment of chemical concentrations in sediment and for deriving guidelines to meet relevant endpoints. BSAFs calculated with empirical data show little differences between sites and can be applied on a wide scale, though sampling protocols and the foraging ecology of the species must be considered to avoid potentially under and over-estimating BSAFs. Bioaccumulation modeling allows BSAFs to be estimated for more species than often feasible with empirical

sampling, and has been shown to calculate BSAFs with good agreement in a variety of sites in B.C.

Using BSAFs to assess the current SQG shows that the method used to derive SQG in British Columbia, Canada and many other jurisdictions fails to account for the biomagnifying properties of chemicals, which can result in a failure to meet environmental and human health related protection goals. The SQG for a biomagnifying chemical such as PCB are not protective of fish and shellfish populations or fisheries, potentially leading to closures of economically important fisheries. Current SQG fail to protect the health of fish-eating birds as these species would be expected to experience adverse health effects as a result of PCB exposure through their diet. Marine mammals, such as Harbor seals, Steller sea lions, and Orca whales - which are economically important organisms for tourism in B.C., are also unprotected by current SQG and would be expected to experience adverse immunotoxicity and endocrine disrupting effects as a result of PCB concentrations in sediment that meet the current guideline value. Lastly, human health is placed at risk as a result of current SQG. PCB concentrations in sediments equal to the guideline value would result in increased risk of acute toxicity and increased lifetime excess cancer risks well above the benchmarks considered acceptable for human health. These risks are significantly amplified for populations that are heavily reliant on marine organisms as a food source, such as the many First Nation groups residing in British Columbia. The current method does not accurately represent the relationship between sediment concentrations of PCB and concentrations of PCB in aquatic

biota. Until this is corrected, SQG will not meet protection goals for biomagnifying chemicals.

Considering SQGs are needed for assessing ecosystem health, regulating disposal of sediments at sea and remediation of contaminated sites, a fundamental flaw in the derivation process should not be ignored. Regulators need accurate SQG to effectively evaluate risks to aquatic biota and human health. Using current guidelines, Disposal at Sea programs may unintentionally place marine mammals at significant risk as a result of disposing contaminated sediments in sensitive habitats. Fisheries may require to be closed or consumption limits placed on food as a result of PCB concentrations above the legal standards for consumption because risk assessors may inaccurately determine PCB concentrations in sediments below the SQG are of an acceptable risk. Sediments are also the primary media for remediation in aquatic sites and must be remediated down to the CCME guideline. However if this guideline is not as protective of aquatic and human health as expected, risk may go unmanaged. The management of the risk of chemicals in the environment is reliant on having benchmarks that are developed using the best science, and which accurately express the expected risk to the ecosystem at that chemical concentration. The current SQG in Canada do not offer this for PCB, as shown in this project, and this must be corrected for effective risk management.

Recent research has shown that emerging chemicals of concern such as PDBE, have BSAF values for some shellfish that are higher than for PCBs (Dangerfield, 2011). SQG for PDBE are still in development for Canada, however

if the current method is used, it is very likely these will also fail to protect upper trophic level organisms and human health. The inability of SQG to protect ecosystems and human health from PCB concentrations results from the derivation method and its failure to consider the biomagnification of certain chemicals. Until a new derivation method is developed, this problem will persist and other biomagnifying chemicals may be poorly managed as well.

Using BSAFs, whether derived using empirical data or bioaccumulation modeling, allows a tool for deriving guidelines that meet protection goals for the health of aquatic ecosystems and human health across British Columbia. Risk assessments, following the methodology used here, gives regulators a tool to ensure that protection goals are met. Bioaccumulation modeling of BSAF to accurately represent the relationship between sediment and biota concentrations of PCB or other chemicals of concern allows regulators to identify the most sensitive organism in a system and derive a SQG which ensure this and all other species meet protection goals. The use of BSAF for deriving SQG is a step toward ensuring the best science is used for protecting aquatic ecosystems.

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7.0 APPENDIX

7.1 Appendix Tables

See Excel file: REM 699 J. Arblaster – Appendix Tables on attached CD

Table A1: Concentrations of PCB Congeners (pg/g) in Crab Species from Vancouver

Table A2: Concentration of PCB congeners (pg/g ww) in Crab Species from the Strait of Georgia

Table A3: Concentrations of PCB Congeners (pg/g ww) in Crab Species from Victoria

Table A4: Concentrations of PCB Congeners (pg/g ww) in Crab Species from the Central Coast

Table A5: Concentrations of PCB Congeners (pg/g ww) in Mussel species from Vancouver

Table A6: Concentrations of PCB Congeners (pg/g ww) in Mussel species from the Strait of Georgia

Table A7: Concentrations of PCB Congeners (pg/g ww) in Clam species from the Strait of Georgia

Table A8: Concentrations of PCB Congeners (pg/g ww) in Mussel species from Victoria

Table A9: Concentrations of PCB Congeners (pg/g ww) in Clam species from the Central Coast

Table A10: Concentrations of PCB Congeners (pg/g ww) in Fish from Vancouver

Table A11: Concentrations of PCB Congeners (pg/g ww) in Fish from the Strait of Georgia

Table A13: Concentrations of PCB Congeners (pg/g ww) in Fish from the Central Coast

Table A14: Concentrations of PCB Congeners (pg/g ww) in Harbor Seals from Vancouver

Table A15: Concentrations of PCB Congeners (pg/g ww) in Harbor Seals from the Strait of Georgia

Table A16: Concentrations of PCB Congeners (pg/g ww) in Harbor Seals from Victoria

Table A17: Concentrations of PCB Congeners (pg/g ww) in Harbor Seals from the Central Coast

Table A18: Concentrations of PCB Congeners (pg/g ww) in Sediment samples from Vancouver

Table A19: Concentrations of PCB Congeners (pg/g ww) in Sediment samples from the Strait of Georgia

Table A20: Concentrations of PCB Congeners (pg/g ww) in Sediment samples from Victoria

Table A21: Concentrations of PCB Congeners (pg/g ww) in Sediment samples from the Central Coast

