THE BIOACCUMULATION OF POLYCHLORINATED BIPHENYLS (PCBs) IN A MARINE FOOD WEB

By

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ABSTRACT

Polychlorinated biphenyls (PCBs) are a group of synthetic chemicals whose production in North America was banned in 1977 due to their toxicity, persistence, and ability to bioaccumulate. Although PCB bioaccumulation has been well-studied, the relative contribution of bioconcentrating and biomagnifying processes remains a topic of debate. This study aimed to investigate evidence of PCB biomagnification in a marine food web. The distribution of PCBs was characterized in seawater, sediment, and eighteen marine organisms from three sampling sites in False Creek Harbour, Vancouver, Canada. Twenty PCB congeners/coeluters were selected for analysis based on a range of chemical properties and on their widespread occurrence in environmental samples. Food web structure was expressed as trophic position (TP) (from literature diet data) and as stable nitrogen isotope ratios ($\delta^{15}N$). PCB concentrations increased significantly and substantially with TP and $\delta^{15}N$. Food Web Magnification Factors (FWMFs) from the regressions for log [PCB]-vs-TP and log [PCB]-vs-$\delta^{15}N$ ranged from 2.0 to 7.5 and from 1.8 to 9.8, respectively, providing evidence of biomagnification. For congeners with intermediate log K_{ow}, fish BAFs were above predicted BCFs providing further evidence of biomagnification. Both FMWF and BAF showed a curvilinear relationship with log K_{ow}. In comparison between FWMF and BAF, BAF mis-classified certain congeners as non-bioaccumulative according to CEPA (1999), whereas FWMFs identified the same congeners as being biomagnified. The results of this study has implications for evaluating bioaccumulative substances and for setting sediment quality guidelines.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS AND ACRONYMS

Bioaccumulation	=	The process by which an aquatic organism achieves an increased chemical concentration compared to that in water due to uptake from all routes of exposure (*e.g.*, dietary absorption, transport across respiratory surfaces, dermal absorption, inhalation) (Gobas and Morrison, 2000; Mackay and Fraser, 2000)
BAF	=	Bioaccumulation Factor; The ratio of the chemical concentrations in the organism to those in water, as a result of chemical uptake through all routes of exposure (Gobas and Morrison, 2000).
Bioconcentration	=	The "process in which the chemical concentration in an aquatic organism exceeds that in water as a result of exposure to waterborne chemical" (Gobas and Morrison, 2000).
BCF	=	Bioconcentration Factor; The ratio of the chemical concentrations in the organism to those in water, as a result of exposure to waterborne chemical (Gobas and Morrison, 2000).
Biomagnification	=	The "process in which the chemical concentration in an organism achieves a level that exceeds that in the organism's diet, due to dietary absorption" (Gobas and Morrison, 2000).
Colloid	=	Nonsettling particles between the particulate phase (> 1 μm) and the dissolved phase (< 10 nm) (Burgess *et al*., 1996a,b; Gschwend and Wu, 1985).
Ectotherm	=	An animal that must use environmental energy and behavioral adaptations to regulate its body temperature, such as fish, reptiles, or amphibians.
Endotherm	=	An animal that uses metabolic energy to maintain a constant body temperature, such as a bird or mammal.
FWMF	=	Food Web Magnification Factor; The overall food web biomagnification factor calculated from the slopes of logarithmic concentration of contaminants vs trophic position (or $\delta^{15}N$ values) of food web components (Fisk *et al.*, 2001)
Interim Sediment Quality Guideline (ISQG)	=	The "concentration below which adverse biological effects are expected to occur rarely" (CCME, 2001)
LDSM	=	Operationally-defined as 'large diameter suspended matter', this referred to the particulate matter captured by the glass fibre filter, which had a pore size of 0.45 μm in diameter

MRL	=	Minimum Reportable Level; A threshold, above which PCB concentrations are considered truly above background levels, defined as the average concentration in the blanks plus three times the standard deviation.
Native	=	A term used to refer to chemicals (in this case PCBs) that is present in environmental samples and that has not been added to the sample as in the case of surrogates. Native PCBs are comprised almost exclusively of carbon-12.
ND	=	Not Detected; A term used to designate a concentration that was below a detection limit set by the HRGC/HRMS.
NDR	=	Not Detected due to Ratio; A term used to designate a concentration in which the isotope ratio was outside of the acceptable range.
Probable Effects Level (PEL)	=	The "level [or concentration] above which adverse effects are expected to occur frequently" (CCME, 2001)
Relative Response Factors (RRFs)	=	For the native compounds, the RRF was defined as the ratio between the response factors of the analyte and the corresponding surrogate internal standard. For the surrogate internal standards, the RRF was defined as the ratio between the response factor of the surrogate internal standard and the corresponding surrogate recovery standard.
SDSM	=	Operationally-defined as 'small diameter suspended matter', this referred to the particulate matter captured by the C_{18} extraction disks, which had diameters less than 0.45 μm (the pore size of the glass fibre filter)
Sorbent	=	A chemical or particle that takes up and holds onto a chemical through either adsorption or absorption
Surrogate	=	A term used to refer to a chemical standard of a known amount which is added to the environmental sample for the purpose of quantifying the 'native' concentrations. PCB surrogate internal standards in this study were isotope-labelled with carbon-13.
Trophic Position (TP)	=	The relative position of an organism in a food chain based on their main nutritional source. Primary producers occupy a TP of 1, while primary consumers (*i.e.*, herbivores) occupy a TP of 2. Secondary and tertiary consumers occupy TPs of 3 and 4, respectively.

1. INTRODUCTION

Polychlorinated biphenyls (PCBs) are a group of compounds that were used primarily as dielectric fluids until their production was banned in 1977 (CCREM, 1986; Sather *et al.,* 2001). First synthesized in 1881, PCBs were not commercially produced until 1929 (CCREM, 1986). Their resistance to breakdown by heat, acids, bases, and light, as well as their low electrical conductivity made them ideal for use as insulation in electrical equipment (CCREM, 1986; Sather *et al.,* 2001). Their physicochemical properties also made them useful as lubricants, fire retardants, plasticizers, and sealants (see Table A-1 in Appendix A for other reported uses of PCBs). An estimated 635 000 metric tones of PCBs were produced in North America prior to 1977, the bulk of which was manufactured by Monsanto Corporation (Safe, 1984; CCREM, 1986; McDonald and Tourangeau, 1996). No PCBs were ever produced in Canada and it has been estimated that 40 000 metric tones have been imported into Canada from all sources (CCREM, 1986; McDonald and Tourangeau, 1996). (A national inventory of PCBs in Canada for 2002 can be found on Environment Canada's website at http://www2.ec.gc.ca/pcb/pdf/ NI2002_e.pdf.) Their extensive use raised few concerns over possible environmental impacts until Swedish scientists reported their detection in birds, sediment, and water in 1966 (Safe, 1984). Soon afterwards, analytical studies detected their presence in almost every component of the global ecosystem and, today, PCBs are detected in even the most remote areas (Kidd *et al.,* 1998a; Fisk *et al.,* 2001).

Each PCB molecule is comprised of two benzene rings linked by a single carbon-carbon bond (*i.e.,* a biphenyl molecule) and of chlorine and hydrogen atoms (see Figure 1-1). Each carbon in the biphenyl molecule allows for a single attachment and thus, there are 209 possible congeners. The experimental conditions determined the degree of chlorination, but the resultant product was always a mixture of isomers, congeners and impurities (Safe, 1984; Environment Canada 1997). For each congener, the physical-chemical properties depend on the degree of chlorination. For example, the hydrophobicity, as measured by the *n*-octanol-water partition coefficient (K_{ow}), increases as the number of chlorine atoms increases on a PCB molecule. Although sold and used as mixtures[1], distribution of PCBs within the environment ultimately depends on the physical-chemical properties of individual PCB congeners and on the biotic and abiotic characteristics of the receiving environment.

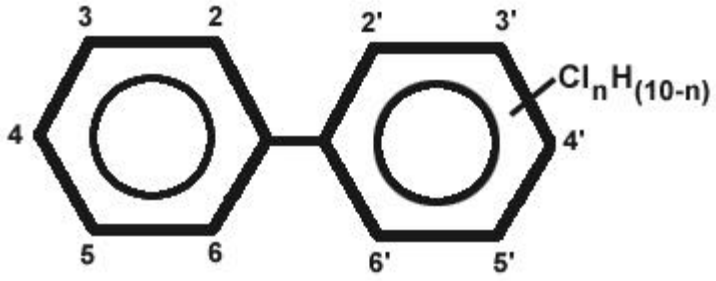

Figure 1-1. Generalized structure of a PCB molecule. Each carbon atom allows for a single attachment for chlorine or hydrogen.

Although PCBs share the same general structure as shown in Figure 1-1, the toxicities of the individual congeners are not the same and can be classified into two categories: dioxin-like and non-dioxin-like. Dioxin-like toxicity is produced by the coplanar PCBs, which lack complete substitution in the ortho positions (*i.e.*, positions 2,

[1] In North America, PCBs were primarily sold as mixtures under the trade name Aroclor (Sather *et al.*, 2001). Other trades names are listed in McDonald and Tourangeau (1996).

2', 6, and 6' in Figure 1-1) of the biphenyl structure (Bergen *et al*., 1996). Of the 209 congeners, only 20 can achieve the coplanar configuration and of these, three (PCB-77, PCB-126, and PCB-169) have demonstrated acute toxicity similar to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and 2,3,7,8-tetrachlorodibenzofuran (Hong *et al.*, 1993; Bergen *et al*., 1996; Fischer *et al*., 1998; Andersson *et al*., 2000). The mechanism of toxic action of coplanar PCBs has been well studied. The toxicity of PCBs has been linked to binding of PCB molecules to the Ah receptor (Safe, 1984; Andersson *et al*., 2000). It has been proposed that the binding of the Ah receptor allows for the passage of the complex through the nuclear membrane and causes the induction of cytochrome P-450 enzymes. This, in turn, increases the number of detoxifying enzymes in the system, which increases the formation of highly reactive epoxides of aromatic hydrocarbons. Epoxides, being highly unstable, react quickly with neighbouring molecules. In the presence of DNA, epoxide formation has been linked to the formation of DNA adducts, which interfere with the normal functions of the cell and can lead to carcinogenesis and cell death. Although Ah receptor-mediated toxicity has been studied mainly in mammals, cytochrome P-450 enzymes have been detected in fish (James *et al.*, 1997; Grinwis *et al.*, 2001) and bivalves (Livingstone *et al.*, 1997). Non-dioxin-like toxicity is produced by the non-coplanar PCBs, which contain at least one chlorine substituent in the ortho positions. Non-coplanar PCBs do not bind with high affinity to the Ah receptor. Hence, it was originally assumed that their toxicity was minimal (Kafafi *et al*., 1993; Fischer *et al*., 1998). However, in a review by Fischer *et al*. (1998), various toxic effects were listed that were attributable to non-coplanar PCBs, including neurotoxicity (such as "decreased catecholamine levels in certain brain regions and behavioural changes in

laboratory animals"), increased insulin release, neutrophil activation, and activation of ryanodine-sensitive Ca^{2+} channels. Overall, PCB toxicity can result from exposure to either coplanar or non-coplanar congeners.

Persistent organic pollutants, such as PCBs, are known to reach elevated concentrations within organisms relative to their environment, a phenomenon termed 'bioaccumulation'. Bioaccumulation is the process by which an aquatic organism achieves an increased chemical concentration compared to that in water due to uptake from all routes of exposure (*e.g.*, dietary absorption, transport across respiratory surfaces, dermal absorption, inhalation) (Gobas and Morrison, 2000; Mackay and Fraser, 2000). Bioaccumulation can be divided into two processes: bioconcentration and biomagnification. Bioconcentration is the "process in which the chemical concentration in an aquatic organism exceeds that in water as a result of exposure to waterborne chemical" (Gobas and Morrison, 2000). Biomagnification is the "process in which the chemical concentration in an organism achieves a level that exceeds that in the organism's diet, due to dietary absorption" (Gobas and Morrison, 2000). The relative importance of bioconcentration and biomagnification has been, and continues to be, a topic of debate (*e.g.*, Leblanc, 1995; Randall *et al.*, 1998; Gary, 2002), despite the overwhelming abundance of literature supporting the importance of biomagnification, especially for PCBs (*e.g.*, Fisk *et al.*, 2001; Hop *et al.*, 2002; Hoekstra *et al.*, 2003). The bioaccumulation of PCBs has been well-studied, although at the start of this study most bioaccumulation studies involved freshwater food webs (*e.g.*, Oliver and Niimi, 1988; Pereira *et al*., 1988; Kidd *et al.*, 2001).

Recently, studies of PCB bioaccumulation in Arctic marine food webs have been published. Hoekstra *et al.* (2003) reported significant increases in log-transformed, lipid-normalized organochlorine concentrations with δ^{15}N-determined trophic levels from a food web comprised of zooplankton, fish species (including arctic cod, arctic char, pink salmon, and fourhorn sculpin), and marine mammals (including bowhead whales, beluga whales, ringed seals and bearded seals). Ruus *et al.* (2002) reported significant increases in log organochlorine concentrations (including PCBs) with δ^{15}N-determined trophic levels in a Norwegian marine food web comprised of a polychaete, the lesser sandeel, three species of gobys, bullrout, cod, herring gull, and harbour seals. Hop *et al.* (2002) found similar observations for ectothermic and endothermic food webs from the Barents Sea. Other studies of organochlorine bioaccumulation (including PCBs) in the Arctic include Fisk *et al.* (2001), who studied another Arctic marine food web, and Kidd *et al.* (1998a,b) who studied freshwater food webs. All of these studies have attributed the increase in lipid-normalized organochlorine concentrations to biomagnification.

Biomagnification of PCBs has recently been quantified through the calculation of Food Web Magnification Factors (FWMFs) (Fisk *et al.*, 2001; Ruus *et al.*, 2002; Hop *et al.*, 2002; Hoekstra *et al.*, 2003). FWMFs are derived from the slope of the linear regressions between the logarithm of PCB concentrations and the trophic positions of the organisms comprising the food web. By definition, FWMFs greater than one indicate biomagnification of chemicals. Essentially, FWMFs are similar to biomagnification factors, except that they incorporate full food webs. For the above-mentioned Arctic food webs, Hoekstra *et al.* (2003) reported food web magnification factors (FWMFs) that ranged from 1.29 (for PCB-28) to 6.69 (PCB-153), while the FWMF for ΣPCB was 3.26;

Ruus *et al.* (2002) reported a FWMF of 6.2 for ΣPCB; Hop *et al.* (2002) reported FWMFs in the range of 3-4 for ectothermic food webs and in the 28-32 range for the same food web that included endotherms.

The primary aim of this study was to characterize PCB biomagnification in a marine food web. Some authors (*e.g.*, Leblanc, 1995; Randall *et al.*, 1998; Gary, 2002) have repeatedly argued that biomagnification does not exist and that aquatic organisms acquire their PCB body burden from the water. For example, Leblanc (1995) concluded that biomagnification (which the author refers to as "trophic level differences in bioconcentration") is due "largely to increased lipid content and decreased chemical elimination efficiency of organisms occupying increasing trophic levels". However, the authors compare wet weight concentrations amongst aquatic organisms from different studies. As well, the author attributed apparent evidence of biomagnification from the Oliver & Niimi (1988) study to sampling artefacts. Indeed, the sampling program in Oliver & Niimi (1988) was poorly designed with biota samples collected from various locations within Lake Ontario and with sampling times that spanned five years. Hence, the present study examined biomagnification in a small-scale, relatively enclosed ecosystem and attempted to minimize errors due to spatial differences in PCB concentrations, errors due to sampling over a long period of time, and errors due to inconsistent sampling design. In addition, there have been no comparable studies in the more temperate climate of the southern west coast of British Columbia and in which the distribution of PCBs was investigated with such a well-characterized marine food web.

The objectives of this thesis included (1) to determine how lipid-normalized PCB concentrations in biota varied with trophic position, as defined by literature diet

composition and by stable nitrogen isotope ratios; (2) to quantify the extent of biomagnification by calculating FWMFs; (3) to examine the relationship between observed bioaccumulation factors (BAFs), biota-sediment accumulation factors (BSAFs), and predicted values; (4) to examine the relationships between FWMFs, BAFs, BSAFs between PCB congeners by comparing them to the log K_{ow} of each congener; and (5) to determine whether BAFs and FWMFs agree with each other with respect to the potential of a chemical for bioaccumulation or biomagnification.

2. METHODS

OVERVIEW: Biota, sediment, and seawater samples were collected from False Creek Harbour in Vancouver, BC, by Cheryl Mackintosh. All samples were analyzed concurrently for both phthalate esters (PEs) and polychlorinated biphenyls (PCBs) at the Institute of Ocean Sciences (IOS) by Audrey Chong, Jody Carlow, Hongwu Jing, Zhongping Lin, Natasha Hoover, Linda White, and Joel Blair. Water samples were filtered by Cheryl Mackintosh at SFU prior to chemical analysis at IOS. All results regarding PEs can be found in Mackintosh (2002). As this study used the same samples as in Mackintosh (2002), diet-based trophic positions and the three-phase aqueous model were obtained from Cheryl Mackintosh. For PCBs, quality assurance and control (QA/QC) of the biota data was performed by this author, while Tamara Fraser at IOS performed the QA/QC of the sediment and seawater data. The analysis of PCB concentrations was performed by this author.

2.1. STUDY SITE AND DESIGN

2.1.1. Site History

The site selected for this field study was False Creek Harbour in Vancouver, BC, Canada (see Figure 2-1). It is a small inlet for the marine waters of the Strait of Georgia. It is characterized by relatively well-mixed shallow waters (~20 ft.) and an average salinity of approximately 30 ppt (Mackintosh, 2002). The annual daily mean temperature for the area is 11.0°C and the mean precipitation is 1588.6 mm per year (Environment Canada, 2003). Although the land immediately surrounding the harbour is now primarily

residential, it was mainly used for industrial purposes between the 1900s and 1980s (Gourley, 1997). It has been, and continues to be, the site of a Canadian Pacific Railway terminal and is the site of a large marina.

2.1.2. Study Design

This study was designed by Dr. Frank Gobas and Cheryl Mackintosh. It was comprised of three sampling sites within False Creek, which were designated "North-Central", "Marina", and "East-Basin" (see Figure 2-1). Triplicate samples of sediment, water, and biota were collected from each site. The latitudes and longitudes for each location are:

North-Central: 49°16'13"N, 123°07'40"W

Marina-South: 49°16'09"N, 123°07'15"W

East-Basin: 49°16'28"N, 123°06'18"W

Supplementary sediment and water samples were also collected from a fourth station:

Cambie Bridge: 49°16'18"N, 123°07'04"W

In July of 1998, a pilot study was performed with the Institute of Ocean Sciences (IOS) to develop analytical methods for the simultaneous extraction of PCBs and phthalate esters from environmental samples. A limited number of samples consisting of sediment (n=8), mussel (n=8), clam (n=3), and oyster (n=3) samples were collected during this time (Mackintosh, 2002).

Sediment and biota samples for this study were collected from May to October 1999 by Cheryl Mackintosh and were pooled with the 1998 samples. Surf scoter samples from the False Creek area, which were collected during this same period, were provided by Laurie Wilson of the Canadian Wildlife Service. Water samples from False Creek and from Lynn Headwaters Regional Park (LHRP) (North Vancouver, BC) were collected in 1999 and July of 2000. False Creek water samples from 2000 were used for the data analysis. Water samples from LHRP were used as negative controls, or "blanks".

All samples were sent to the Institute of Ocean Sciences (IOS) in Sidney, BC, for chemical analysis. Sub-samples of tissue samples were sent to the University of California (Davis) for stable isotope analysis. PCB data analysis was performed by this author.

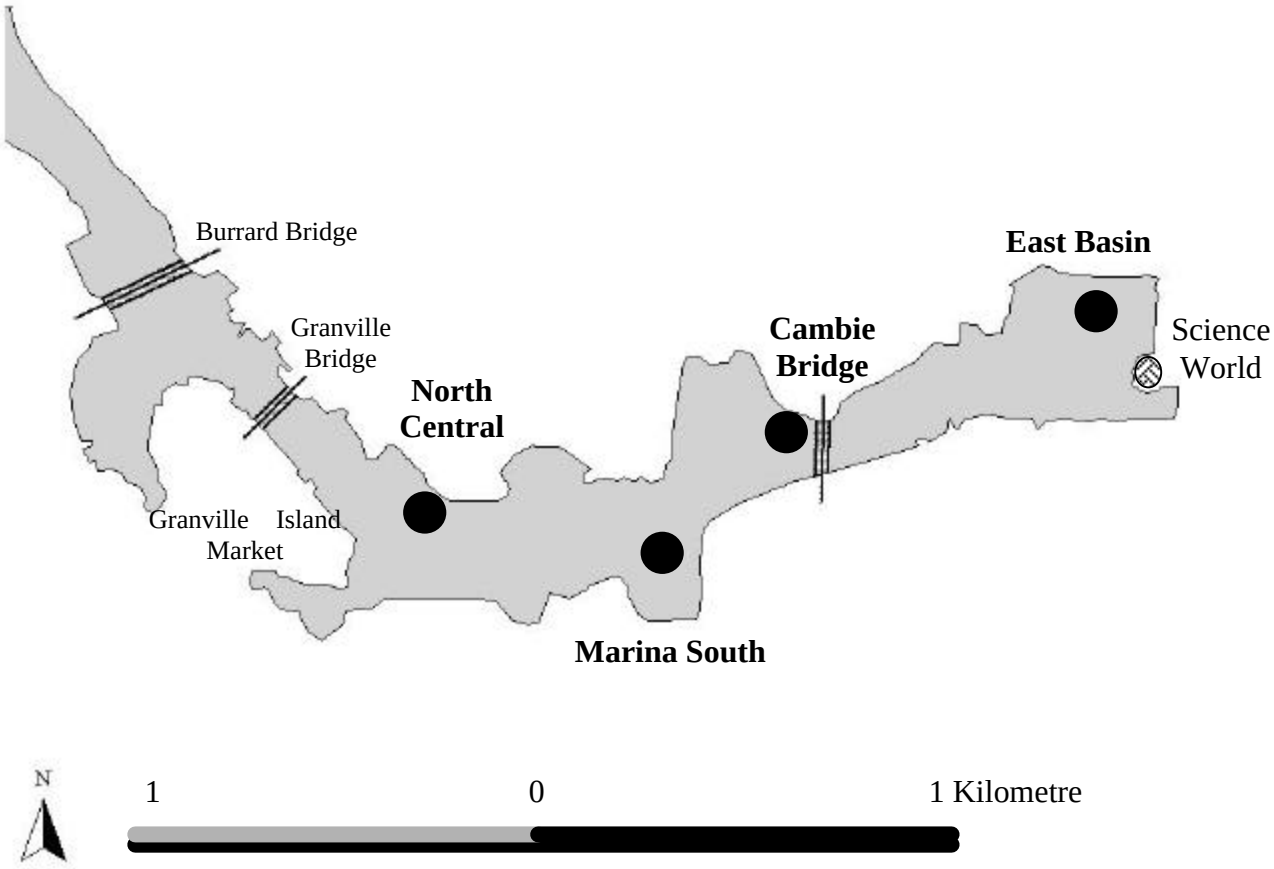

Figure 2-1 – Map of Field Study Site: False Creek Harbour, Vancouver, British Columbia, showing locations of four sampling stations: "North Central", "Marina – South", "Cambie Bridge", and "East Basin".
(Used with permission from Mackintosh 2002)

2.2. FIELD SAMPLING

NOTE: All preparatory steps and field sampling were performed by Cheryl Mackintosh. The following field sampling methods were summarized from Mackintosh (2002).

2.2.1. Preliminary Steps

The ubiquitous nature of both phthalate esters (PEs) and PCBs required several preparatory steps to reduce background contamination in all sampling equipment. Prior to use, all equipment, which was made of glass or stainless steel, was washed with lab-grade detergent and rinsed twice with distilled hexane, iso-octane, and dichloromethane (DCM). The equipment was then heated in a muffler oven at 400°C for a minimum of 10 hours, after which it was re-rinsed three times with distilled acetone, hexane, iso-octane, and DCM. Aluminium foil, which had been rinsed with distilled acetone and hexane and baked at 350°C for 10 hours, was used to cover cleaned equipment. Solvent-rinsed metal lids were used to cap glass vials. The only exception to the above procedures was the petit ponar sediment grab sampler, which although washed with lab-grade detergent and rinsed three times with distilled acetone, hexane, and DCM could not be baked due to its size.

2.2.2. Sediment Sampling

Sediment samples were collected from each sampling site using a petit ponar grab sampler (see Figure 2-2A) and transferred onto aluminium foil. The top 0.5 to 1.0 cm of sediment, representing the ‘active layer’, was collected with a metal spoon and transferred into glass vials. The vials were the covered with aluminium foil and sealed

with metal lids. The vials were immediately placed on ice and then stored in the dark at –20°C until analysis.

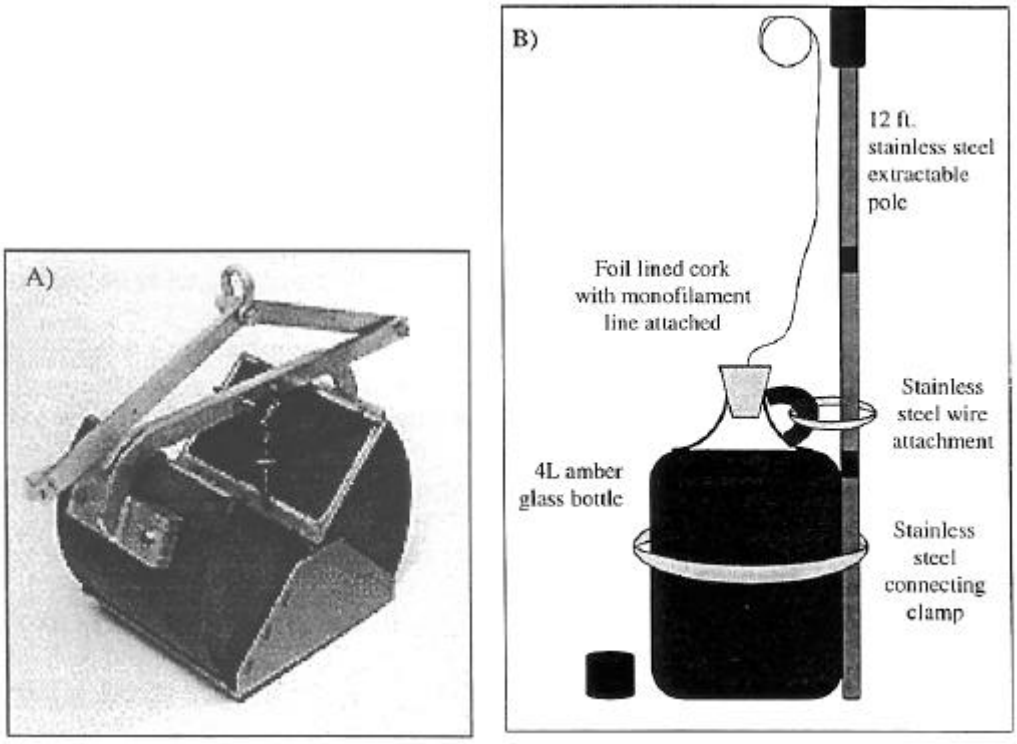

Figure 2-2 - Sediment & Water Sampling Equipment. A. Petit Ponar Sediment Grab Sampler. B. Seawater collection apparatus: 4 L amber glass bottle attached to stainless steel extendible pole. (Used with permission from Mackintosh 2002.)

2.2.3. Water Sampling

Water samples were collected from mid-ocean depth (~10-12 ft.) at each sampling site using the set-up in Figure 2-2B. The 4L amber glass bottle was attached to an extendible stainless steel pole and lowered to the appropriate depth. The plug was then pulled out and the bottle was raised after it had filled. The bottles were immediately placed on ice and then transferred to a refrigerator at the SFU laboratory where they were kept at 4°C until filtration. Well water from Lynn Headwaters Regional Park (North Vancouver, BC) was used for procedural blanks. Sample spiking (using internal

standards), filtration and extraction occurred within 12 hours of collection (see Section 2.4.4.).

2.2.4. Biota Sampling

Eighteen marine organisms representing various feeding strategies and life-histories were collected from three sites within False Creek Harbour (see Figure 2-1). The methods of collection are listed in Table 2-1. Representatives of both benthic and pelagic food webs were selected and included the primary producers (eg. plankton and algae), filter feeders (eg. blue mussels), deposit feeders (eg. geoduck clams), rapidly-maturing, short-lived species (eg. striped seaperch), and slow-growing, long-lived species (eg. dogfish). Selected species were relatively abundant within False Creek and were considered as resident, or non-migratory, species, with the exception of the dogfish shark and the surf scoter. Residency was considered important for obtaining tissue concentrations that were representative of the water and sediment concentrations to which the organisms were exposed. Plankton samples were collected in pre-cleaned 250 mL vials and all other biota were wrapped in solvent-rinsed aluminium foil and frozen at ~20°C until analysis. Surf scoter liver samples were provided by the Canadian Wildlife Service. Further information on the trophodynamic interactions and the life histories of False Creek species can be found in Appendix B of Mackintosh (2002).

Table 2-1. Species Information and Sampling Methods[e] for Marine Organisms Collected from False Creek Harbour, Vancouver, Canada[a].

Trophic Group	Common Name	Latin Name	Mean Length (Range) (cm)	Mean Weight (Range) (g)	Collection Methods
Primary Producers	Green Algae	*Enteromorpha intestinalis*	NA[b]	NA	Collected from shore at low tide
	Brown Algae	*Nereocystis luetkeana*	NA	NA	Collected from water
		Fucus gardneri			Collected from shore at low tide
	Plankton[c]	NA	NA	NA	Plankton tow net ~236 µm mesh size
Benthic Invertebrates	Blue Mussels	*Mytilus edulis*	NA	Individual shellfish were pooled to obtain samples of ≥ 10 g.	Collected from pilings during low tide
	Pacific Oysters	*Crassostrea gigas*			Collected off rocks during low tide
	Geoduck Clams	*Panopea abrupta*			Dug up from mud shore during low tide
	Manila Clams	*Tapes philippinarum*			Dug up from mud shore during low tide
	Dungeness Crabs	*Cancer magister*	12.4 (9.3-16.0) carapace width	252 (102-514)	Stainless steel crab traps and bait
	Purple Seastar	*Pisaster ochraceus*	NA	NR[b]	Collected from rocks and pilings during low tide
Small Forage Fish	Shiner Perch	*Cymatogaster aggregata*	Individuals ranged in size from approx. 2.5 - 10 cm	Individuals were pooled to obtain samples of ≥ 5 g.; Individual minnows ranged from approx. 1 –20 g.	Beach seining net - ¼″ mesh size
	Pacific Staghorn Sculpin	*Leptocottus armatus*			
	Cutthroat Trout	*Salmo clarki clarki*			
	Three Spine Stickleback	*Gasterosteus aculeatus*			
	Whitespotted Greenling	*Hexagrammos stelleri*			
	Starry Flounder	*Platichthys stellatus*			

[a] Used with permission from Mackintosh (2002).
[b] NA - Not Applicable; NR – Not Reported/recorded.
[c] The plankton sample was a composite of phytoplankton, zooplankton, and other pelagic invertebrates and algae.
[d] The starry flounder (adult) sample was pooled from 3 individuals.
[e] Samples were taken in triplicate from each site.

Table 2-1 (Continued). Species Information and Sampling Methods for Marine Organisms Collected from False Creek Harbour, Vancouver, Canada[a].

Trophic Group	Common Name	Latin Name	Mean Length (Range) (cm)	Mean Weight (Range) (g)	Collection Methods
Forage Fish (Adults)	Pacific Herring	*Clupea harengus pallasi*	11 – 18	45 – 160	Herring gill nets - 1″ mesh size
	Surf Smelt	*Hypomesus pretiosus pretiosus*	15	30	
	Northern Anchovy	*Engraulis mordax mordax*	13	28	
	Pile Perch	*Rhacochilus vacca*	14.1 (13.5 – 15.0)	54 (49 –60)	Beach seine net - ¼″ mesh size AND Herring gill nets - 2″ mesh size
	Striped Seaperch	*Embiotoca lateralis*	14.2 (12.5 – 17.5)	73 (49 – 174)	
Predatory Fish	Pacific Staghorn Sculpin	*Leptocottus armatus*	17.4 (12.0 – 29.5)	106 (22 – 344)	Stainless steel prawn traps & bait
	English Sole	*Parophrys vetulus*	15	74	Sinking gill net - 2″ mesh size
	Starry Flounder[2]	*Platichthys stellatus*	15 (11 – 22)	NR	
	Whitespotted Greenling	*Hexagrammos stelleri*	20 (18.5 – 21.5)	126 (100 – 241)	Stainless steel prawn traps & bait
	Spiny Dogfish	*Squalus acanthias*	82 (61 – 104)	ca. 2000	Long-line fishing
Marine Bird	Surf Scoter	*Melanitta perspicillata*	NA	NR	Collected by the Canadian Wildlife Service

[a] Used with permission from Mackintosh (2002).
[b] NA - Not Applicable; NR – Not Reported/recorded.
[c] The plankton sample was a composite of phytoplankton, zooplankton, and other pelagic invertebrates and algae.
[d] The starry flounder (adult) sample was pooled from 3 individuals.
[e] Samples were taken in triplicate from each site.

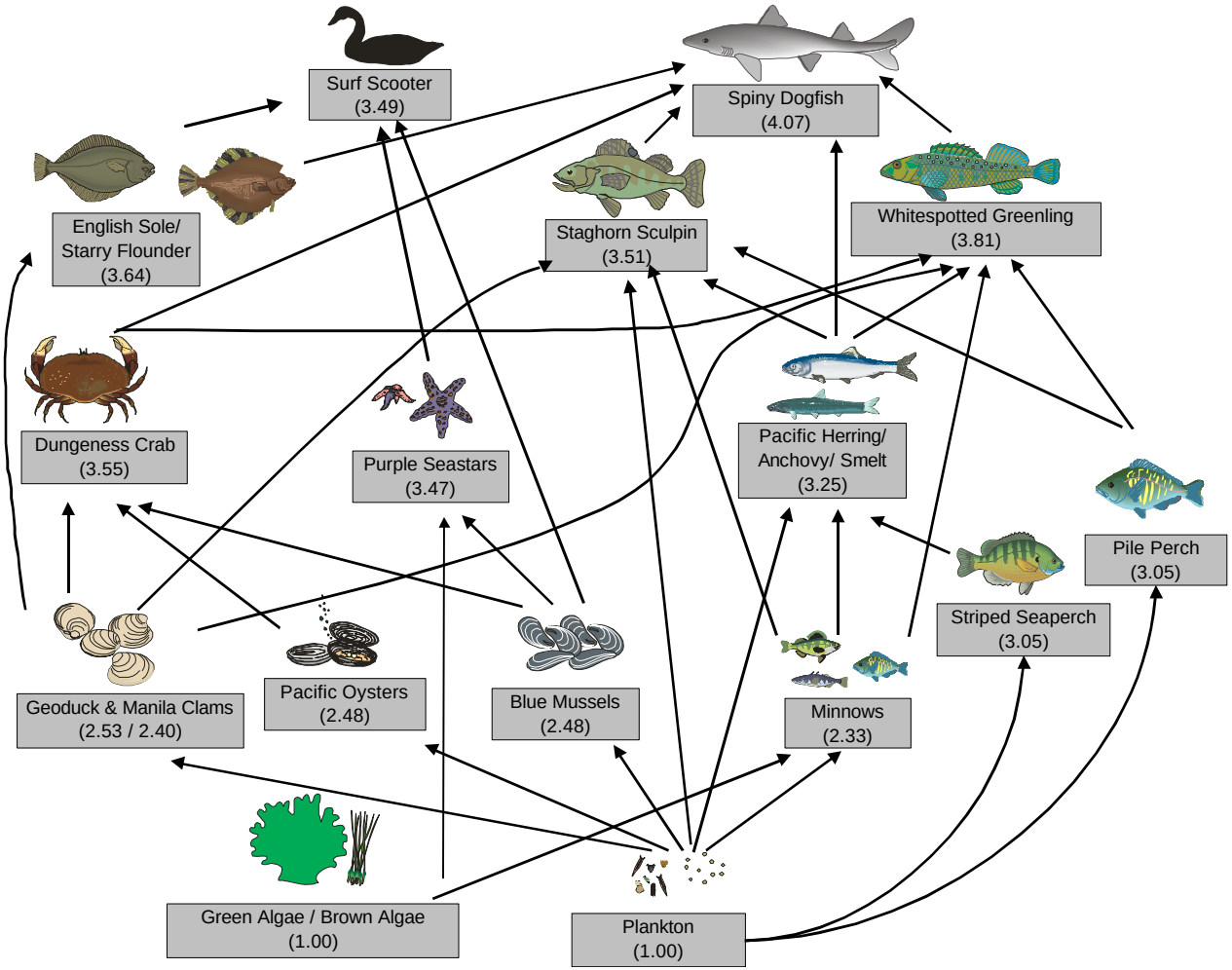

Figure 2-3. Generalized Food Web for False Creek Harbour, showing trophic linkages and diet-based trophic positions (in parentheses). (Used with permission from Mackintosh, 2002)

2.3. DETERMINATION OF LIPID, MOISTURE, ORGANIC CARBON, & PARTICULATE MATTER CONTENT

2.3.1. Lipid Content in Biota Samples

Biota samples were analyzed for lipid content at the Regional Dioxin Lab (RDL) at the Institute of Ocean Sciences (IOS) in Sidney, BC, according to the protocols in Ikonomou *et al.* (2001). Briefly, 5 g of a biota sample were weighed and transferred quantitatively to a porcelain mortar with 100 g of anhydrous, granular sodium sulphate. The mixture was ground until it was homogeneous and then transferred to a glass extraction column. The column was packed with glass wool at the tip and a TurboVap sample tube (Zymark Ltd., Mississauga, Ontario) was placed under the column. The aluminium weighing boat, mortar and pestle, funnel and spatula were rinsed three times with 1:1 dichloromethane (DCM):hexane (both solvents pesticide residue analysis grade, Caledon Laboratories Ltd., Georgetown, Ontario). The column was eluted with 100 mL of 1:1 DCM:hexane. The solvent was reduced to approximately 1 mL in the TurboVap and quantitatively transferred with 1:1 DCM:hexane to a pre-weighed aluminium weighing boat. The weighing boat and solvent were dried in a 40°C vented oven overnight. The samples were then cooled completely in a desiccator over anhydrous calcium sulphate. Their weights were recorded, yielding the lipid weight, and lipid content was calculated using Equation 1:

$$\text{Lipid Content} = \left(\frac{\text{Lipid Weight}}{\text{Wet Sample Weight}} \right) \cdot 100\% \quad \textbf{(Eqn 1)}$$

2.3.2. Moisture Content in Biota and Sediment Samples

Biota and sediment samples were analyzed at the RDL at IOS for moisture content, according to the protocols in Ikonomou *et al*. (2001). Briefly, two 3 gram portions from each biota sample were weighed (yielding the wet weight), dried in a 40°C vented oven for at least 48 hours, cooled in a desiccator, and weighed again (yielding the dry sample weight). Moisture content was calculated using the mean wet and dry sample weights (from the duplicate samples) in Equation 2:

$$\text{Moisture Content} = \left[\frac{(\text{Wet Sample Weight} - \text{Dry Sample Weight})}{\text{Wet Sample Weight}}\right] \cdot 100\% \quad \textbf{(Eqn 2)}$$

2.3.3. Organic Carbon (OC) Content

Sediment, algae, plankton, and particulate matter were analysed for organic carbon (OC) content at IOS using the methodology outlined in Van Iperen and Helder (1985). The following methods were summarized from Mackintosh (2002).