Table A22: Environmental Input Parameters in all sites used in the BSAF Model

Table A23: Chemical properties of PCB congeners used in the BSAF Model

Table A24: Biological Input parameters for General Aquatic Biota

Table A25: Species specific input parameters for Invertebrates and Fish

Table A26: Species specific input parameters for Birds

Table A27: Species specific input parameters for Marine Mammals

Table A27 - Congener specific and Total PCB log BSAF (kg dw/kg ww) and log BSAF (kg OC/kg lipid) in the Strait of Georgia

Table A28 - Congener specific and Total PCB log BSAF (kg dw/kg ww) and log BSAF (kg OC/kg lipid) in the Strait of Georgia

Table A29 - Congener specific and Total PCB log BSAF (kg dw/kg ww) and log BSAF (kg OC/kg lipid) in Vancouver Harbor

Table A30 - Congener specific and Total PCB log BSAF (kg dw/kg ww) and log BSAF (kg OC/kg lipid) in Victoria Harbor

Table A31 - Congener specific and Total PCB log BSAF (kg dw/kg ww) and log BSAF (kg OC/kg lipid) in the Central Coast

7.2 Appendix Figures

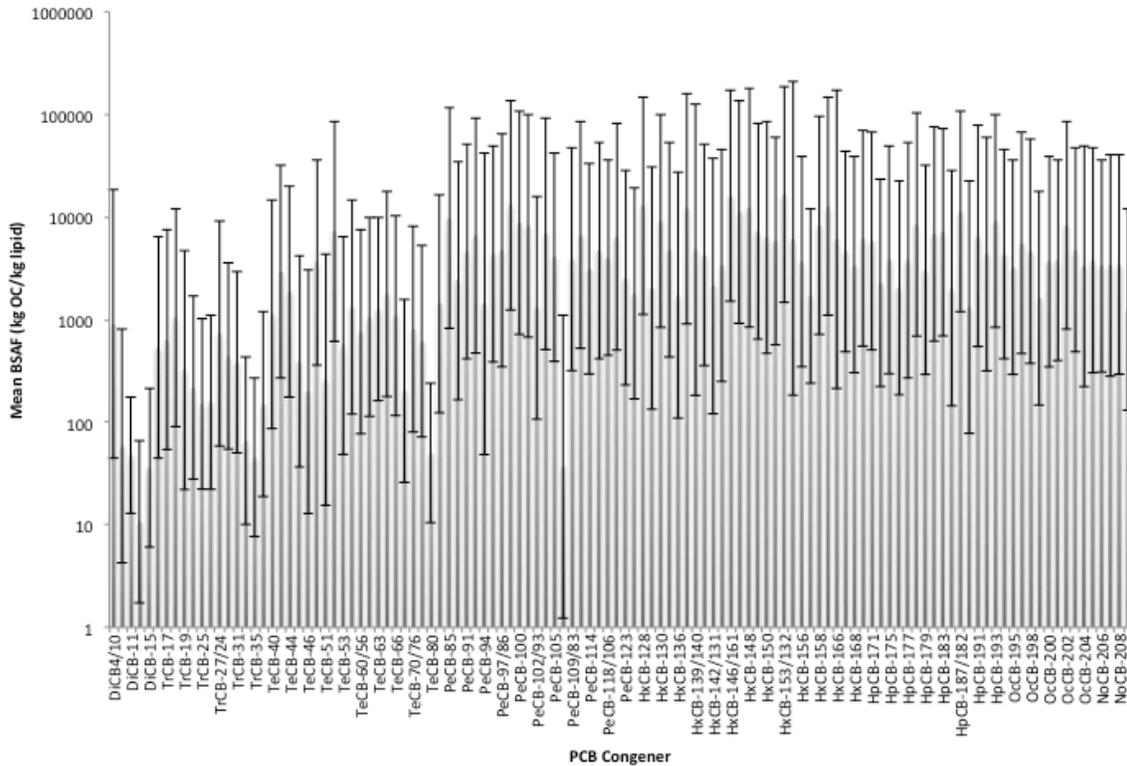


Figure A1a: Congener specific log BSAF values in kg OC/kg lipid for Dungeness Crab in Vancouver Harbor. Error bars represent ± 1 SD from the mean.

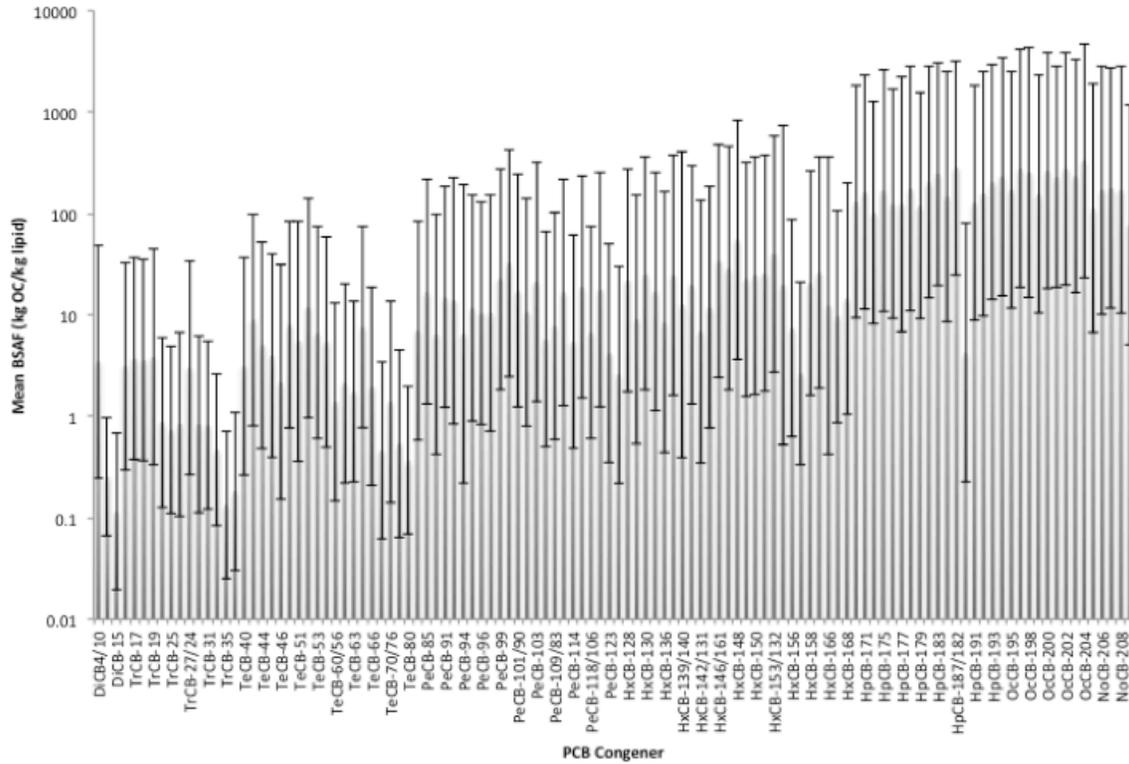


Figure A1c: Congener specific log BSAF values in kg OC/kg lipid for English Sole in Vancouver Harbor. Error bars represent ± 1 SD from the mean.