2.3.3.1. Sediment

Carbonates were removed from sediment by acidifying approximately 500 mg of dried sediment in a clean crucible with 1N HCl. The acidified sample was then dried in an oven at 70°C for 2 hours followed by another 2 hours at 105°C. The sample was then hydrated for 2.5 hours prior to analysis. 8-10 mg sub-samples were weighed into tin cups for carbon/nitrogen analysis on a Leemans 440 Elemental Analyzer. Acetanilide standards, containing 71.09% carbon and 10.36% nitrogen, were included in the sediment batches and samples duplicates were analyzed (pooled standard deviation for sample

duplicates was 0.23%, where n = 3 sample pairs). OC content was expressed on a dry weight basis as g OC/g dry sediment.

2.3.3.2. Algae

To prevent non-algal contributions to total organic carbon content (TOC) measurement, green and brown algae samples were rinsed with double-milli-q (dmq) water, removing sand, shell fragments, and other inorganic substances. The rinsed samples were dried overnight at 60°C and then homogenized. 2-3 mg sub-samples were then analyzed in a Leeman's Elemental Analyzer that had been calibrated with acetanilide.

Green and brown algae samples were rinsed with double-milli-q (dmq) water to remove sand, shell fragments, and other inorganic substances that might contribute to the total organic carbon content (TOC) measurement. Algae samples were dried overnight at 60°C to achieve a stable weight, homogenized, and then subsampled for TOC measurement. A 2-3 mg sample was then analyzed in a Leeman's Elemental Analyzer, which was calibrated with acetanilide. OC content was expressed on a dry weight basis as g OC/ g wet algae.

2.3.3.3. Plankton

Plankton samples were cleared of wood pieces, leaves, and non-planktonic materials, although small pieces of algae were left in. The samples were homogenized and sub-samples were filtered with double-milli-q water on acid-washed, combusted 47 mm – 0.8 mm nucleopore filters to remove salts. Samples were then oven-dried at 60°C until their weight was stable and sieved through a 1000 mm mesh for further cleaning.

The dried matter was then ground with a mortar and pestle, transferred to a clean vial, and acidified with 4% HCl to remove inorganic carbon (*i.e.,* $CaCO_3$). The ground homogenate was transferred to a combusted 25 mm nucleopore filter and rinsed three times with dmq water to remove the acid. The sample was oven-dried at 60°C to a stable weight and a 2-3 mg sample was analyzed in Leeman's Elemental Analyzer that had been standardized with acetanilide. OC content was expressed on a wet weight basis as g OC/g wet plankton.

2.3.3.4. Suspended Particulate Matter

Three litres of each water sample were pumped through the filtration system depicted in Figure 2-4 (and described in Section 2.4.4.2). After weighing (see Section 2.3.4 below), glass fibre filters containing the operationally-defined 'large diameter suspended matter' (LDSM) were fumed with concentrated HCl to remove inorganic carbon. The samples were then analyzed on the Leeman's Elemental Analyzer. OC content was expressed on a wet weight basis as g OC/g wet particulate matter.

2.3.4. Quantification of Suspended Particulate Matter in Water Samples

Suspended particulate matter was quantified for both False Creek and LHRP water samples by first pumping 3 litres of water (from the 4-L samples) through the filtration system shown in Figure 2-4 (see Section 2.4.4.2 for more information on the filtration system). This step was performed at SFU by Cheryl Mackintosh. The amount of suspended particulate matter was calculated by subtracting the pre-filtered dry weights of the glass fibre (GF) and C_{18} disks from the post-filtered dry weights. Particulate matter on the GF filter, which was greater than 0.45 μm in diameter, was operationally

defined as 'large diameter suspended matter' (LDSM). C_{18} disks, which were supposed to capture freely dissolved PCBs and PEs, were found to also capture fine grained particulate matter. This fine-grained material on the C_{18} disks was operationally defined as 'small diameter suspended matter' (SDSM). Once filtered, the GF filters were used for quantification of OC content (see Section 2.3.3.4 above).

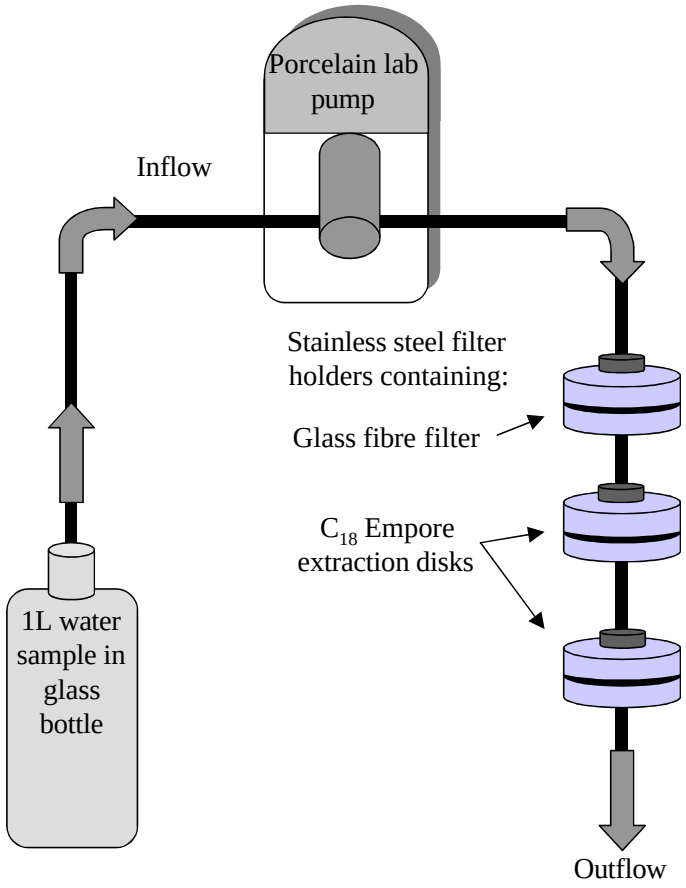

Figure 2-4. Schematic of Apparatus for Filtering PCBs from Water.
Water was extracted using a FMI Valveless Laboratory Pump and Three 47 mm Stainless Steel In-line Filter Holders Housing a Glass Fibre Filter (0.45 μm diameter pore size) in Holder #1, and an Octadecyl (C_{18}) Empore Extraction Disk in Holders #2 and #3. (Obtained with permission from Mackintosh, 2002).

2.4. PCB ANALYSIS

OVERVIEW: Biota and sediment samples and GF and C_{18} filters were transferred to the Regional Dioxin Laboratory (RDL) at IOS for PCB analysis. Water samples were spiked at the SFU laboratory with isotope-labelled internal standards. Phthalate esters (PEs) and PCBs were concurrently extracted from each sample using protocols modified from Ikonomou *et al*. (2001). Chemical analyses at IOS were performed by Audrey Chong, Joel Blair, Jody Carlow, Hongwu Jing, Zhongping Lin, Natasha Hoover, Linda White, and Joel Blair. All samples were analyzed using pre-extracted glassware and included 1-2 procedural blanks per batch of 4-8 samples/blanks. Each blank was processed in the same manner as the environmental samples and was comprised of sodium sulphate. Lynn Headwaters Regional Park (LHRP) water samples were treated as the procedural blanks for False Creek water samples. A summary of the analytical methods can be found in Figure 2.5 (reproduced with permission from Mackintosh, 2002).

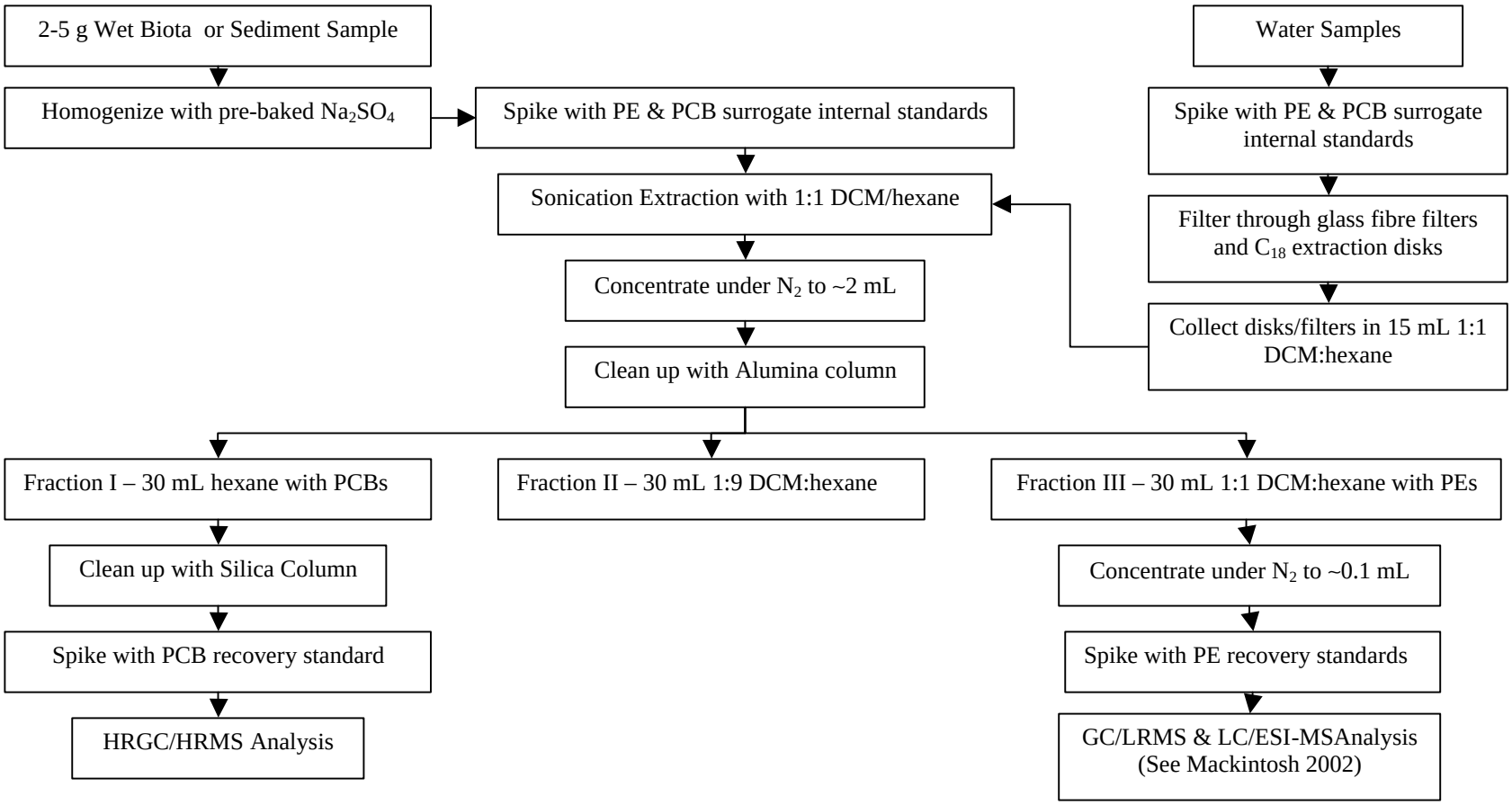

Figure 2-5. Summary of the Extraction and Analytical Procedures for the Concurrent Analysis of PCBs and PEs in Sediment, Biota, and Seawater Samples.
(Reproduced with permission from Mackintosh, 2002)

2.4.1. Materials

Two types of isotope-labelled standards (IS) were used: surrogate internal standards (SIS) and recovery standards (RS). SIS were added to each sample before any processing was performed and were used to estimate the loss of chemicals throughout the processing, extraction, and clean-up procedures. RS were added immediately before GC-MS analysis and used to estimate loss during the GC-MS analysis. All standard solutions were prepared by IOS personnel. The following information was summarized from Mackintosh (2002).

A stock solution (*a.k.a.*, BIG SIS) was prepared in *n*-nonane and contained the sixteen PCB SIS listed in Table 2-2. For information on the phthalate ester (PE) standards, please refer to Mackintosh (2002). All IS were purchased from Cambridge Isotope Laboratories (Andover, MA, U.S.A.). Spiking solutions were prepared by diluting the BIG SIS in toluene for the biota and sediment samples or in HPLC-grade methanol for the seawater and well water samples. Each PCB spike consisted of 75 µL of the diluted BIG SIS (*i.e.*, 25 µL of non-ortho PCB IS, 25 µL of mono-ortho PCB IS, and 25 µL of di-ortho PCB IS) and contained 1.0 – 1.2 ng of each SIS. The PCB RS was comprised solely of ^{13}C-PCB-111. All solutions were kept at 4°C in the dark.

Table 2-2. PCB Composition[a] of the BIG Surrogate Internal Standard (SIS).

Di-Ortho PCBs	^{13}C-PCB-52, -101, -128, -180, -194, -208, and -209
Mono-Ortho PCBs	^{13}C-PCB-28, -105, -118, and -156
Non-Ortho PCBs	^{13}C-PCB-15, -77, -126, and -169; and d_5-PCB-38

[a]The 'di-ortho' designation includes PCBs with 2 or more chlorines in the *ortho* position. Mono-ortho PCBs contain only one chlorine in the *ortho* position, while 'non-ortho' lack chlorine substition in the *ortho* position.

All solvents were 'distilled-in-glass' grade (Caledon, ON, Canada) and reagent water was high-purity HPLC grade (Burdick and Jackson, MI). Alumina (neutral) was purchased from ICN Biomedicals (Germany). Sodium acetate and anhydrous sodium sulphate (granular) were purchased from Aldrich. Neutral 100-200 mesh silica was purchased from Mallinckrodt Baker, Inc. (Paris, Kentucky). H_2SO_4 was ACS-assured grade and was purchased from BDH Inc. (Toronto, Ontario). NaOH was prepared using Milli-RX 20-processed water (15 megohm-cm, 50 ppb total organic carbon), which was purchased from Millipore (Canada) Ltd. (Nepean, Ontario) and was washed twice with toluene (pesticide residue analysis grade; Caledon Laboratories Ltd., Georgetown, Ontario).

2.4.2. Preparation of Reagents and Glassware

In an effort to minimize background contamination, the following preparatory methods were taken. Solvents were doubly distilled. Solvent rinses were collected and processed in the same manner as real samples and then analyzed by GC-MS to ensure that background PE levels were below the machine detection limit. Alumina and sodium sulphate were baked at 200°C and 450°C, respectively, for at least 24 hours, cooled and stored in a desiccator. Laboratory glassware was washed with lab-grade detergent, rinsed with distilled water, and then rinsed with doubly-distilled acetone, hexane, iso-octane, and dichloromethane (DCM). Glassware was then baked at 400°C for at least 10 hours and stored in clean aluminium foil. Mortars and pestles were cleaned in the same manner as the glassware, but were baked at 150°C for 10 hours. Other materials which were not able to be baked, such as Teflon™ stoppers, GC septa, and caps of sample vials, were washed extensively with 1:1 DCM:hexane.

2.4.3. Extraction and Clean-up of Sediment and Biota Samples

2.4.3.1. Extraction

Biota and sediment samples were thawed and the sediment samples were thoroughly mixed prior to weighing to ensure homogeneity. 2-5 g of wet biota sample or wet sediment were weighed and 15-20 g of Na_2SO_4 were added to each sample or blank. The sample or blank was then ground in a 750 mL-capacity porcelain mortar with a 215 mm porcelain pestle until a free-flowing mixture was attained. The mixture was then transferred to a round-bottom flask and spiked with 100 ng of PE IS (see Mackintosh, 2002) and 75 µL of the BIG IS (1.0 – 1.2 ng of each SIS; see Section 2.4.1 and Table 2-2). Syringes were washed with toluene before and after use and with 1:1 DCM:hexane in between uses. 50 mL of 1:1 DCM:hexane were added to the flask and the flask was sonicated for 15 min. in a Branson 5210 ultrasonic water bath (Branson Ultrasonics Co., CT). The flask was then placed on a shaker table (Eberbach Co., MI) for 10 min., after which the suspended particles were allowed to settle and then the supernatant was removed and placed into a fresh, clean flask. The extraction was repeated twice more and the supernatants were combined. The combined extracts were concentrated to ~ 5 mL under a gentle stream of high purity nitrogen.

2.4.3.2. Alumina Chromatography (De-activated)

Alumina chromatography is a conventional clean-up tool used by IOS that uses a highly porous and granular form of aluminium oxide to separate compounds of interest from interfering materials based upon differing chemical polarities. Although available in basic (pH 9-10) or acidic (pH 4-5) forms, the RDL uses neutral alumina (super 1

activity) to separate out compounds such as aldehydes, ketones, quinines, esters, lactones and glycosides.

40 cm custom glass columns with reservoir (30 cm long x 12 mm o.d. x 10 mm i.d., 100 mL reservoir, 10 mm o.d. coarse glass frit and plug end (8 mm i.d.), straight pore Teflon™ stopcock and burette tip (Kimble Glass Inc., Vineland, New Jersey, U.S.A.)) were rinsed with hexane and allowed to dry in a fume hood. Alumina was activated at a minimum of 200°C overnight and cooled to room temperature in a desiccating chamber. 15 g of activated alumina were weighed out per column (90 g/batch for 6 columns) and then deactivated by adding HPLC-grade water to make 15% water w/w (13.5 mL/batch). The mixture was shaken until there were no visible lumps. 15 g of the hydrated alumina were then added to each column, followed by 2 cm of Na_2SO_4. The columns were then conditioned with 15-20 mL of hexane leaving 1 cm of solvent in the column before adding the sample. The concentrated sample from the extraction procedure was then quantitatively transferred to a column. Three consecutive 30 mL elutions were then added: (1) hexane; (2) 1:9 DCM:hexane; and (3) 1:1 DCM:hexane. The first fraction, containing PCBs in hexane, was evaporated to near dryness under nitrogen, re-dissolved in 5 mL in hexane, and further cleaned-up in a silica column (see Section 2.4.3.3 below). The second fraction was discarded. The third fraction contained PEs in 1:1 DCM:hexane and was analysed according to methods presented in Mackintosh (2002).

2.4.3.3. Silica Chromatography

Acidic/basic silica chromatography is another standard tool for 'cleaning-up' samples before analysis. This process uses the oxidative power of concentrated sulphuric acid to remove polar lipids and polar matrix components from the sample.

Neutral 100-200 mesh silica was activated overnight at 200°C and then cooled to room temperature in a desiccating chamber over anhydrous calcium sulphate. Acidic and basic silica layers were prepared in separate flasks according to the following recipe: 2.7 g Si + 1.3 g conc. H_2SO_4 and 1.5 g Si + 0.5 g 1M NaOH, respectively. The layers were shaken until there were no visible lumps. The prepared layers were dry-packed into 40 cm glass columns (30 cm long x 12 mm o.d. x 10 mm i.d., 100 mL reservoir, 10 mm o.d. coarse glass fritted plug end (8 mm i.d.), straight bore Teflon™ stopcock and burette tip; Kimble Glass Inc., Vineland, New Jersey, U.S.A.) in the amounts and the order illustrated in Figure 2-6. 1 g of Na_2SO_4 was placed on top of the silica layers and then each column was rinsed with 50 mL 1:1 DCM:hexane. The concentrated sample from fraction #1 from the alumina chromatography procedure was then loaded quantitatively into the column with 1:1 DCM:hexane. The column was eluted with 60 mL of 1:1 DCM:hexane and the fraction was collected in a 250 mL round bottom flask. The fraction was concentrated to near dryness under nitrogen and then allowed to go to dryness at room temperature. The sample was re-dissolved in 5 mL of hexane and further cleaned-up in a dry-packed activated alumina column (see Section 2.4.3.4).

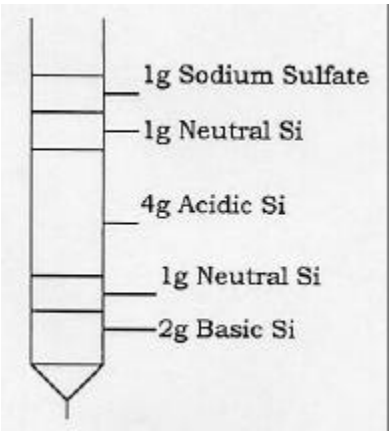

Figure 2-6. Silica Column Preparation

2.4.3.4. Alumina Chromatography (Activated)

This procedure was similar to the aforementioned clean-up with alumina except for the following changes. The glass column was dry-packed with 10 g of activated alumina (no HPLC-grade water was added) followed by 1 g Na_2SO_4. The column was rinsed with 25 mL of hexane and the sample from the previous step was loaded quantitatively into the column with hexane. 25 mL of hexane were passed through the column, collected, and discarded. 60 mL of 1:1 DCM:hexane were then passed through the column and collected in a 250 mL round bottom flask. The sample was concentrated to 1 mL under nitrogen and transferred to centrifuge tubes. The sample was further concentrated to 0.5 mL under nitrogen and transferred to a HR autosampler vial. Finally, the sample was concentrated to 0.1 mL under nitrogen and was ready for GC-MS analysis.

2.4.4. Filtration, Extraction, and Clean-up of Water Samples

2.4.4.1. Introduction

All water samples were collected and filtered at the SFU laboratory by Cheryl Mackintosh and the filters were sent to IOS for analysis. In total, there were 12 seawater samples from False Creek harbour: 3 from the North Central (NC) site, 3 from the East Basin (EB) site, and 6 from the Marina (Ma) site. As well, there were 10 well water samples from Lynn Headwaters Regional Park. Samples were spiked with 75 µL of BIG IS (1.0 – 1.2 ng of each SIS; see Section 2.4.1 and Table 2-2) one hour prior to filtration.

2.4.4.2. Filtration

Each water sample was pumped through three separate filters at a flow rate of 8-10 mL using a FMI valveless pump (see Figure 2-4). The first was a 47 mm glass fiber

(GF) filter of 0.45 μm diameter pore size (Gelman Laboratory, Pall Corporation, Ann Arbor, Michigan), which separated out the operationally-defined 'large diameter suspended matter' (LDSM). The second and third filters were consecutive 47 mm octadecyl (C_{18}) extraction disks (3M, St. Paul, MN) and separated out the operationally-defined 'small diameter suspended matter' (SDSM), as well as the freely-dissolved chemicals. It must be noted that in other studies, C_{18} has been used either in columns (Burgess *et al.*, 1996a) or on silica beads (Burgess and Ryba, 1998) and not as a filter. Each C_{18} disk was housed in separate 47 mm stainless steel in-line filter holders (Gelman Laboratory, Pall Corporation, Ann Arbor, Michigan) and had a typical composition of 90% octadecyl bonded silica particles and 10% matrix PTFE by weight.

2.4.4.3. Extraction and Clean-up

After filtration, the GF filter and C_{18} disks were removed from the filtration apparatus and placed into separate glass vials containing 15 mL 1:1 DCM:hexane. Both C_{18} disks were placed into the same glass vial. The vials were refrigerated at 4°C and then transferred to the IOS lab. GF and C_{18} filters were extracted independently by three subsequent 5 min sonications with 20 mL 1:1 DCM:hexane. The extracts from each sonication were combined and concentrated to 3-5 mL under a gentle stream of high purity nitrogen. The concentrated extract was then quantitatively transferred to neutral de-activated alumina column for clean-up (see Section 2.4.3.2). Clean-up and sample preparation followed the same methods outlined above for sediment and biota analysis. PCBs were fractioned out at the end of the de-activated alumina clean-up and were subsequently cleaned-up through silica (see Section 2.4.3.3) and activated alumina

columns (see Section 2.4.3.4). The final extract was concentrated to 0.1 mL under nitrogen and was ready for GC-MS analysis.

2.4.5. HRGC/HRMS Analysis of Environmental Samples

PCB RS, *i.e.,* ^{13}C-PCB-111, (30 μL) was added to the concentrated sample from the dry-packed alumina clean-up procedure and the vials were capped. The vials were then placed in the GC autosampler and analyzed by a high-resolution gas chromatography/ high-resolution mass spectrometry (HRGC-HRMS) machine.

Due to the time span of this study, two HRGC-HRMS machines and software were used. The first machine (HRGC/HRMS #1) was used to analyze the biota and water (1st analysis) samples. It consisted of a Hewlett-Packard (Palo Alto, CA) model 5890 series II high-resolution gas chromatograph that delivered the sample through a splitless injector port to the high-resolution mass spectrometer, a VG-AutoSpec-S (FISONS Instruments, VG-Analytical, Manchester, UK). Programming and operation of both the GC and the autosampler was controlled from the MS's data system, OPUS version 2.1E (FISONS Instruments, VG Analytical, Manchester, UK). The two most abundant isotope ions, M+ and (M+2)+ in most cases, of known relative abundance are monitored for each homologue series and ^{13}C labelled surrogate standard. Raw data was presented as ion chromatograms, with final reports presenting sample weights, concentrations of native compounds, amounts of surrogates added, calculated limits of detection, and percent surrogate recoveries. Quantification was accomplished according to the methods in Section 2.4.6 with minimum machine detection limits listed in Section 2.4.6.2. Paper reports were then subject to Quality Assurance/Quality Control (QA/QC) protocols described in Section 2.4.7 below.

The second machine (HRGC/HRMS #2) was used to analyze the sediment and water (2nd analysis) samples. It consisted of an AutoSpec-Ultima NT HRGC-HRMS and used Quanlynx (v.3.5) software. Both the GC-MS and software were purchased from Micromass (Floats Road, Wythenshawe, Manchester, M23-9LZ, UK). Chromatograms were generated electronically and converted to Excel™ format. Excel™ reports included sample weights, concentrations of native compounds, amounts of surrogates added, calculated limits of detection, and percent surrogate recoveries. Final reports from this machine were subjected to QA/QC protocols by Tamara Fraser at IOS.

2.4.6. Quantification of PCBs in Environmental Samples

2.4.6.1. Criteria for Positive Peak Identification

Before compounds could be quantified, the HRGC/HRMS software required that the following identification (outlined in Ikonomou *et al*., 2001) criteria were met: (1) For each congener, the two isotopes had to be detected at their exact m/z (Table B-1 in Appendix B) at a minimum 10k RP during the entire chromatographic run; (2) Both of the isotope signals in criterion 1 had to be present and had to maximize within ± 2 seconds of one another; (3) The retention time of every congener had to be within 3 seconds of established retention times. Where a congener had its surrogate analogue, the native and surrogate ion peak maxima had to coincide within 3 seconds; (4) The signal-to-noise ratio of each of the isotope m/z channels had to be ≥ 3 for a sample extract and ≥ 10 for a calibration standard; (5) The ratio between the top and bottom mass channels (*i.e.*, the isotope ratio) had to be within the range outlined in Table B-1 in Appendix B.

2.4.6.2. Minimum HRGC/HRMS Detection Limits

The minimum HRGC/HRMS detection limits for di-ortho, mono-ortho, and coplanar PCBs were 1.8 pg/g, 0.20 pg/g, and 0.08 pg/g, respectively, for a 5 g sample. Detection limits were inversely proportional to the sample weight. For example, for di-ortho PCBs, 1 g sample had a minimum machine detection limit of 9.0 pg/g.

2.4.6.3. Calculations

PCB quantification was determined using the isotope dilution method. Known amounts of surrogate internal and recovery standards were added to every sample prior to extraction. Final native concentrations were based on the assumption that native and surrogate compounds behaved similarly during sample preparation and HRGC/HRMS analysis. For both native and surrogate compounds, PCB concentrations were calculated using relative response factors (RRFs). For the native compounds, the RRF was defined as the ratio between the response factors (RFs) of the analyte and the corresponding surrogate internal standard (Ikonomou *et al*., 2001). For the surrogate internal standards, the RRF was defined as the ratio between the RF of the surrogate internal standard and the corresponding surrogate recovery standard (Ikonomou *et al*., 2001). Equation 3 illustrates the RRF calculation for both native and surrogate compounds, where "i" and "j" represent either the surrogate internal standard and the recovery standard, respectively, or the test analyte and the surrogate internal standard, respectively. The mean RRF is calculated from five calibration solution runs where the concentration of "j" is kept constant and the concentration of "i" is incrementally increased from 0.5 to 200 pg/μL. These RRFs were constant over the concentration range for which the MS response was linear. Percent recovery of the surrogate internal standard (SIS) was

calculated using the spike amount and total peak area of the SIS and the recovery standard (^{13}C-PCB-111; RS) and the RRF of the native version of the SIS relative to the SIS (Equation 4). Using mean RRFs determined from calibration standards, along with native and surrogate responses from the samples, PCB concentrations (C_{PCB}) were calculated by the HRGC/HRMS software using Equations 5, 6, and 7. Percent recoveries, PCB concentrations, and detection limits for ^{12}C-PCB-118 and its surrogate internal standard, ^{13}C-PCB-118, were manually calculated by this author using Equations 5, 6, and 7, where intensities were measured in ion counts and heights were measured in mm from chromatograms.

$$RRF_{\frac{i}{j}} = \frac{\text{Total Peak Area}_i}{\text{Total Peak Area}_j} \cdot \frac{\text{Mass}_j}{\text{Mass}_i} \quad \textbf{(Eqn 3)}$$

$$\%\ \text{Recovery} = \frac{\text{Total Peak Area of SIS}}{\text{Total Peak Area of RS}} \cdot \frac{\text{RS Spike Amt. (pg)}}{RRF_{\frac{\text{Native}}{\text{SIS}}} \cdot \text{SIS Amt. (pg)}} \cdot 100\% \quad \textbf{(Eqn 4)}$$

$$C_{PCB}\ (\text{pg/g}) = \frac{\text{Total Peak Area of PCB}}{\text{Total Peak Area of SIS}} \cdot \frac{\text{SIS Spike Amt (pg)}}{\text{mean RRF} \cdot \text{Sample Weight (g)}} \quad \textbf{(Eqn 5)}$$

$$\text{Noise Intensity} = \frac{\text{Noise Height}}{\text{Full Scale Height}} \cdot \text{Full Scale Intensity} \quad \textbf{(Eqn 6)}$$

$$DL_{PCB}\ (\text{pg/g}) = \frac{\left[\text{Noise Intensity in } ^{12}\text{C channel}\right] \cdot \left(C_{PCB}\right) \cdot 3}{\text{Native PCB Intensity in } ^{12}\text{C Channel}} \quad \textbf{(Eqn 7)}$$

2.4.7. Quality Assurance/Quality Control (QA/QC)

2.4.7.1. Preliminary QA/QC

In general, the criteria for identification and quantification of all analytes, as well as the quality control measures undertaken, were based upon protocols for the analysis of

polychlorinated dibenzo-p-dioxins and furans established in Environment Canada report EPS 1/RM/19 (Environment Canada, 1992) and reported in Ikonomou *et al*. (2001). After chromatograms were printed, IOS staff performed preliminary data quality assurance/quality control (QA/QC) work on the MS-processed data. Samples with chromatogram peak intensities greater than 3×10^8 counts were diluted and reanalyzed. Samples that showed a 5% contribution from the preceding sample due to carryover were reanalyzed. Samples that showed a greater than 120% recovery of the surrogate internal standards were further cleaned up, diluted and re-spiked, or peak-area adjusted, depending on the possible source of error. Similarly, samples with less than 20% recovery of the surrogate internal standards had to be reanalyzed. Samples that were re-analyzed and that were not able to recover greater than 20% of internal standards were eliminated from further calculations.

2.4.7.2. QA/QC of PCB Reports

For the biota samples, 20 PCB congeners/co-eluters were selected for QA/QC evaluation based on their range of K_{ow} and on their presence in the great majority of samples. The PCBs[2] QA/QC-evaluated included congeners 18, 16/32, 73/52, 47/75/48, 101/90, 99, 110, 118, 149, 132/153, 138/160/163/164, 187/182, 177, 180, 203/196, 194, 200, 208, 206, and 209. For sediment and water samples, 154 congeners (33 of which co-eluted with other congeners) were QA/QC evaluated (by Tamara Fraser at IOS). The guidelines and protocols for QA/QC evaluations are summarized here from Appendix XIII in Ikonomou *et al*. (2001).

[2] PCBs are referred to in this thesis according to BZ numbers (first numbered by Ballshmiter and Zell, 1980), which are currently identical to numbers assigned by IUPAC.

QA/QC first involved screening all isotope ratios and comparing them to the acceptable ranges listed in Table B-1 in Appendix B. Isotope ratios were calculated by the HRGC/HRMS software using the peak areas from top and bottom mass channels. Native isotope ratios that were outside of acceptable ranges were labelled 'Not-Detected due to Ratio' or 'NDR' and omitted from further calculations. In certain cases, the HRGC/HRMS software improperly integrated a native peak area. This occurred when two congeners or coeluters had similar elution times (*i.e.,* the peaks were too close together) or when the peak intensity was near detection limits. In these cases, the improperly integrated peak areas were manually recalculated using one of two methods (*i.e.,* Equation 8 or 9). Since peak area was related to the peak height (in mm), the peak height and area of a different native congener (whose peak area was properly integrated) from the same mass channel could be used to estimate the peak area of the congener of interest. For example, Equation 8 illustrates the recalculation of the peak area (PA) for PCB-52/73, where the peak height (PH) and PA of the properly integrated congener (*e.g.,* PCB-47/75/48) were from the same mass channel, PH's were measured directly from the chromatograph (in mm), and PA (PCB-47/75/78) was read from the HRGC/HRMS output table.

$$\text{PA (PCB - 52/73)} = \frac{\text{PH (PCB - 52/73)}}{\text{PH (PCB - 47/75/48)}} \cdot \text{PA (PCB - 47/75/48)} \quad \textbf{(Eqn 8)}$$

An alternate method was to use the peak height, area, and intensity of the corresponding surrogate internal standard (SIS) to recalculate the peak area for the native congener of interest. First, the native peak height was converted to a peak intensity (PI), measured in ion counts, using the full-scale height and intensity, as in Equation 9a. Then, the ratio of

peak area to peak intensity for the SIS was used to convert the native peak intensity from Equation 9a to a new peak area, as in Equation 9b. For example, the recalculation of a peak area for PCB-52/73 is illustrated in Equations 9a and 9b using ^{13}C-PCB-52 (*i.e.*, the corresponding SIS).

$$\text{PI (PCB - 52/73)} = \text{PH (PCB - 52/73)} \cdot \frac{\text{Full Scale Intensity}}{\text{Full Scale Height}} \quad \textbf{(Eqn 9a)}$$

$$\text{PA (PCB - 52/73)} = \text{PI (PCB - 52/73)} \cdot \frac{\text{PA } (^{13}\text{C - PCB - 52})}{\text{PI } (^{13}\text{C - PCB - 52})} \quad \textbf{(Eqn 9b)}$$

Once a new peak area was calculated, the new isotope ratio was checked to ensure that it fell within acceptable limits. If so, the new peak area was used to recalculate the total peak area and the new total peak area was used in Equation 5 to recalculate the concentration. The new PCB concentration was checked against new detection limits, which were recalculated using Equations 6 and 7.

Finally, since some congener concentrations were occasionally calculated using average homologue RRFs, RRFs were checked against the accepted congener-specific RRFs listed in Table B-2 of Appendix B. In cases that needed adjustment, new concentrations were calculated using Equation 10.

$$\text{New } C_{PCB} \text{ (pg/g)} = C_{PCB} \text{ (pg/g)} \cdot \frac{\text{Average Homologue RRF}}{\text{Congener - Specific RRF}} \quad \textbf{(Eqn 10)}$$

2.5. $d^{15}N$ & $d^{13}C$ ANALYSIS

Stable nitrogen isotopes have been significantly correlated with the bioaccumulation of organochlorines and so are also useful in predicting bioaccumulation (Cabana and Rasmussen, 1994; Vander Zanden & Rasmussen, 1996; Kidd *et al.*, 1998a;

Fisk *et al.*, 2001; Hop *et al.*, 2002; Ruus *et al.*, 2002; Hoekstra *et al.*, 2003). Sediment and biota sub-samples were sent to the Stable Isotope Facility at the University of California-Davis (Davis, CA, USA) for $\delta^{15}N$ and $\delta^{13}C$ analysis. Dried surficial sediment (30 mg) (n=4) or dried biota tissue (n=3 of each species) (1 mg) were finely ground using an acid washed mortar and pestle, and enclosed in 8 x 5 mm tin capsules from Costech Technologies (Valencia, CA). Samples were analyzed on a continuous flow Europa Scientific Hydra 20/20 Isotope Ratio Mass Spectrometer. Stable isotope ratios (parts per thousand, ‰) were calculated according to Equations 11 (nitrogen), and 12 (carbon), where the $\delta^{15}N$ standard is from nitrogen in the air, and the $\delta^{13}C$ standard is from Pee Dee Belomite limestone. Machine precision was assessed by analyzing 13 replicates of a prepared standard ($\delta^{15}N$ = 1.33‰ and $\delta^{13}C$ = -23.83‰) for which reproducibility was SD = 0.11‰ and 0.07‰ for $\delta^{15}N$ and $\delta^{13}C$, respectively.

$$d^{15}N = \frac{(^{15}N/^{14}N \text{ sample} - {}^{15}N/^{14}N \text{ standard})}{^{15}N/^{14}N \text{ standard}} \cdot 1000 \quad \textbf{(Eqn 11)}$$

$$d^{13}C = \frac{(^{13}C/^{12}C \text{ sample} - {}^{13}C/^{12}C \text{ standard})}{^{13}C/^{12}C \text{ standard}} \cdot 1000 \quad \textbf{(Eqn 12)}$$

2.6. DATA ANALYSIS

2.6.1. Recovery of Surrogate Internal Standards

To ensure the validity of the HRGC/HRMS analysis, the recoveries of the surrogate internal standards were recorded. Table 2-3 lists the mean recoveries and standard deviations for the biota, sediment, and seawater samples and their sodium sulphate blanks.