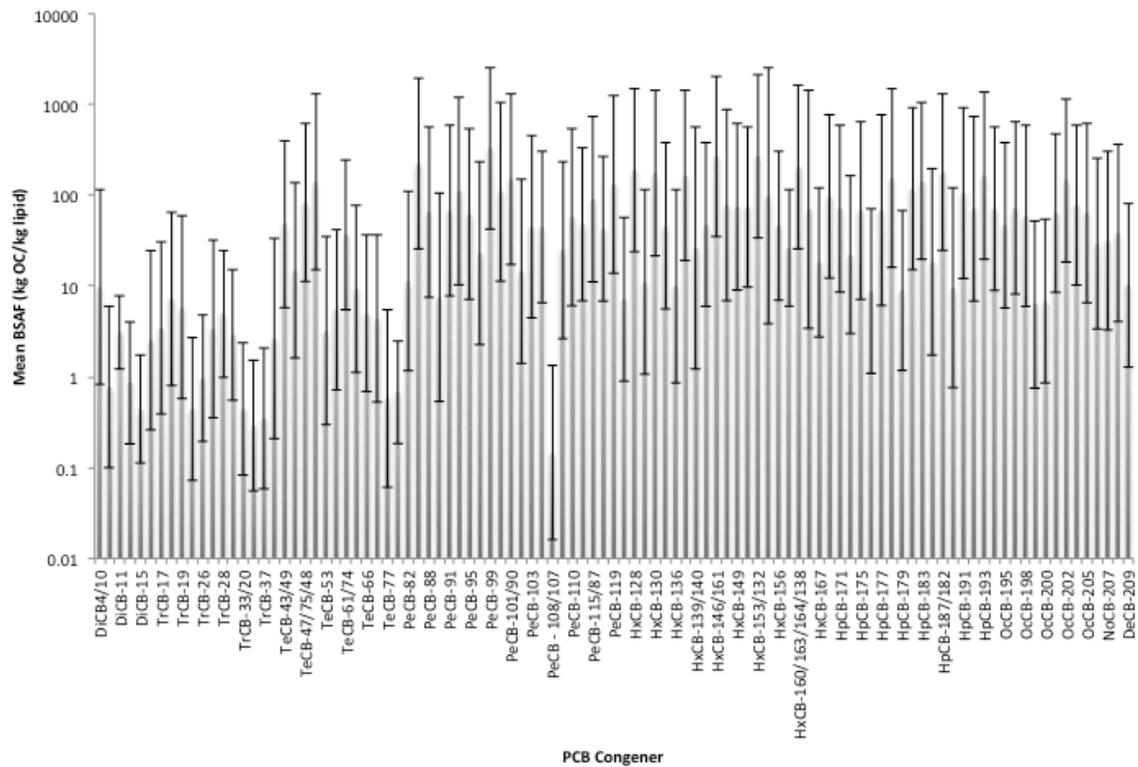


Figure A1d: Congener specific log BSAF values in kg OC/kg lipid for Harbor Seals in Vancouver Harbor. Error bars represent ± 1 SD from the mean.

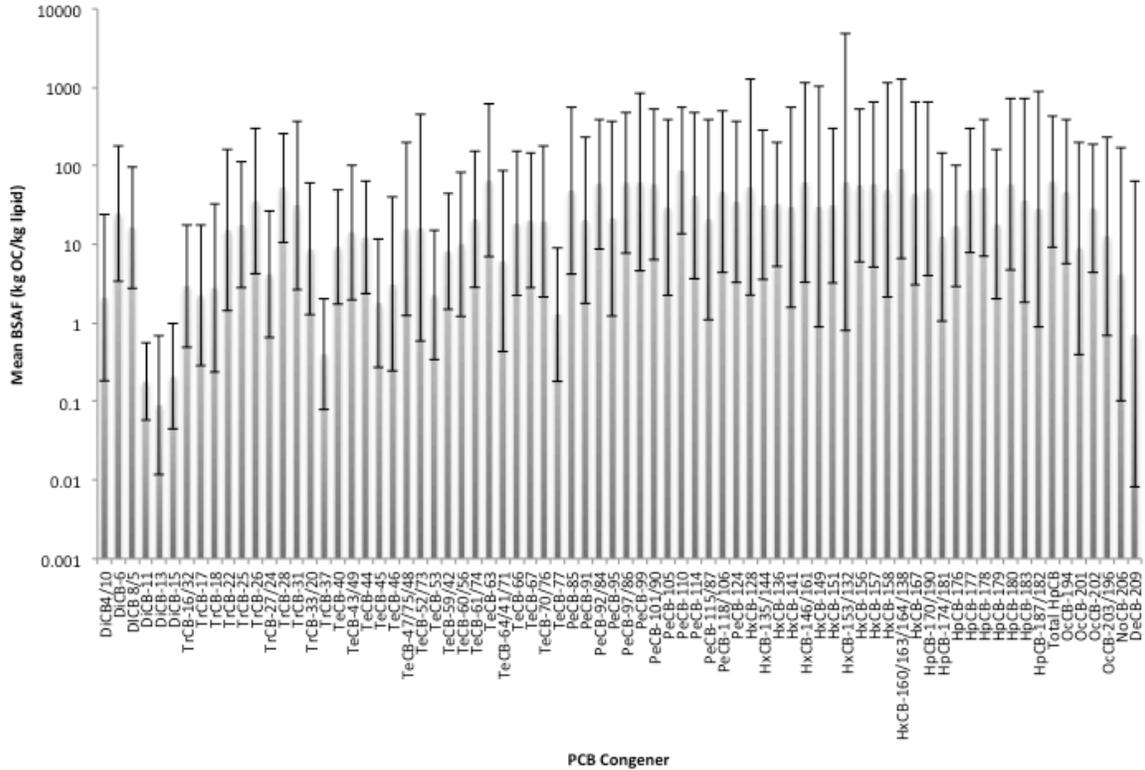


Figure A2a: Congener specific log BSAF values in kg OC/kg lipid for Dungeness Crab in the Strait of Georgia. Error bars represent ± 1 SD from the mean.