Table 2-3. Mean Percent Recovery (and Standard Deviation) of Surrogate Internal Standards from Biota, Sediment, and Seawater Samples and their Sodium Sulphate Blanks.

Media	Material	^{13}C-PCB-28	^{13}C-PCB-52	^{13}C-PCB-101	^{13}C-PCB-118	^{13}C-PCB-128	^{13}C-PCB-180	^{13}C-PCB-194	^{13}C-PCB-208	^{13}C-PCB-209
Biota	False Creek	46 (14)	64 (16)	71 (19)	71 (15)	43 (16)	74 (18)	79 (21)	75 (18)	71 (19)
	Na_2SO_4 Blanks	36 (15)	54 (16)	62 (14)	68 (12)	31 (14)	71 (13)	76 (16)	75 (15)	74 (15)
Sediment	False Creek	37 (14)	44 (11)	48 (11)	51 (25)	58 (9)	45 (11)	56 (14)	44 (13)	47 (14)
	Na_2SO_4 Blanks	27 (28)	29 (26)	47 (26)	50 (18)	63 (8)	47 (18)	55 (21)	49 (22)	50 (22)
Seawater (C18)	False Creek	74 (31)	50 (22)	84 (26)	93 (11)	58 (18)	77 (17)	77 (18)	80 (20)	57 (19)
	Na_2SO_4 Blanks	65 (20)	60 (10)	79 (15)	101 (6)	73 (7)	77 (8)	81 (12)	80 (9)	76 (11)
Seawater (GF)	False Creek	69 (33)	43 (16)	87 (25)	93 (14)	55 (17)	74 (19)	72 (19)	76 (21)	52 (20)
	Na_2SO_4 Blanks	53 (32)	45 (18)	68 (21)	103 (9)	66 (13)	70 (14)	73 (17)	74 (14)	71 (14)

2.6.2. Calculation of Minimum Reportable Levels (MRLs)

To quantify concentrations that were significantly above background levels, all data were screened against Minimum Reportable Levels (MRLs). The MRLs were defined as the mean of the response of all blanks plus three times the standard deviation of all the blank concentrations in the biota [n = 63] and seawater [n = 1 (Batches A & D), n = 2 (Batches B & C), n = 10 (all blanks)] analyses. For the water blanks, when only one blank value was available in a batch, the standard deviation was estimated using either the remaining batches or all the blanks (n = 10). For the sediment data, since only two procedural blanks were run with the sediment samples, MRLs were set as the maximum PCB concentration detected in the two blanks. Values that were below the HRGC/HRMS detection limits (*i.e.,* classified 'Not-Detected', or 'ND') were omitted from the calculation of means and standard deviations.

2.6.3. Biota Concentration Data

Prior to further analysis, the biota data, which were in picograms (pg), were converted to concentrations (pg/g ww) by dividing by the sample weights. To estimate the concentrations above background levels, the biota data were blank-corrected. Each batch of samples included 1 or 2 sodium sulphate procedural blanks and was comprised of 4 to 8 samples. Blank-corrections were performed on a batch basis. First, the mean blank amount had to be determined for each PCB congener in each batch. If a batch contained two values for blanks above the HRGC/HRMS Detection Limit (DL), the average of the two values was used as the mean blank amount of that batch. If a batch contained only one reliable value above the DL, the single value was used as the mean amount. If no value was above the DL, the mean amount of the blanks in all other batches of samples in the biota analysis was used as the mean blank amount. The mean blank concentration (pg/g ww) was then calculated by dividing the mean amount (pg) detected in the blank by the corresponding biota sample's weight (g ww). This concentration was then subtracted from the biota concentrations (pg/g ww) in the biota samples to calculate the blank-corrected chemical concentration. After the blank-corrections, the biota data were screened against the MRLs calculated in Section 2.6.2 and values below the MRLs were omitted from further calculations and analyses.

Because PCBs are known to partition into the lipid compartment of organisms (Rasmussen *et al.*, 1990; Hebert and Keenleyside, 1995; van Wezel and Opperhuizen, 1995), blank-corrected, MRL-screened biota data were lipid-normalized using Equation 13 or 14. For all the biota except plankton and algae, wet weight concentrations were divided by the lipid content of each sample, as in Equation 13, where C_{lipid} (pg/g lipid)

was the lipid-normalized concentration, C_{wet} (pg/g wet tissue) is the wet weight concentration, and L is the lipid content (unitless) of the tissue.

$$C_{lipid} = \frac{C_{wet}}{L} \quad \textbf{(Eqn 13)}$$

Plankton and algae were lipid- and organic carbon-normalized according to Equation 14, where f_{OC} is the fraction of non-lipid organic carbon in the wet sample (g OC / g wet sample), and 0.35 is a proportionality constant recommended by Seth *et al.* (1999) for relating the sorbing properties of organic carbon to those of octanol. The rationale for combining lipid and organic carbon normalization can be found in Mackintosh (2002) which states that because algae and plankton "possess low lipid contents, and relatively high organic carbon contents" the organic carbon fraction of algae and plankton can be expected to be an important site for chemical accumulation in these organisms.

$$C_{lipid} = C_{wet} / \left[L + \left(0.35 \cdot f_{oc}\right)\right] \quad \textbf{(Eqn 14)}$$

In preparation for the calculation of the geometric mean of the concentrations for False Creek, a one-way ANOVA analysis was performed using JMP IN 4 statistical software to verify that the concentrations between sites in False Creek were not significantly different from each other. PCB concentrations were then tested for normality by Kolmogorov-Smirnov and Shapiro-Wilk normality tests and found to be log normally distributed. Geometric means of PCB concentrations in each organism were calculated and reported with Upper Limits (UL) and Lower Limits (LL), representing one geometric standard deviation above and below the mean, respectively.

2.6.4. Seawater Concentration Data

Seawater C_{18} and GF concentrations were screened against MRLs (see Section 2.6.2) on a batch basis using the water blanks obtained from Lynn Headwaters Regional Park. Values below the MRLs were omitted from further calculations. Values above MRLs were blank-corrected according to the following procedure. Mean blank PCB concentrations were calculated for each PCB congener on a batch basis. In cases where only one value was available for the blanks in a batch, the single value was used as the average and the standard deviation was estimated from the average standard deviation of the other batches or the standard deviation of all the blank data. Mean blank PCB concentrations were then subtracted from the MRL-screened seawater data.

Due to the low number of values above MRLs in seawater, tests for normality and tests for difference between sampling sites were not meaningful. However, it was assumed that water concentrations were log normally distributed since both sediment and biota concentrations were log normally distributed. In addition, it was assumed that no significant difference existed between sampling locations. Geometric means were then calculated and reported along with Upper Limits (ULs) and Lower Limits (LLs), representing one geometric standard deviation above and below the mean, respectively.

2.6.5. Sediment Concentration Data

As described in Section 2.6.2, MRLs were calculated as the mean blank concentration plus three times the standard deviation of the data. Sediment concentrations below the MRLs were omitted from further calculations. Average blank concentrations were calculated for each PCB congener. This average concentration was then subtracted from each sediment concentration on a congener-specific basis. Blank-

corrected concentrations were then divided by moisture contents to obtain dry-weight concentrations. Since the concentration of non-polar compounds, like PCBs, have been found to correlate with the organic carbon (OC) content of the sediment (Karichkoff *et al.*, 1979; Means *et al.*, 1980; Schwarzenbach and Westall, 1981; Gshwend and Wu, 1985; Brownawell and Farrington, 1986), dry-weight concentrations were OC-normalized by dividing by the OC content (f_{oc}) of the sediment.

To ensure the sediment concentrations could be combined from each site, the sediment concentrations were analyzed for differences between sites using a one-way ANOVA analysis (JMP IN 4 statistical software). Combined data was tested for normality by Kolmogorov-Smirnov and Shapiro-Wilk normality tests and found to be log-normally distributed. Sediment concentrations from all sampling locations were then used for calculating geometric means. Geometric means were then calculated and reported along with Upper Limits (ULs) and Lower Limits (LLs), representing one geometric standard deviation above and below the mean, respectively.

2.6.6. Calculations

2.6.6.1. Total Water Concentration

Total water concentrations (C_{total}) were calculated through the addition of the mean PCB concentrations in the C_{18} (C_{C18}) and glass fibre (0.45 μm pore size; C_{GF}) filters (Equation 15).

$$C_{total} = C_{C18} + C_{GF} \quad \textbf{(Eqn 15)}$$

2.6.6.2. C_{18} Fraction of Total Water Concentration

For each PCB congener, the mean PCB concentration on the C_{18} filter (C_{C18}) was divided by the total water concentration (C_{total}) to obtain the fraction of concentration captured by the C_{18} filter. PCB congeners that were not detected on both C_{18} and glass fibre filters were omitted from the calculation of average C_{18} fractions.

2.6.6.3. Freely-Dissolved Water Concentrations

Freely-dissolved PCB concentrations were estimated using a three-phase model, where PCBs were either freely-dissolved, bound to small diameter suspended matter (SDSM), or bound to large diameter suspended matter (LDSM). First, the fraction of chemical captured by the C_{18} extraction disks was related to the concentration of SDSM (β_{SDSM}; kg organic carbon/L water), the concentration of LDSM (β_{LDSM}; kg organic carbon/L water) and the organic carbon-water partition coefficient (K_{oc}) using Equation 16 (Mackintosh, 2002). β_{SDSM} and β_{LDSM} values were calculated by fitting both phthalate ester (PE) and PCB data (*i.e.*, C_{18} fractions and K_{ow}'s) to Equation 16 and by minimizing the sum of squared deviations between observed and predicted values, resulting in values of 5.71E-5 and 7.14E-5 respectively. Both PE and PCB data were used in order to calibrate the model over a log K_{ow} range of 1 to 10, which was deemed appropriate given that PCBs showed similar C_{18} fractions as PEs over the same range of log K_{ow}. For co-eluting PCBs, K_{ow}'s were estimated using weighted averages based on the PCB compositional patterns of Aroclor 1016, as reported in Frame *et al.* (1996). All K_{ow}'s used in the model were seawater-corrected according to Xie *et al.* (1997) (see Section 2.6.6.4). Freely-dissolved concentrations were then calculated by first calculating the

freely-dissolved fraction using Equation 17 and then multiplying the fraction by the total water concentrations.

$$f_{C_{18}} = \frac{1 + (b_{SDSM} \cdot \mathrm{K_{ow}})}{1 + (b_{SDSM} \cdot \mathrm{K_{ow}}) + (b_{LDSM} \cdot \mathrm{K_{ow}})} \quad \textbf{(Eqn 16)}$$

$$f_{FDW} = \frac{1}{1 + (b_{SDSM} \cdot \mathrm{K_{OC}}) + (b_{LDSM} \cdot \mathrm{K_{OC}})} \quad \textbf{(Eqn 17)}$$

2.6.6.4. Seawater-Corrected K_{ow}'s for PCB Congeners/Co-eluters

To compensate for reduced solubility of PCBs in marine waters, freshwater *n*-octanol-water partition coefficients (K_{ow}'s) reported in Hawker and Connell (1988) were converted to seawater-corrected K_{ow}'s using a relationship reported by Xie *et al.* (1997) and shown in Equation 18, where V_H is the LeBas Molar Volume (cm^3/mol).

$$\text{Seawater - Corrected } \mathrm{K_{ow}} = \text{Freshwater } \mathrm{K_{ow}} \cdot 10^{(0.0009 \cdot \mathrm{V_H})} \quad \textbf{(Eqn 18)}$$

Since some of the PCB's co-eluted in the analysis, K_{ow}'s for each set of co-eluters had to be estimated. PCB composition patterns of water and sediment were compared to various Aroclor composition patterns as reported in Schulz *et al.* (1989), Frame *et al.* (1996), and Frame *et al.* (1997). Aroclor composition patterns that most closely matched water and sediment compositional patterns were used to estimate the contribution of each PCB congener to the PCB co-eluting set. A weighted-average approach based on the most closely matched Aroclor was then used to estimate the K_{ow} for a co-eluting set of congeners.

2.6.6.5. Diet-Based Trophic Position

One method of investigating bioaccumulation in a food web is through the comparison of contaminant concentrations with trophic position. In her study on the distribution of phthalate esters in environmental samples, Mackintosh (2002) calculated trophic positions (TP) using a food chain model developed by Vander Zanden and Rasmussen (1996). Diet compositions, where p_i is the proportion of prey item *i* in the diet of the predator, were used to estimate a fractional measure of each species' trophic position (Equation 19). For the purpose of direct comparison with her study, trophic positions from her study were used in this study.

$$TP_{predator} = \sum\left(TP_{prey} \cdot r_{prey}\right) + 1 = \left(TP_1 \cdot r_1\right) + \left(TP_2 \cdot r_2\right) + \left(TP_i \cdot r_i\right) + 1 \quad \textbf{(Eqn 19)}$$

The calculated trophic positions can be found in Table C-1 in Appendix C (obtained from Mackintosh 2002 with permission). Plankton and algae were assigned a trophic position of 1.00, as in Vander Zanden and Rasmussen (1996). Juvenile cutthroat trout, Pacific staghorn sculpin, shiner perch, starry flounder, three-spine stickleback, whitespotted greenling, and shrimp were grouped together into the trophic guild of 'small forage fish'. Northern anchovy, Pacific herring, and surf smelt were grouped together into the trophic guild of 'forage fish' and English sole and starry flounder were grouped as 'sole'.

2.6.6.6. Food Web Magnification Factor (FWMF)

A Food Web Magnification Factor (FWMF) represents a useful measure of biomagnification in a food web (Fisk *et al.,* 2001; Hop *et al.,* 2002). FWMFs are

calculated from the slopes of the linear regressions between PCB concentrations (log [PCB]) and trophic position (TP) or $\delta^{15}N$ (Equations 20 and 21, respectively):

$$\log[PCB] = (b \times TP) + a \quad \textbf{(Eqn 20)} \qquad \log[PCB] = (b \times d^{15}N) + a \quad \textbf{(Eqn 21)}$$

For the log [PCB]-vs-TP regression (Equation 20), the FWMF was calculated as the antilog of the slope of the regression (Equation 22). For the log [PCB]-vs-$\delta^{15}N$ regression, the FWMF was calculated as 3.4 times the slope of the regression (Equation 23). The value of 3.4 represents the average $\delta^{15}N$ increase (‰) per trophic level (Minegawa and Wada, 1984).

$$FWMF = 10^{b} \quad \textbf{(Eqn 22)} \qquad FWMF = 10^{3.4 \times b} \quad \textbf{(Eqn 23)}$$

2.6.6.7. Bioaccumulation Factor (BAF)

Bioaccumulation factors were calculated using wet weight (BAF, Equation 24) and lipid-normalized (BAF_L, Equation 25) biota concentrations and with total, operationally-defined 'freely-dissolved' (*i.e.*, C_{18}), and model-predicted freely-dissolved water concentrations.

$$BAF\ (\text{L water/kg organism}) = \frac{C_{biota}}{C_{water}} \quad \textbf{(Eqn 24)}$$

$$BAF_L\ (\text{L water/kg lipid}) = \frac{C_{lipid}}{C_{water}} \quad \textbf{(Eqn 25)}$$

Predicted wet weight bioconcentration factors (BCF) can be calculated as the product of lipid content (L) and K_{ow}, according to equilibrium partitioning theory (Mackay, 1982). Predicted lipid-normalized bioconcentration factors (BCF_L) then are simply equal to the K_{ow} of a chemical (*i.e.*, $BCF_L = K_{ow}$).

2.6.6.8. Biota-Sediment Accumulation Factor (BSAF)

$BSAF_L$s were calculated using the geometric means of lipid-normalized biota concentrations (pg PCB / kg lipid) and OC-normalized sediment concentrations (pg PCB / kg OC) (Equation 26). Theoretical $BSAF_L$s were predicted using equilibrium partitioning theory. At equilibrium, lipid-normalized concentrations (C_{lipid}) are related to water concentrations (C_{water}) by a chemical's K_{ow} (*i.e.*, $C_{lipid} = K_{ow} \times C_{water}$) and organic carbon-normalized concentrations in sediment (C_{oc}) are related to water concentrations by the organic carbon-water partition coefficient (K_{oc}) (*i.e.*, $C_{oc} = K_{oc} \times C_{water}$). Additionally, Seth *et al.* (1999) found that K_{oc} was related to K_{ow} by a factor of 0.35 (*i.e.*, $K_{oc} = 0.35\ K_{ow}$) and that this relationship varied by a factor of 2.5 (*i.e.*, the upper limit of K_{oc} was $0.88\ K_{ow}$ and the lower limit was $0.14\ K_{ow}$). Therefore, a predicted $BSAF_L$ is equal to 1/0.35 or 2.86 (with upper and lower limits of 7.14 and 1.14, respectively).

$$BSAF_L\ (\text{kg OC/kg lipid}) = \frac{C_{lipid}}{C_{oc}} \quad \textbf{(Eqn 26)}$$

3. RESULTS AND DISCUSSION

3.1. BIOTA CONCENTRATIONS

3.1.1. PCB Concentrations in Biota Blanks

Because PCBs are ubiquitous contaminants, a study of their bioaccumulation first required the determination of background levels. Sixty-three sodium sulphate blanks were analysed alongside the biota samples. Mean PCB concentrations (and standard deviations), as well as Minimum Reportable Levels (MRLs), are reported in Table D-1 in Appendix D. Octa-chlorinated biphenyls (PCB-200, -194, -203/-196), nona-chlorinated biphenyls (PCB-206 & -208), and PCB-209 were not detected in any of the blanks, while the tri-chlorinated biphenyls (PCB-18 & -16/-32) were found at the highest concentrations.

3.1.2. PCB Concentrations in Biota Samples

PCB concentrations from each sampling site were compared using the Tukey-Kramer HSD All-Pairs Comparison test. Table 3-1 summarizes the comparison and reports which PCBs were significantly different between sites ($\alpha = 0.05$) and which were not. Table 3-2 summarizes which congeners were not detected in the biota samples. Although there was a general trend of greater PCB contamination in the East Basin site compared to Marina and North Central sites, the majority of PCB congeners showed no significant differences between sampling sites. For congeners that were significantly higher in the East Basin site, no significant difference was observed between Marina and North Central sites. However, it should be noted that at most three samples per site were

collected and not every sample contained the same detectable PCB congeners, so the small sample size did not provide sufficient power to detect differences between sites. For the purpose of this study, it was deemed acceptable to compile the data from each sampling site into one value for False Creek for each PCB and for each organism.

The data for each organism were compiled from each sampling site and their distribution was analyzed using the Kolmogorov-Smirnov and Shapiro-Wilk normality tests (Table I-4 in Appendix I). Although an analysis of concentration distribution is difficult for left-censored data sets (*i.e.*, blank-corrected and MRL-screened) (Clark and Whitfield, 1994), an effort to characterize the distribution was still carried out and, in general, PCB concentrations were found to be log-normally distributed. This was not unexpected since environmental concentrations are frequently found to be log-normally distributed. The data was then log transformed and geometric means were calculated.

Table 3-1. Results of Tukey-Kramer HSD All-Pairs Comparison Test of Wet Weight PCB Concentrations From East Basin (EB), Marina (Ma), and North Central Sampling Sites. Statistics performed using JMP IN (v.4).

Species[a]	No Sig. Diff. Btn. Sites	Sig. Diff. Btn. Sites	Site Comparison
P	101/90, 149, 132/153, 187/182, 180	110, 130/160/163/164	EB > Ma; EB˜ NC; Ma˜ NC
		118	EB > Ma; EB > NC; Ma˜ NC
GA	99, 203/196	101/90, 110, 118, 149, 132/153, 177, 138/160/163/164	EB > Ma; EB > NC; Ma˜ NC
		187/182, 180, 194	EB > NC; EB˜ Ma, Ma˜ NC
GC	73/52, 47/75/48, 101/90, 99, 149, 132/153, 138/160/163/164, 187/182, 177, 180, 200, 194, 203/196	110, 118	EB > NC; EB˜ Ma, Ma˜ NC
BM	101/90, 99, 118, 149, 132/153, 138/160/163/164, 187/182, 177, 180, 200, 194, 203/196	110	EB > Ma & NC; Ma˜ NC
PO	73/52, 47/75/48, 99, 132/153, 187/182, 200	101/90, 110, 118, 149, 138/160/163/164, 177, 180	EB > Ma; EB˜ NC, Ma˜ NC

Table 3-1 (Continued). Results of Tukey-Kramer HSD All-Pairs Comparison Test of Wet Weight PCB Concentrations From East Basin (EB), Marina (Ma), and North Central Sampling Sites. Statistics performed using JMP IN (v.4).

Species	No Sig. Diff. Btn. Sites	Sig. Diff. Btn. Sites	Site Comparison
WG	18, 47/75/48, 101/90, 99, 110, 118, 149, 132/153, 138/160/163/164, 187/182, 177, 180, 200, 194, 203/196	16/32, 73/52, 206, 208, 209	NC > Ma
PSS	73/52, 47/75/48, 101/90, 99, 110, 118, 149, 132/153, 138/160/163/164, 187/182, 177, 180, 200, 194, 203/196, 206, 208, 209		
SS	73/52, 47/75/48, 101/90, 99, 110, 118, 149, 132/153, 138/160/163/164, 187/182, 177, 180, 200, 194, 203/196, 206, 208, 209		

[a] P – plankton; GA – green algae; GC – geoduck clams; BM – blue mussels; PO – Pacific oysters; WG – whitespotted greenling; PSS – Pacific staghorn sculpin; SS – striped seaperch.

Table 3-2. PCBs Detected Above MRLs in At Least One Sample of Each Marine Organism

ORGANISM	PCB CONGENERS NOT DETECTED
Plankton	18, 208, 209
Brown Algae	18, 16/32, 47/75/48, 177, 200, 194, 203/196, 206, 208, 209
Green Algae	18
Manila Clams	(All 20 PCBs detected)
Blue Mussels	18, 208, 209
Pacific Oysters	208
Geoduck Clams	(All 20 PCBs detected)
Minnows	(All 20 PCBs detected)
Striped Seaperch	18, 16/32
Pile Perch	18, 16/32
Forage Fish	(All 20 PCBs detected)
Purple Seastar	209
Surf Scoter	18, 16/32
Pacific Staghorn Sculpin	(All 20 PCBs detected)
Dungeness Crab	(All 20 PCBs detected)
Sole	(All 20 PCBs detected)
Whitespotted Greenling	(All 20 PCBs detected)
Spiny Dogfish Muscle	(All 20 PCBs detected)
Spiny Dogfish Embryo	18
Spiny Dogfish Liver	(All 20 PCBs detected)

Previous studies have observed strong positive correlations between lipid contents and PCB concentrations of different species (Rasmussen *et al.*, 1990; Stow *et al.*, 1997). In this study, wet weight PCB concentrations were compared to lipid contents prior to

making interspecies comparisons. Figure 3-1 depicts the relationship between the logarithm of 'Sum 20 PCB' concentrations and the logarithm of equivalent lipid content for algae and plankton and the logarithm of lipid content for all other species. Table 3-3 reports the slopes, intercepts, R^2, and p-values for all congeners. As shown in Figure 3-1, the R^2 value for the correlation increased from 0.2509 to 0.4624 when the algae and plankton were removed from the comparison. In fact, R^2 values increased for all PCBs (except PCB-18) when algae and plankton were removed from the correlations (Table 3-3), suggesting that PCB concentrations for algae and plankton were lower than expected by the PCB:lipid relationship. For brown algae, this could be explained by the species that compose the grouping: *Nereocystis luetkeana* and *Fucus gardneri*. *Nereocystis luetkeana* (*a.k.a.* bull kelp) is known to grow 17 cm (7") per day from March to September (Druehl, 2000). As this algal sample was collected in June, its growth rate was likely larger than the uptake rate resulting in decreased algal PCB concentrations. *Fucus gardneri* (*a.k.a.* rock weed) was collected from an intertidal area with a rocky shoreline, as were the green algae. Intertidal organisms are less exposed to contaminated water than continuously submerged organisms, resulting in lower than expected PCB concentrations. The plankton samples likely contained a mixture of zooplankton, phytoplankton, and other organic matter, which likely influenced the PCB concentrations detected. Although the relationship between PCB and lipid was not strong with the algae and plankton, the relationship was strong enough without these organisms to warrant lipid-normalization of PCB concentrations for inter-species comparisons. Table E-1 in Appendix E reports the lipid-normalized PCB concentrations for all species sampled in False Creek.

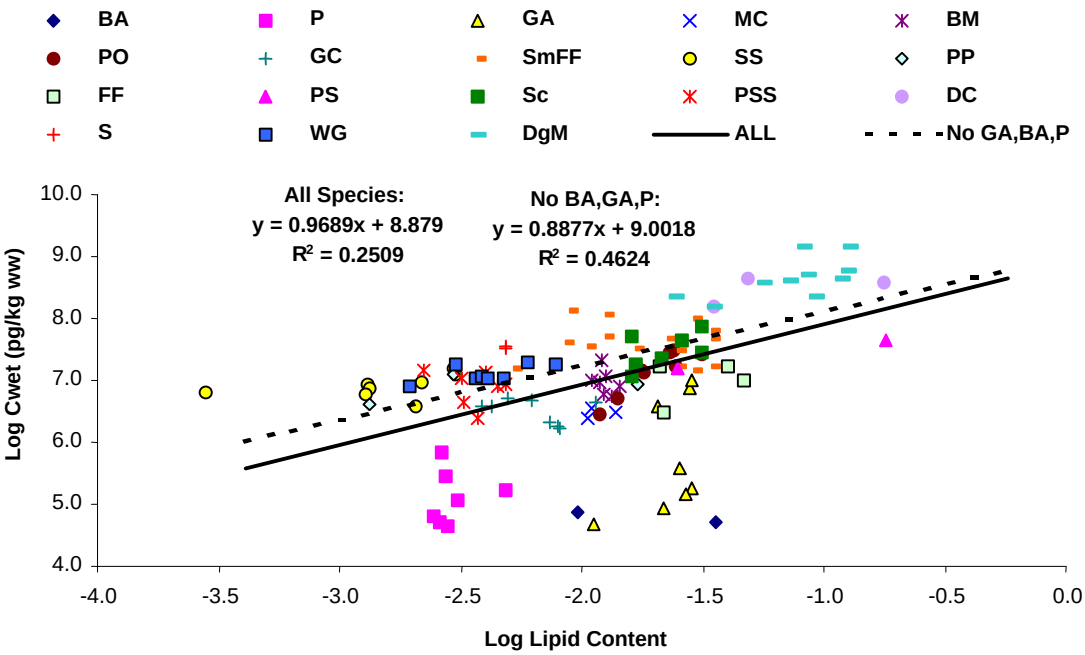

Figure 3-1. Logarithm of Wet Weight PCB concentrations (pg/kg ww) in Biota versus Logarithm of Lipid Content. PCB Concentrations are for 'Sum 20 PCBs'.
The two regression lines include either all species (solid line; p << 0.0001) or omit algae and plankton (broken line; p << 0.0001). Abbrev.: P - plankton; BA - brown algae; GA - green algae; MC - manila clam; BM - blue mussel; PO - Pacific oyster; GC - geoduck clam; SmFF - small forage fish; SS - striped seaperch; PP - pile perch; FF - forage fish; PS - purple seastar; Sc - surf scoter; PSS - Pacific staghorn sculpin; DC - Dungeness crab; S - sole; WG - whitespotted greenling; DgM - spiny dogfish muscle.

Figure 3-2 shows the contribution of each PCB class (*i.e.*, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, and deca-chlorinated biphenyls) to the sum of 20 PCBs, calculated using the sum of the geometric means of each PCB within each PCB class. As can be seen in Figure 3-2, the penta- and hexa-chlorinated biphenyls make up the majority of the PCBs within each organism. The contribution of tri- and tetra-chlorinated biphenyls decreased from plankton to spiny dogfish. In contrast, the contribution of hepta-chlorinated biphenyls to the sum total increases from plankton to spiny dogfish.

These trends will be further discussed in Section 3.4 (PCB Concentrations versus Trophic Position).

Table 3-3. Summary of Linear Regression Information[a] for Log Wet Weight Concentration (pg/kg ww) versus Log Lipid Content (unitless) for 20 PCB Congeners and 'Sum 20 PCBs'. Summary includes information for regressions that include all species and that omit algae and plankton.

	All Species Included			Algae & Plankton Omitted[b]		
PCB Congener	**Slope**	**Y-Int.**	**R^2**	**Slope**	**Y-Int.**	**R^2**
18	0.6281	6.3107	0.4816	0.6281	6.3107	0.4816
16/32	0.7050	6.4480	0.4865	0.7163	6.4882	0.5140
52/73	0.6681	7.1386	0.2756	0.6715	7.2334	0.3585
47/75/48	0.8762	7.1016	0.4589	0.8771	7.1602	0.5245
101/90	0.7910	7.4939	0.1865	0.7426	7.6489	0.3269
99	0.8083	7.5154	0.2575	0.8586	7.7509	0.4407
110	0.8330	7.4262	0.2112	0.7551	7.5117	0.3176
118	0.9826	7.9320	0.2403	0.8979	8.0573	0.4434
149	0.9944	7.7157	0.3160	0.9340	7.8346	0.5330
132/153	0.9749	8.1729	0.2325	0.8939	8.3079	0.4124
138/160/163/164	1.0056	8.1995	0.2500	0.9188	8.3177	0.4390
187/182	0.9943	7.6360	0.2936	0.9628	7.8035	0.4889
177	0.9335	7.0813	0.2897	0.9615	7.3130	0.5225
180	0.9359	7.5600	0.2448	0.8628	7.6448	0.3425
200	0.8243	6.2776	0.3758	0.8307	6.3212	0.3926
194	0.8033	6.4232	0.2124	0.8510	6.6093	0.2646
203/196	0.7137	6.3285	0.1681	0.7573	6.5057	0.2072
206	0.7413	5.9378	0.2845	0.7665	6.0408	0.3221
208	0.7854	5.6391	0.4248	0.8031	5.6926	0.4432
209	0.7825	5.6771	0.4907	0.8233	5.7925	0.5569
Sum 20 PCBs	**0.9689**	**8.8790**	**0.2509**	**0.8877**	**9.0018**	**0.4624**

[a] All slopeslinear regressions were significantly greater than zero ($p << 0.0001$).
[b] Linear regressions include all species except algae and plankton

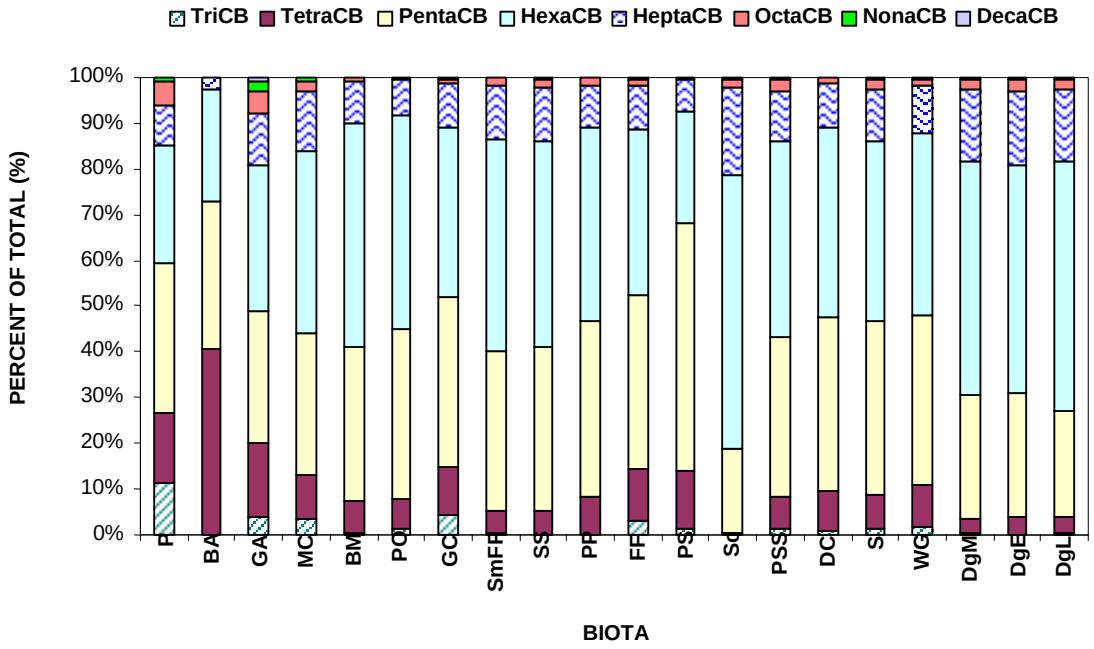

Figure 3-2. Contribution of Each PCB Class (*i.e.*, Tri-, Tetra-, Penta-, Hexa-, Hepta-, Octa-, Nona-, and Deca-Chlorinated Biphenyls) to the Sum of 20 PCBs for Each False Creek Marine Organism. Abbrev.: P - plankton; BA - brown algae; GA - green algae; MC - manila clams; BM - blue mussels; PO - Pacific oyster; GC - geoduck clams; SmFF - small forage fish; SS - striped seaperch; PP - pile perch; FF - forage fish; PS - purple seastar; Sc - surf scoter; PSS - Pacific staghorn sculpin; DC - Dungeness crab; S - sole; WG - whitespotted greenling; DgM - spiny dogfish muscle; DgE - spiny dogfish embryo; DgL - spiny dogfish liver.

3.2. SEAWATER CONCENTRATIONS

3.2.1. PCB Concentrations in Water Blanks

To provide an estimate of background PCB concentrations, eleven well water samples from Lynn Headwaters Regional Park served as blanks for the seawater samples. Table 3-4 reports the range of concentrations in the blanks observed within each chlorination class of PCB (*i.e.*, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, and deca-chlorinated biphenyls). Background concentrations were highest for the di-, tri-, and tetra-chlorinated biphenyls, while nona- and deca-chlorinated biphenyls were absent. This was expected as lighter chlorinated PCBs are more water-soluble and thus more likely to be found at higher concentrations in background levels. The mean blank concentrations from the C_{18} extraction disks and glass fibre (GF) filters, as well as

Minimum Reportable Levels (MRLs; see Section 2.6.2), are reported in Tables D-2 and D-3 in Appendix D, respectively.

Table 3-4. Range of PCB Concentrations (by PCB Class) found in C_{18} and Glass Fibre Filters from the Water Blanks.

PCB Class[a]	C_{18} Extraction Disks		Glass Fibre Filters	
	Min (pg/L)	Max (pg/L)	Min (pg/L)	Max (pg/L)
Σ Di-CB	188.85	396.57	81.11	958.62
Σ Tri-CB	391.99	786.67	363.92	1851.55
Σ Tetra-CB	152.53	322.11	105.78	619.23
Σ Penta-CB	35.59	119.46	9.42	113.63
Σ Hexa-CB	22.90	90.02	8.41	56.24
Σ Hepta-CB	4.27	46.58	6.90	40.93
Σ Octa-CB	8.63	10.22	3.50	3.86
Σ Nona-CB	ND[c]	ND	ND	ND
Deca-CB	ND	ND	ND	ND
Total PCBs[b]	**877.25**	**1594.88**	**486.00**	**3522.29**

[a] CB = chlorinated biphenyl
[b] Total PCBs includes the sum of 121 congeners/coeluters. Of 121, 26 represent coeluting PCBs.
[c] ND = Not Detected above Minimum Reportable Levels (MRLs).

3.2.2. PCB Concentrations in Seawater Samples

Seawater concentrations of detected PCB congeners were insufficient within the three sampling sites for inter-site statistical comparisons. Thus, for this study, the concentrations from each sampling site were compiled into one set of values for False Creek. Those congeners with sufficient concentration values were subjected to tests for normality using the Kolmogorov-Smirnov and Shapiro-Wilk normality tests (Table I-3 in Appendix I) and found to be log-normally distributed. Thus, the concentrations were log-transformed and reported as geometric means (pg/L) with upper and lower standard deviations for C_{18}, glass fibre (GF), and total water (Table E-2 in Appendix E). PCB concentrations on the large-diameter suspended matter (μg/kg LDSM), *i.e.*, particulate matter captured by the glass fibre, are reported in Table E-3 of Appendix E.

PCB concentrations in seawater are often viewed as existing in three phases: particulate, colloidal, and dissolved (Gschwend and Wu, 1985; Brownawell and Farrington, 1986; Baker *et al.*, 1986; Eadie *et al.*, 1990; Burgess *et al.*, 1996a,b; Butcher *et al.*, 1998; Lee & Kuo, 1999; Pedersen *et al.*, 1999; Poerschmann & Kopinke, 2001). The particulate phase includes PCBs that are associated with the suspended solids in the water column. The colloidal phase includes PCBs that are associated with nonsettling particles between the particulate phase (> 1 μm) and the dissolved phase (< 10 nm) (Gschwend and Wu, 1985; Burgess *et al.*, 1996a,b). (The definition of a 'colloid' varies between articles, but often is not distinguished from dissolved organic matter (DOM) or dissolved organic carbon (DOC).) The dissolved phase are those PCB molecules that are surrounded by a shell of water molecules and are not associated with any other materials. In biological systems, it is the dissolved phase that is often considered to be the only bioavailable phase, *i.e.*, the phase that is available for uptake by an organism. Thus, the understanding of partitioning between phases is important for the understanding of the mechanism of bioaccumulation.