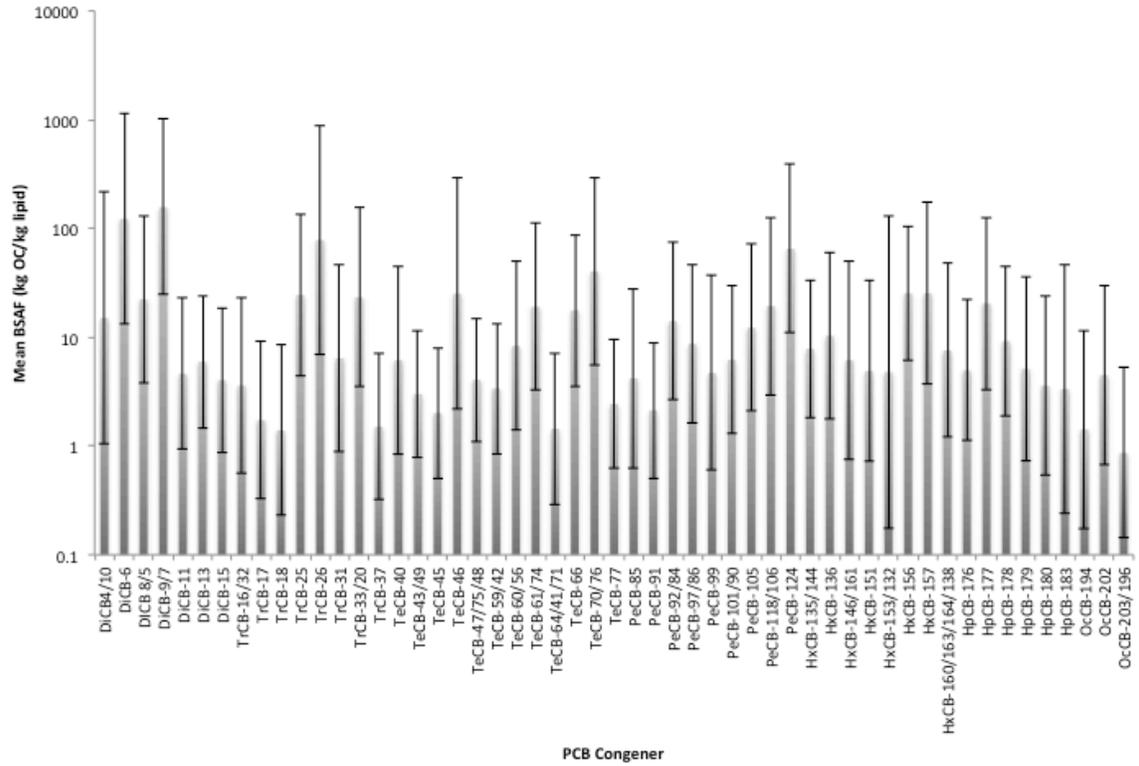


Figure A2b: Congener specific log BSAF values in kg OC/kg lipid for bivalves in the Strait of Georgia. Error bars represent ± 1 SD from the mean.

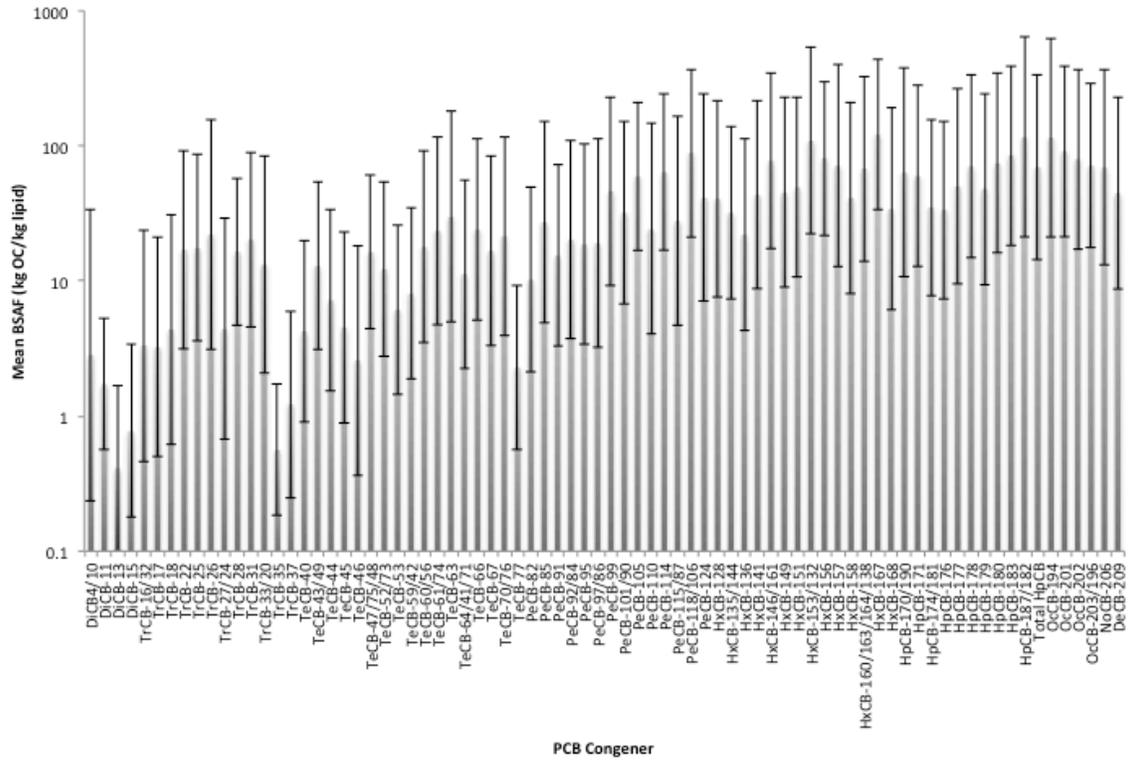


Figure A2c: Congener specific log BSAF values in kg OC/kg lipid for English Sole in the Strait of Georgia. Error bars represent ± 1 SD from the mean.