For nonpolar hydrophobic organic compounds (HOCs), partitioning between particulate, colloidal, and dissolved phases is governed by the properties of a chemical and by the properties of the medium in which it resides. For PCBs, partitioning between phases has often been related to the hydrophobicity of the chemical (*i.e.*, its log K_{ow}) and the organic carbon (OC) content of the particulate and colloidal phases (Karickhoff, 1979; Means *et al.*, 1980; Mackay & Powers, 1987; Seth *et al.*, 1999; Edgar *et al.*, 2003). Other factors have also been found to play a role in the partitioning of PCBs within the water column, such as particle size (Piérard *et al.*, 1996; Carro *et al.*, 2002;

Edgar *et al.*, 2003), particle composition (Edgar *et al.*, 2003), and environmental variables, such as temperature, pH, salinity, and organic matter type and origin (Xie *et al.*, 1997; Doucette, 2000). However, the study of the partitioning of HOCs in the water column has been confounded by difficulties in the separation of phases, especially using filtration and centrifugation methods. Since DOM and DOC are both recognized as sorption matter for hydrophobic contaminants (Boehm and Quinn, 1976; McCarthy *et al.*, 1985; McCarthy and Jimenez, 1985; Kukkonen *et al.*, 1990), inconsistencies in partitioning between phases have often been attributed to sorption onto DOM, DOC, or colloidal matter. Thus, most studies agree that the partitioning of PCBs and other HOCs in the water column is dictated by the log K_{ow} of the chemical and the OC content of particulate and colloidal matter.

In this study, particulate and dissolved phase concentrations were estimated using glass fiber filters (0.45 μm pore size) and octadecyl (C_{18}) extraction disks, respectively. Table E-2 in Appendix E reports the geometric means (and upper and lower standard deviations) for PCB concentrations observed on the glass fibre and C_{18} filters, the total water concentrations based on the sum of the geometric means, the model-derived freely-dissolved concentrations, and the concentrations for the sum of the various chlorination classes of PCBs. On an individual sample basis (not shown), PCB concentrations ranged from 2.71 pg/L to 1.65 x 10^3 pg/L for C_{18} disks and from 2.46 pg/L to 2.30 x 10^3 pg/L for GF filters and ΣPCBs ranged from 27.8 pg/L to 3.16 x 10^3 pg/L for C_{18} disks and from 2.46 pg/L to 3.92 x 10^3 pg/L for GF filters. Although the chemical analysis quantified 121 PCB congeners/coeluters for C_{18} and GF samples, only 48 and 40 congeners/ coeluters were detected above MRLs, respectively. The sum of the geometric means for

all quantified congeners for the C_{18} and GF filters were 1.60 ng/L and 1.97 ng/L, respectively (Table E-2 in Appendix E). The observed total PCB concentration (3.57 ng/L) for False Creek seawater was comparable to other studies of PCBs in various marine and fresh waters, although closest to San Francisco Bay concentrations (Table 3-5). Studies of seawater PCB concentrations for areas closer to Vancouver could not be located. As expected from the water solubilities (Table A2 in Appendix A), the lower chlorinated congeners (*i.e.*, di-, tri-, and tetra-chlorinated biphenyls), which are the most water soluble, were found to be at the highest concentrations for both C_{18} and GF filters.

Table 3-5. PCB Concentrations in Water as Reported in Various Studies

Location	Year Sampled	# of PCBs Totalled	Ave. Total PCB Conc. (ng/L)	Source
San Diego Bay	2000	27	0.054 – 0.419	Zeng *et al.*, 2002
San Francisco Bay	2000		37 ppq – 3.05 ng/L	SFEI, 2000
Gulf of Alaska	1989-1990	40	0.012	Itawa *et al.*, 1993
North Pacific			0.024	
Sea of Japan	1995	30	0.0003 – 0.0017	Kannan *et al.*, 1998
Lake Michigan	1991	85	0.47 ± 0.06	Pearson *et al.*, 1996
Lake Superior	1983	28	0.56	Baker *et al.*, 1985
False Creek	**2000**	**121**	**3.57**	**This Study**

Seawater PCB concentrations were found to be orders of magnitude below their seawater-corrected solubilities (see Table A-2 in Appendix A). Of the PCB congeners analysed (excluding the coeluters), the geometric means of the total water and operationally-defined dissolved (*i.e.*, C_{18}) concentrations ranged from 3.40 pg/L to 419 pg/L and 3.73 pg/L to 238 pg/L, respectively, while the seawater solubilities ranged from 0.00665 μg/L to 569 μg/L. An analysis of the relationship between the logarithm of the ratio of the seawater concentration (C_w) to the seawater solubility (S_w) (*i.e.*, log C_w/S_w)

and log K_{ow} showed a positive linear correlation with strong R^2 values of 0.6083 and 0.7752 for total water and C_{18}, respectively (Figure 3-3). As a comparison, Figure 3-3 also shows the analysis of the relationship between log C_w/S_w and log K_{ow} for the model-derived freely-dissolved (C_{FD}) concentrations. For C_{FD}, a weak (R^2 = 0.1407) negative linear correlation was observed. According to total water and C_{18} concentrations, PCBs approach their solubilities as log K_{ow} increases, whereas the C_{FD} decreases slightly as log K_{ow} increases.

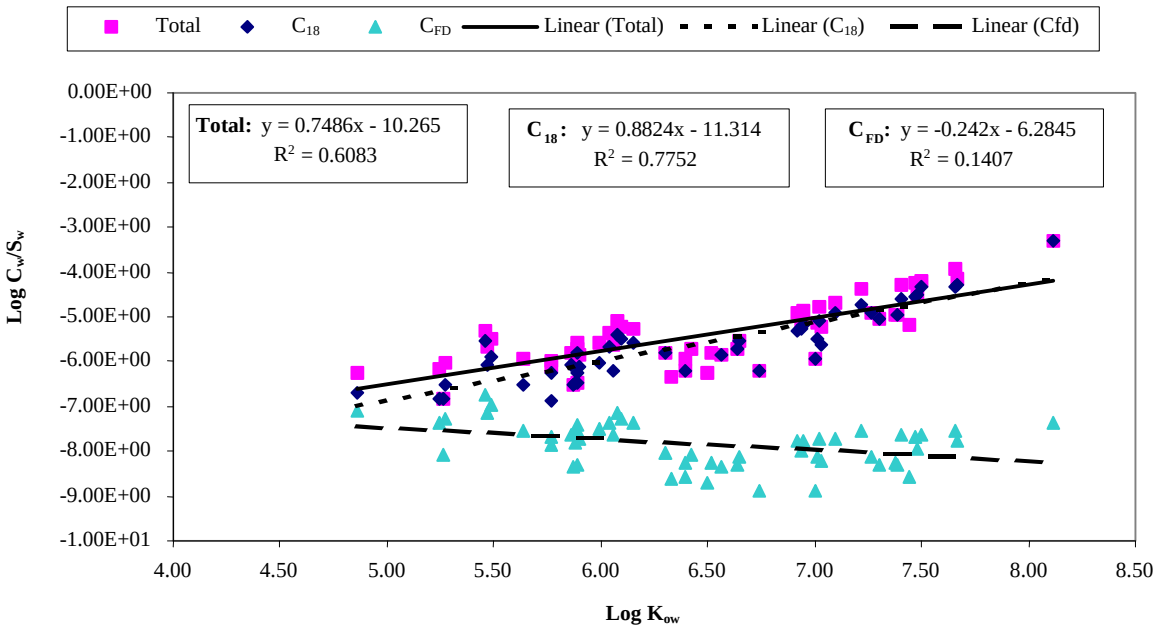

Figure 3-3. Logarithm of the Ratio of Concentration (Total, C_{18}, and Freely-Dissolved) to Solubility in Seawater (Log C_w/S_w) Versus Seawater-Corrected Log K_{ow}.

Over the range of seawater-corrected log K_{ow}'s, approximately 50% of the total PCB concentration in water was captured on the C_{18} disks (Figures 3-4 and 3-5). A comparison of the C_{18} fraction of PCBs and phthalate esters (PEs) from the same water samples (data obtained from Cheryl Mackintosh, Mackintosh 2002) indicated that the C_{18}

fraction of PCBs was similar to that of PEs over the same range of log K_{ow}'s (*i.e.*, log K_{ow} 4 to 8) (Figure 3-4). Frequently, the partitioning of hydrophobic organic compounds (HOCs), like PCBs and PEs, in water has been described by a two-phase model, whereby the chemicals are freely-dissolved (FD) or bound to particulate matter. (Van Hoof and Andren, 1990; Bergen *et al.*, 1993; Butcher *et al.*, 1998; Mackintosh, 2002; Zeng *et al.*, 2002). Figures 3-4 and 3-5 show the FD fraction, based on a two-phase model calibrated to PCB and PE (Mackintosh, 2002) C_{18} fractions. As stated in Mackintosh (2002), C_{18} disks were observed to contain fine particulate matter, operationally-defined as 'small diameter suspended matter' (SDSM), with diameters < 0.45 μm (*i.e.*, smaller than the pore size of the GF filter). The presence of SDSM, in combination with the disagreement between two-phase model predictions and C_{18} fractions, suggested that a three-phase model, where chemicals were either bound to large diameter suspended matter (LDSM), bound to SDSM, or FD, was more appropriate for describing the partitioning of PEs (Mackintosh, 2002). (Further information on this model and its results with regards to PEs can be found in Mackintosh, 2002.) It was concluded that the same three-phase partitioning model could be used to estimate the FD fractions for PCBs. The predictions of the three-phase model are illustrated in Figures 3-4 and 3-5. Figure 3-5 serves as a comparison for the two-phase and three-phase models and shows that FD fractions drop with increasing K_{ow}, whereas predicted C18 fractions (*i.e.*, FD+SDSM) remain constant above a log K_{ow} of 6.

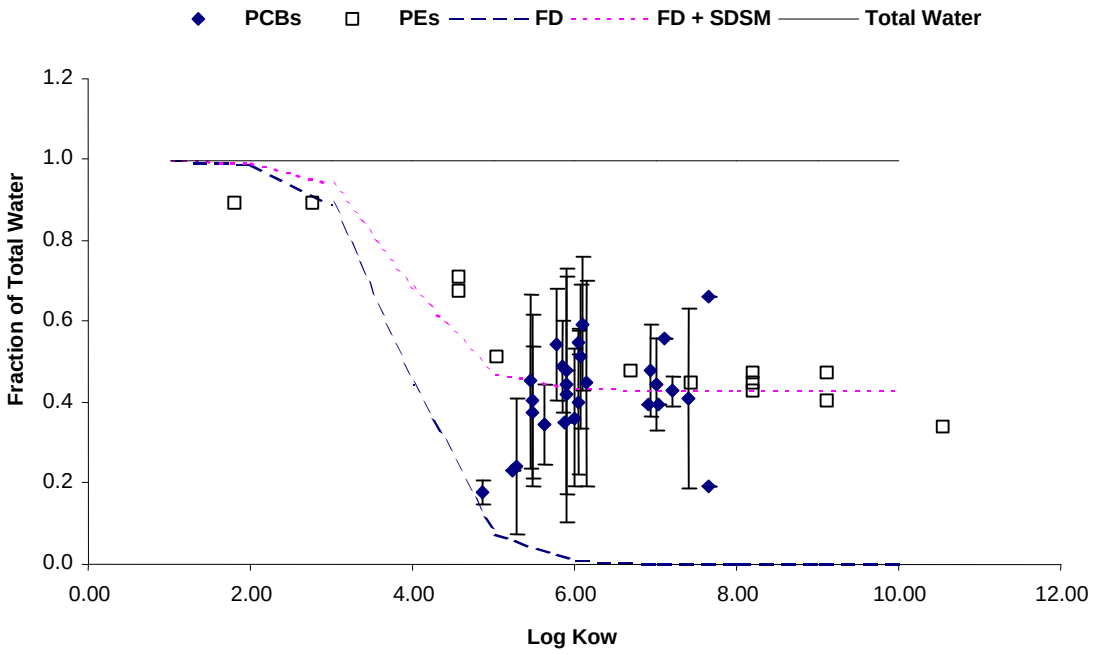

Figure 3-4. C_{18} Fraction of Total Seawater Concentration for PCBs and for PEs (Mackintosh, 2002) versus Seawater Log K_{ow}. Model Predictions for Freely-dissolved (FD) and Freely-Dissolved + SDSM (FD + SDSM) Fractions are Shown (Solid Lines).
Error Bars Depict 1 Std. Dev. For PCB C_{18} Fractions.

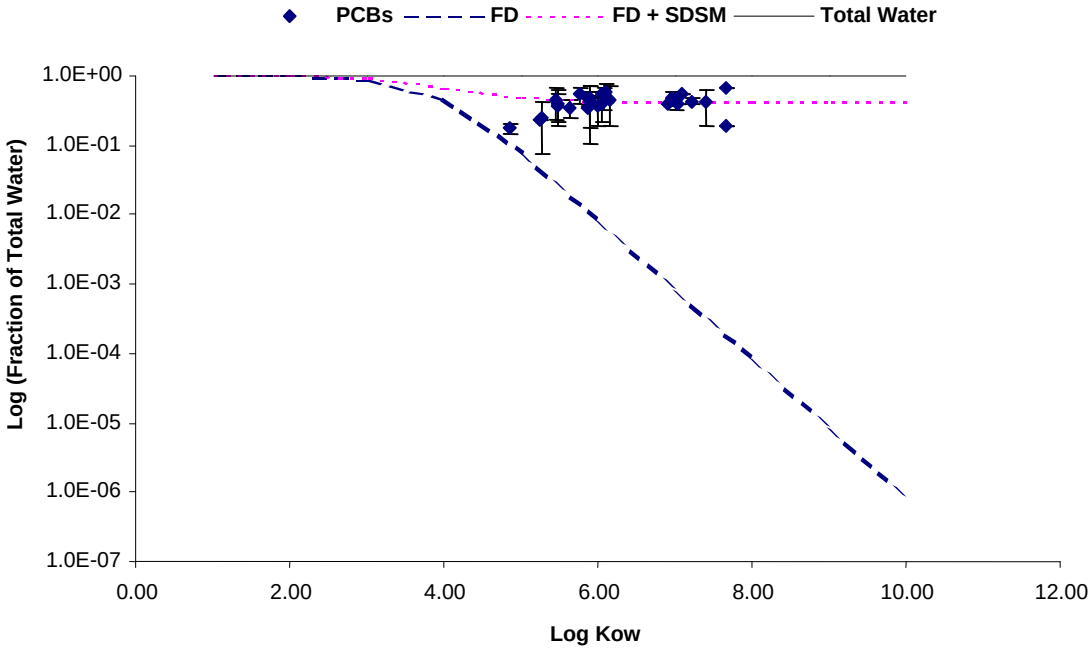

Figure 3-5. Logarithm of C_{18} Fraction of Total Seawater Concentration for PCBs versus Seawater-Corrected Log K_{ow}. Model Predictions for Freely-dissolved (FD) and Freely-Dissolved + SDSM (FD + SDSM) Fractions are Shown (Solid Lines).
Error Bars Depict 1 Std. Dev.

3.3. SEDIMENT DATA

3.3.1. PCB Concentrations in Sediment Blanks

Detected PCB concentrations in the sodium sulphate blanks ranged from 1.26 pg/g ww (2.15 pg/g dw) to 290 pg/g ww (494 pg/g ww). ΣPCB concentrations for the blanks were 2.59 ng/g ww (4.41 ng/g ww) and 1.42 ng/g ww (2.42 ng/g dw). Table D-4 in Appendix D reports the concentrations observed in each sediment blank (in ww and dw), the average concentrations (in ww and dw), and the minimum reportable levels (MRLs) (in ww and dw). Dry weight concentrations were based on a moisture content of 58.6% (*i.e.,* the average moisture content of the sediment samples). Of the 121 congeners/coeluters quantified, 57 congeners/coeluters and 48 congeners/ coeluters were detected in the two blanks. Background contamination was mostly from lower chlorinated congeners (*i.e.,* di-, tri-, and tetra-chlorinated biphenyls).

3.3.2. PCB Concentrations in Sediment Samples

As mentioned in Section 3.2.4 (PCB Concentrations in Seawater), partitioning of hydrophobic organic contaminants in sediment is often described as a three phase model, whereby chemicals partition between particulate, colloidal, and dissolved phases (Gschwend and Wu, 1985; Brownawell and Farrington, 1986; Baker *et al.,* 1986; Eadie *et al.,* 1990; Burgess *et al.,* 1996a,b; Butcher *et al.,* 1998; Lee & Kuo, 1999; Pedersen, 1999; Poerschmann & Kopinke, 2001). In the particulate (and colloidal) phase, concentrations of hydrophobic organic compounds (HOCs), such as PCBs, have been associated with the organic carbon (OC) content of the particulates (Karickhoff, 1979; Means *et al.,* 1980; Mackay & Powers, 1987; Seth *et al.,* 1999; Burgess *et al.,* 2001; Edgar *et al.,* 2003). Although there have been studies relating HOC concentrations to

various other environmental parameters, such as particle size and composition (Piérard *et al.,* 1996; Carro *et al.,* 2002; Edgar *et al.,* 2003), an analysis of the effects of 19 sediment characteristics and 11 humic acid characteristics on the variation in partition coefficients (*i.e.,* $K_{SW} = C_{sediment}/ C_{water}$) found that OC-normalizations reduced the variability in partition coefficients the most for PCB-52 (Burgess *et al.,* 2001). Normalizations based on combinations of humic acid characteristics (*i.e.,* humic acid content + humic oxygen) were found to reduce the variability more so than OC normalizations, but as a sole parameter OC content was found to be superior to any other single characteristic (Burgess *et al.,* 2001).

Figure 3-6 shows the relationship between the logarithm of the dry weight ΣPCB concentrations and the logarithm of OC content. The slope of the log-log relationship was significantly greater than zero ($p = 0.03$) with $R^2 = 0.4239$, suggesting that PCB concentrations are indeed linked to the OC content of the sediment. Thus, differences amongst PCB concentrations in sediment samples were likely due, at least in part, to different OC contents of the sediment samples.