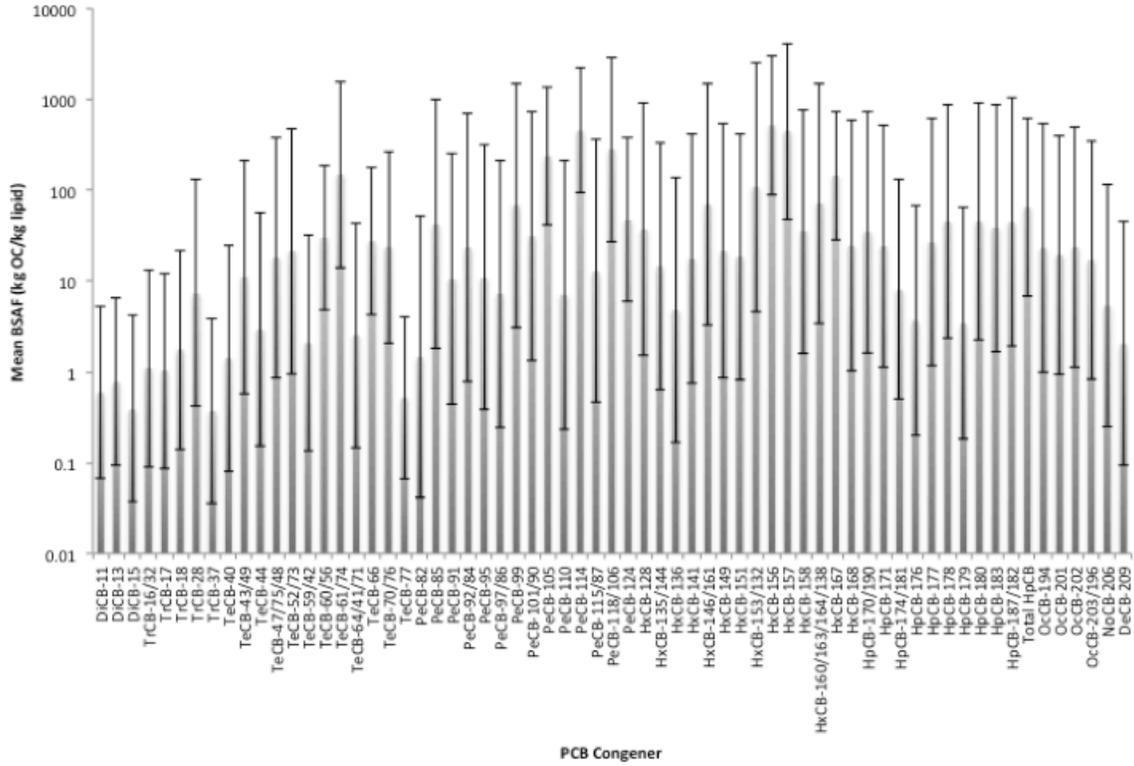


Figure A2d: Congener specific log BSAF values in kg OC/kg lipid for Harbor Seals in the Strait of Georgia. Error bars represent ± 1 SD from the mean.

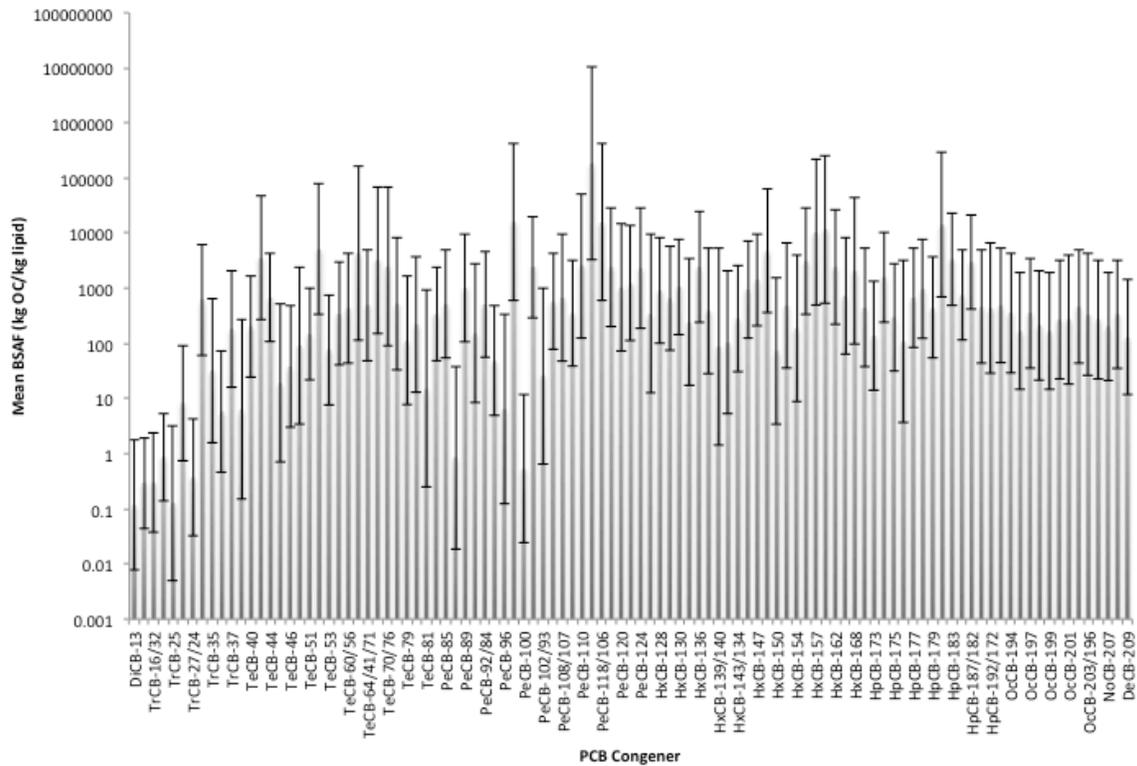


Figure A3a: Congener specific log BSAF values in kg OC/kg lipid for Dungeness Crab in Victoria Harbor. Error bars represent ± 1 SD from the mean.

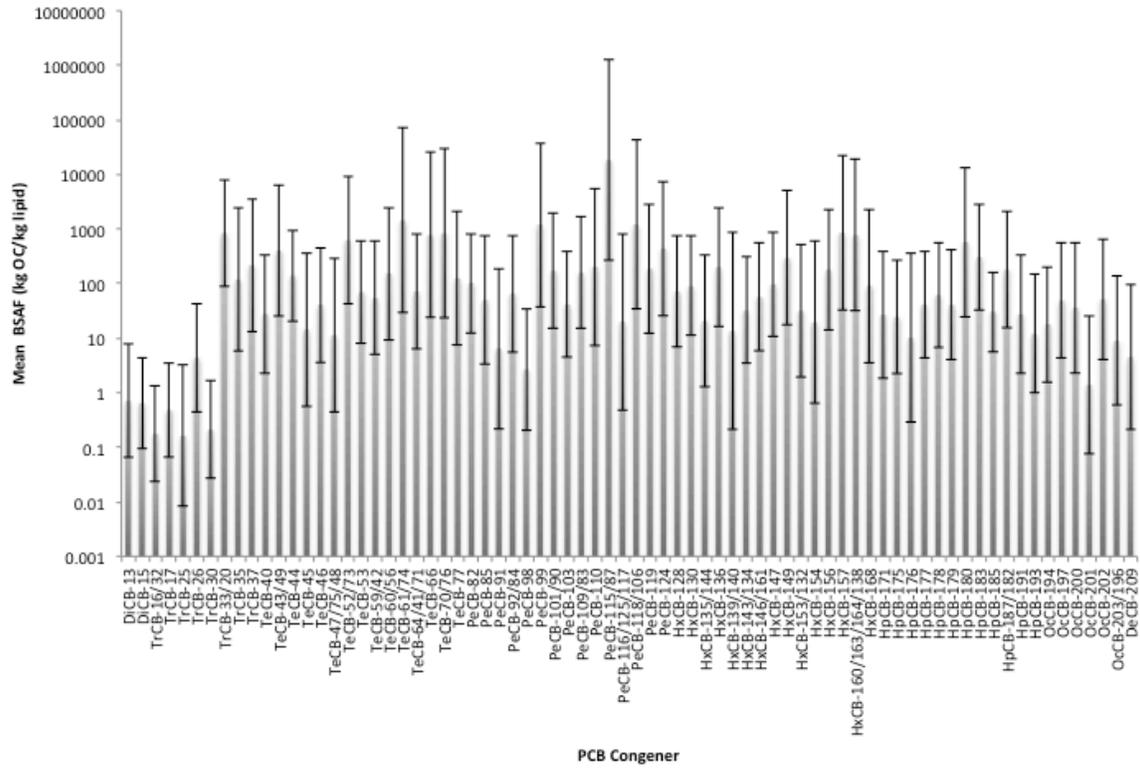


Figure A3b: Congener specific log BSAF values in kg OC/kg lipid for bivalves in Victoria Harbor. Error bars represent ± 1 SD from the mean.

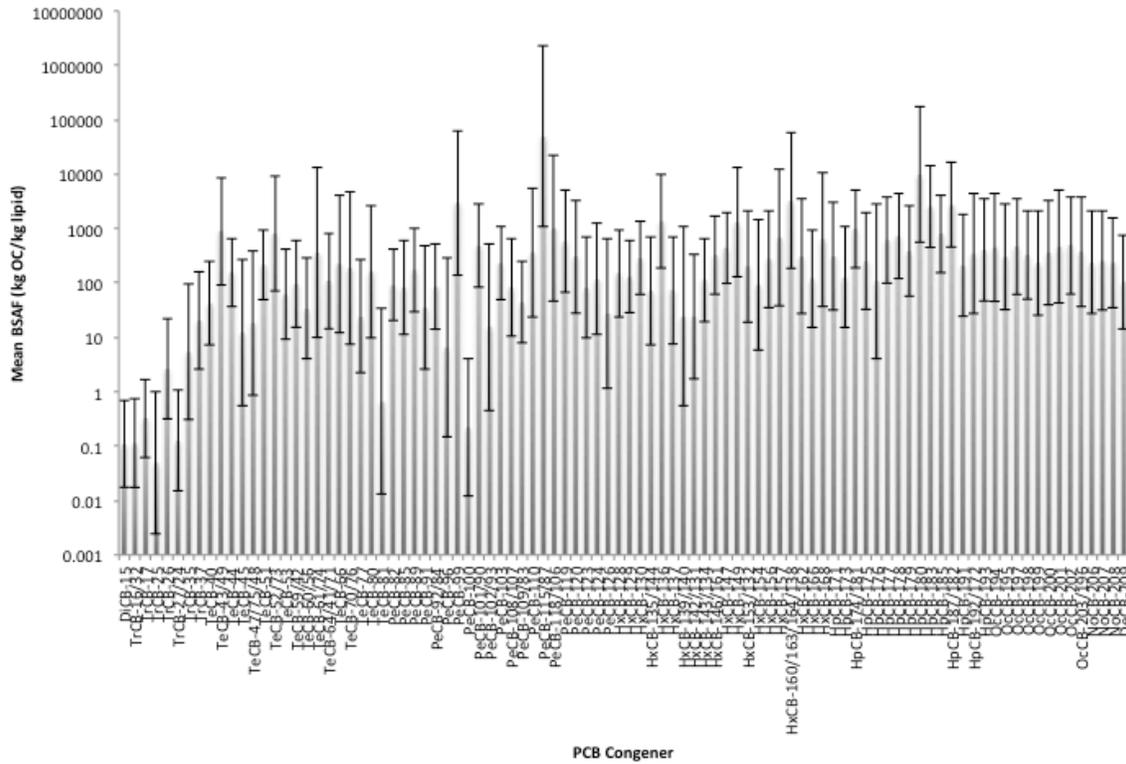


Figure A3c: Congener specific log BSAF values in kg OC/kg lipid for English Sole in Victoria Harbor. Error bars represent ± 1 SD from the mean.

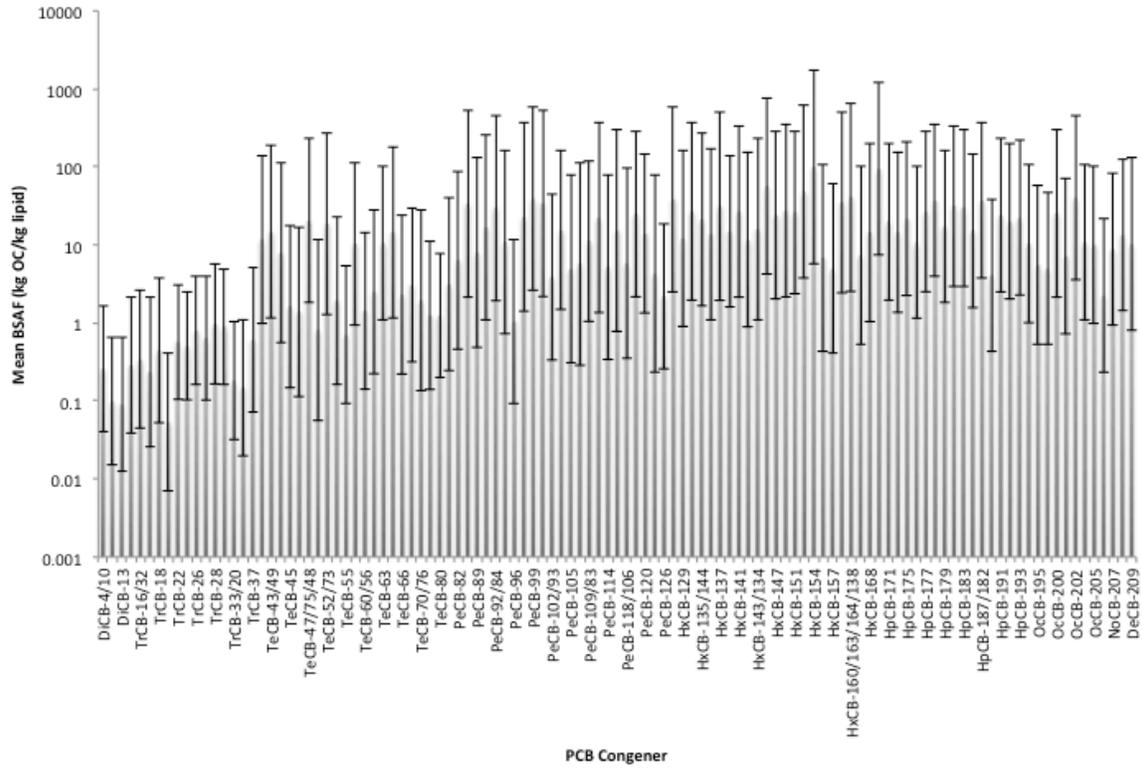


Figure A4a: Congener specific log BSAF values in kg OC/kg lipid for Dungeness Crab in the Central Coast. Error bars represent ± 1 SD from the mean.

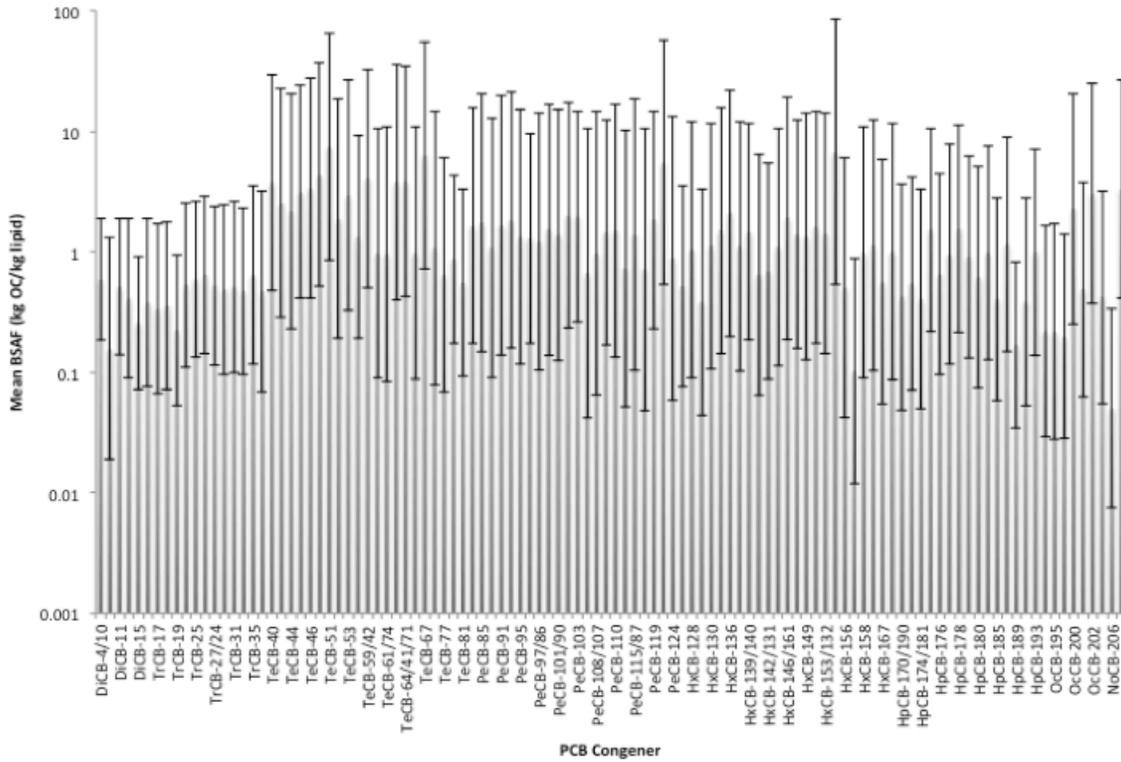


Figure A4b: Congener specific log BSAF values in kg OC/kg lipid for bivalves in the Central Coast. Error bars represent ± 1 SD from the mean.

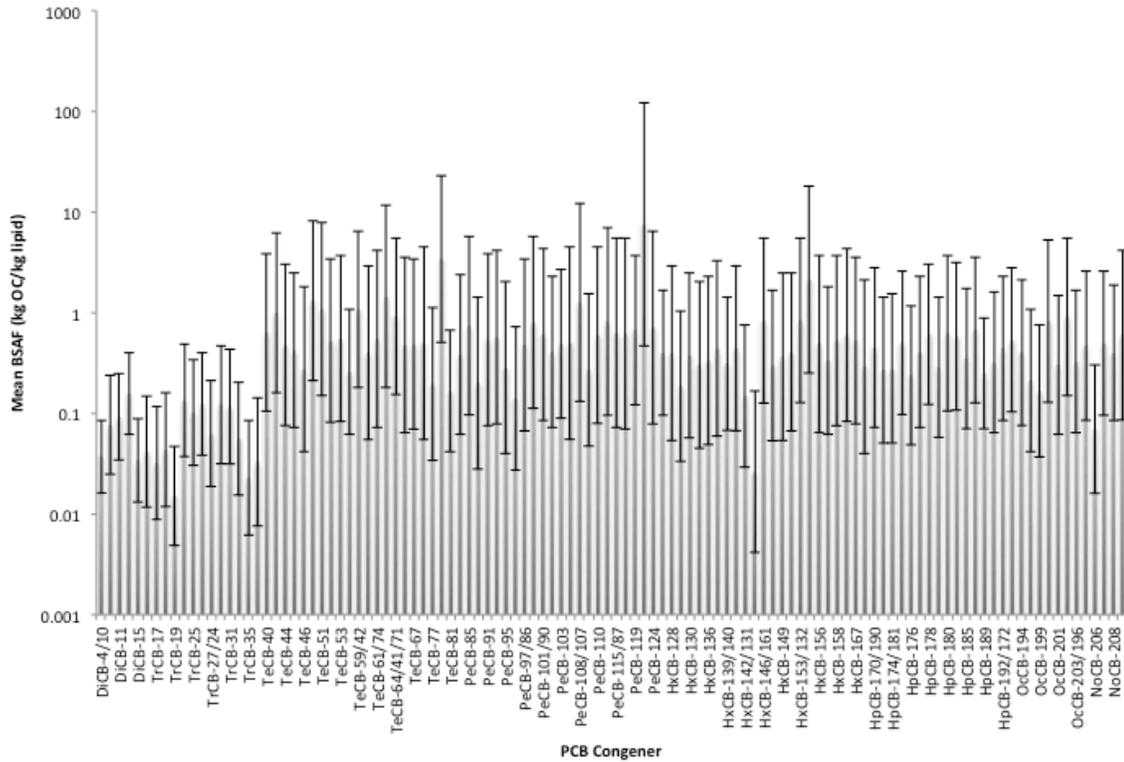


Figure A4c: Congener specific log BSAF values in kg OC/kg lipid for English Sole in the Central Coast. Error bars represent ± 1 SD from the mean.

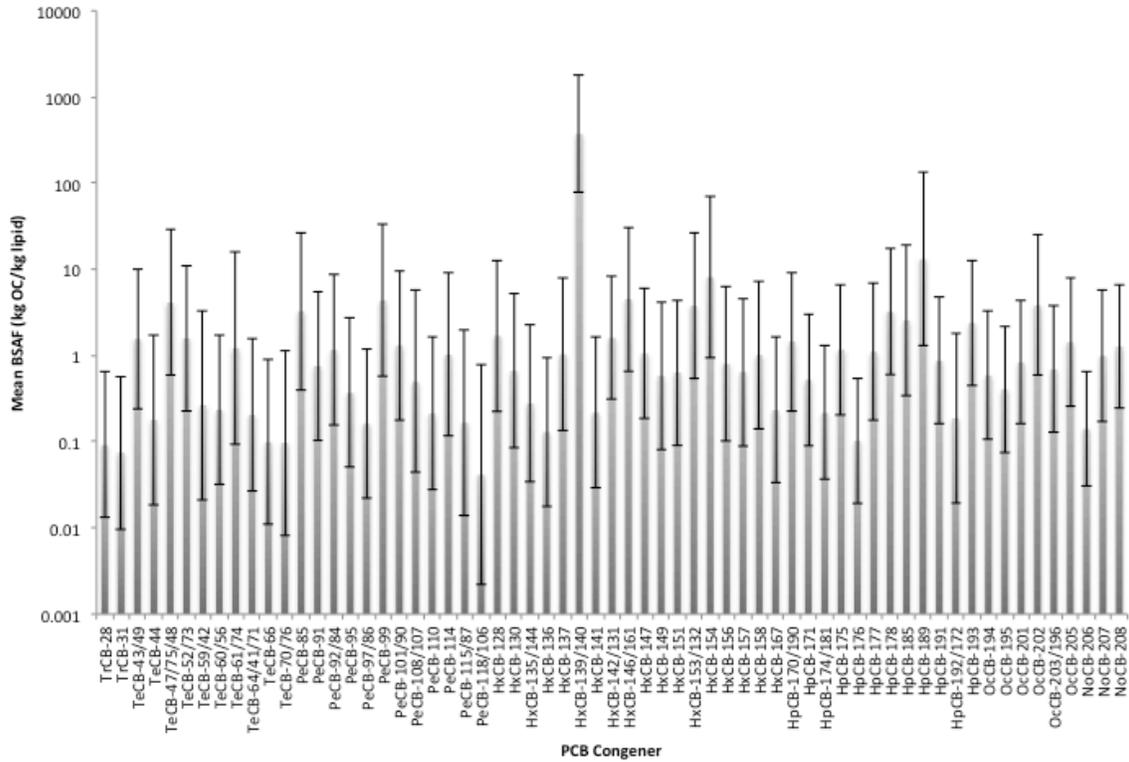


Figure A4d: Congener specific log BSAF values in kg OC/kg lipid for Harbor Seals in the Central Coast. Error bars represent ± 1 SD from the mean.

7.3 Bioaccumulation Models

See attached CD for Bioaccumulation models in Excel 2011

- Vancouver Harbor BSAF Model – Final.xls
- Victoria Harbor BSAF Model – Final.xls
- Strait of Georgia BSAF Model – Final.xls
- Central Coast BSAF Model – Final.xls