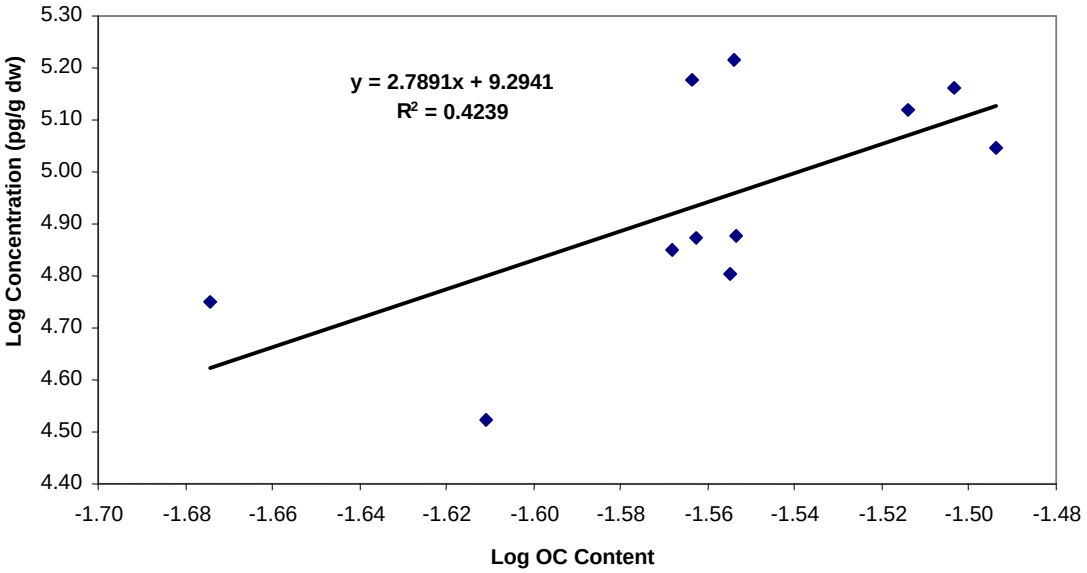

Figure 3-6. Log-Log Plot of Dry-Weight PCB Concentrations in Sediment versus Organic Carbon (OC) Content for ΣPCBs.

Because of the relationship between dry weight sediment concentrations and OC content, OC normalizations were performed to reduce the variability of PCB concentrations between sampling sites. OC-normalized PCB concentrations for each sediment sample are reported in Table E-4 in Appendix E. Differences between sites in OC-normalized PCB concentrations were investigated by using the Tukey-Kramer HSD All-Pairs Comparison test, but was limited due to low sample numbers ($n \leq 3$). Table 3-6 summarizes the conclusions from these comparisons, where the logarithm of PCB concentrations were compared between sites, for each PCB homologue class. ΣPCB concentrations in East Basin were significantly elevated over those at the Marina site, although not significantly different from the other sampling sites. ΣPCB concentrations were not significantly different between other sites. Figure 3-7 shows the differences in concentrations of the PCB homologues between sampling sites, while Figure 3-8 illustrates the differences in ΣPCB concentrations between sampling sites. Since OC-

normalized ΣPCB concentrations in the East Basin site were not significantly different from the Cambie Bridge site and since the concentrations from the Marina and North Central sites were also, in general, not significantly different from the Cambie Bridge site, concentrations from each sampling site were combined into one data set for False Creek.

Table 3-6. Summary of the results for the Tukey-Kramer All Pairs Comparisons Test of OC-Normalized PCB Concentrations from Each Sampling Site in False Creek by PCB Homologue Class.

PCB Class[a]	Results of Tukey-Kramer HSD All Pairs Comparisons Test (q* = 3.31024)
Sum Di-CBs	• Insufficient data for comparison
Sum Tri-CB	• North Central significantly greater than Marina • No significant difference between remaining pairs
Sum Tetra-CB	• No significant difference between all pairs
Sum Penta-CB	• East Basin significantly greater than Marina • No significant difference between remaining pairs
Sum Hexa-CB	• East Basin significantly greater than Marina • East Basin significantly greater than North Central • No significant difference between remaining pairs
Sum Hepta-CB	• East Basin significantly greater than Marina • East Basin significantly greater than North Central • Cambie Bridge significantly greater than North Central • No significant difference between remaining pairs
Sum Octa-CB	• East Basin significantly greater than Marina • East Basin significantly greater than North Central • No significant difference between remaining pairs
Sum Nona-Cs	• No significant difference between all pairs
Deca-CB	• No significant difference between all pairs
SPCB[b]	• East Basin significantly greater than Marina • No significant difference between remaining pairs

[a] CB = Chlorinated biphenyl

[b] SPCBs includes the sum of 121 congeners/coeluters. Of 121, 26 represent coeluting PCBs.

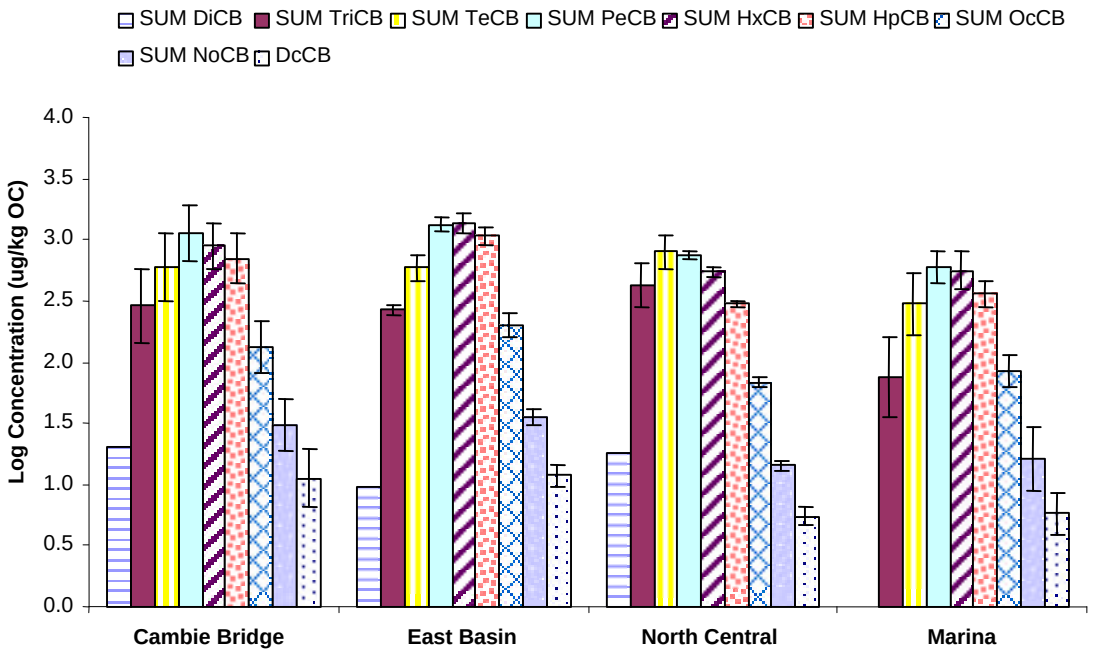

Figure 3-7. Logarithm of Sum PCB Concentrations (mg/kg OC) by Chlorination Class in Sediment from Each Sampling Site in False Creek.
Error Bars Depict One Standard Deviation.

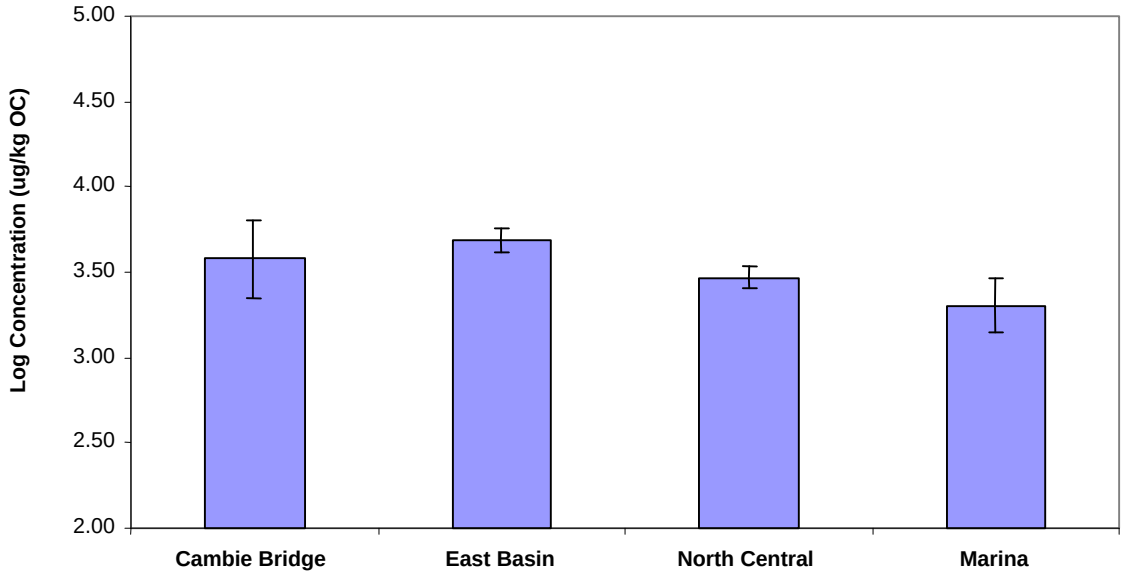

Figure 3-8. Organic Carbon-Normalized SPCB Concentrations (Geometric Means; mg/kg OC) in Sediment from Four Sampling Sites in False Creek.
Error Bars Depict One Standard Deviation.

The distribution of the combined PCB concentrations for False Creek sediment were tested for normality using the Kolmogorov-Smirnov and Shapiro-Wilk normality tests (Table I-1 and I-2 in Appendix I) and found to be log-normally distributed. Hence, the data were log transformed and geometric means (with upper and lower standard deviations) were calculated. Geometric means of OC-normalized PCB concentrations (μg/kg OC) for False Creek sediment ranged from 0.0695 μg/kg OC to 207 μg/kg (Table E-5 in Appendix E).

Sediment ΣPCB concentrations in False Creek sediment were found to be greater than Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (CCME, 2001). The Interim Sediment Quality Guideline (ISQG) for marine sediments, defined as "the concentration below which adverse biological effects are expected to occur rarely", is currently 21.5 μg/kg dry-weight or 779 μg/kg OC (normalized to an average sediment OC content of 2.76%). The Probable Effect Level (PEL) for marine sediments, defined as "the level above which adverse effects are expected to occur frequently", is currently 189 μg/kg dry-weight or 6.85 mg/kg OC (normalized to an average sediment OC content of 2.76%). Thus, the sum of the geometric mean concentrations of each PCB (ΣPCB), 3.11 mg/kg OC, was found to be between the ISQG and the PEL for marine sediments. According to CCME (2001), 37% of adverse effects occur within the range bounded by the ISQG and the PEL and so, sediment concentrations within False Creek are likely causing adverse effects in aquatic organisms.

3.4. BIOACCUMULATION OF PCBS IN FALSE CREEK

3.4.1. Diet-Based Trophic Position versus Stable Nitrogen Isotope Ratios

Food web structure was determined using model-derived diet-based trophic positions (TPs) and stable nitrogen isotope ratios ($\delta^{15}N$). TPs and $\delta^{15}N$ showed a moderate-to-strong linear relationship ($R^2 = 0.5185$; Figure 3-9), indicating that both methods were comparable and that both methods could be used to characterize food web structure. The regression line between TP and $\delta^{15}N$ was based on the liver tissue isotope ratio of the dogfish shark (as well as the remaining organisms), instead of the muscle tissue. Muscle tissue has been previously shown to have a slow isotopic turnover rate (*i.e.,* change in isotope ratio due to growth and metabolic tissue replacement associated with a change in diet) of greater than a year in fish (Hesslein *et al.,* 1993; MacAvoy *et al.,* 2001). Given that spiny dogfish have been observed to be highly mobile, migrating up to 7000 km off the west coast of Canada (McFarlane and King, 2003), the use of isotope ratios from embryos, which are likely newly formed, may better reflect the shark's more recent diet and the False Creek food web. This may especially true since Fisk *et al.* (2002) suggest that high urea levels in shark tissues could affect the $\delta^{15}N$ and underestimate its true trophic position.

As seen in Figure 3-9, the purple seastar (*Pisaster ochraceus*) had a lower $\delta^{15}N$ than predicted by the food web model. This difference between TP and $\delta^{15}N$ may be explained by the fact that the purple seastar sample was comprised of stomach tissue and calcareous ossicles and was not whole body or muscle tissue. Thus, the $\delta^{15}N$ of the seastar may not be representative of the seastar's overall $\delta^{15}N$ and its relative position within the food web. *P. ochraceus* primarily feeds on blue mussels, although they will

eat clams, snails, chitons, barnacles, limpets and occasionally sea anemones (Ricketts *et.al.,* 1985; Nybakken 1997), and should should occupy a higher trophic position (TP) than bivalves. Its $\delta^{15}N$ should also be higher. Alternatively, it is possible that the diet-based TP may have been over-predicted, since it was assumed that seastars ate mainly blue mussels (Mackintosh, 2002). In any case, the disagreement between trophic position and $\delta^{15}N$ suggests that either the TP or the $\delta^{15}N$ is suspicious and that further comparisons between PCB concentrations and TP or $\delta^{15}N$ may not be appropriate for the purple seastar.

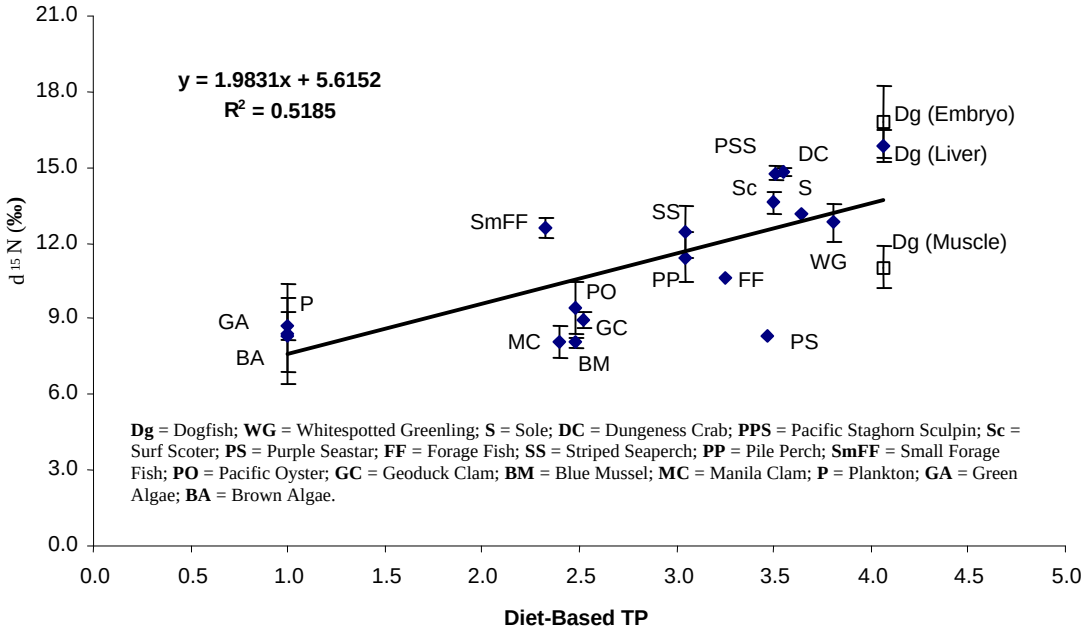

Figure 3-9. $d^{15}N$ **Ratio (‰) versus Diet-Based Trophic Position for False Creek Marine Organisms. Error bars depict one standard deviation. Trendline is based on solid points (*i.e.*, dogfish liver and all other organisms).**

3.4.2. PCB Concentrations versus Trophic Position and versus $d^{15}N$

Figures 3-10 to 3-21 show the comparisons between the logarithm of lipid-normalized concentrations (log [PCB]) and diet-based trophic positions (TP) or $\delta^{15}N$ for PCBs 18, 118, 149, 180, 209, and the sum of 20 PCBs (SPCB). Biomagnification was

observed in all PCBs quantified, whether compared to TP or $\delta^{15}N$. Relationships between log [PCB]-vs-TP and log [PCB]-vs-$\delta^{15}N$ for the remaining 15 PCBs can be found in Appendix F, while Table 3-7 summarizes the linear regressions for all 20 PCBs and for both correlations. (For this section, PCBs were chosen based on their range of log K_{ow}'s and their presence as single congeners.) For the correlations between log [PCB] and TP (Figures 3-10 to 3-20, even numbers): strong positive correlations ($R^2 > 0.6$) were observed for PCBs 47/75/48, 101/90, 99, 118, 149, 132/153, 138/160/163/164, 187/182, 177, 180, SPCB; moderate correlations ($0.4 < R^2 < 0.6$) were observed for PCBs 18, 16/32, 52/73, 110, 200, 194, 203/196, 206, 208; and, a weaker correlation was observed for PCB-209 ($R^2 = 0.3987$). For the correlations between log [PCB] and $\delta^{15}N$ (Figures 3-11 to 3-21, odd numbers): strong correlations ($R^2 > 0.6$) were observed for PCBs 47/75/48, 52/73, 99, 177, 180, 200, 194, 203/196, 206, 208; moderate correlations ($0.4 < R^2 < 0.6$) were observed for PCBs 16/32, 101/90, 110, 118, 149, 132/153, 138/160/163/164, 187/182, 209, 'Sum 20 PCBs'; and, weak correlations ($R^2 < 0.4$) were observed for PCB-18.

All linear regressions from the figures for log [PCB]-vs-TP and log [PCB]-vs-$\delta^{15}N$ (Figures 3-10 to 3-21 and Appendix F) were observed to have slopes significantly greater than zero ($p < 0.05$), with the exception of the correlation between log [PCB-18] and $\delta^{15}N$ ($p = 0.08$). As stated in the introduction, Leblanc (1995) suggested that biomagnification could only occur if organism lipid content increases with increasing trophic position or if chemical depuration rates decrease with increasing trophic level. In addition, Leblanc (1995) suggests that "slight biomagnification (*i.e.,* 2-fold from one trophic level to the next) may occur with compounds having a bioconcentration factor of

> 114 000 or a [log K_{ow}] > 6.3". Given that the regressions were based on lipid-normalized concentrations, the significantly positive slopes in these figures provide evidence for substantial biomagnification, contrary to Leblanc's conclusions. Moreover, evidence for biomagnification (*i.e.*, positive slopes in the above mentioned regressions) was observed throughout the full range of PCB log K_{ow}'s, seawater-corrected log K_{ow} 5.46 to 8.53 (with the possible exception of PCB-18). These observations agree with previous studies on PCB biomagnification in marine food webs (Kiriluk *et al.*, 1995; Kidd *et al.*, 1998a,b; Fisk *et al.*, 2001). For PCB-18, the regression for log [PCB]-vs-$\delta^{15}N$ was not significantly different from zero ($p = 0.08$), which implies that bioconcentration was predominant to biomagnification. This may not be surprising since PCB-18 is the most water-soluble congener of the 20 analyzed, but the lack of significance may simply be a result of a weaker correlation ($R^2 = 0.3335$). The weaker correlation itself may be a result of missing species (*i.e.*, lack of detection of PCB-18 in algal, plankton, blue mussel, striped seaperch, pile perch, and surf scoter samples). Further discussion on biomagnification can be seen in Section 3.4.3 (Food Web Magnification Factors).

In Figures 3-10 to 3-21, the linear regressions were based on all species, except the purple seastars (open squares in figures) and the spiny dogfish liver and embryo tissues (data not shown). As discussed in Section 3.4.1., the disagreement between TP and $\delta^{15}N$ for the purple seastar may indicate a possible error in either TP or $\delta^{15}N$. Inclusion of PCB concentrations for the purple seastar in the linear regressions was then judged to be inappropriate and, although included in the figures, the purple seastar was omitted from regressions.

For the log [PCB]-vs-TP_{diet} relationships, correlations were weakened by the lower-than-expected chemical concentrations of the spiny dogfish shark. Although the spiny dogfish had the highest diet-based trophic position, PCB concentrations were not significantly different from those of whitespotted greenling, sole, striped seaperch, pile perch, and dungeness crabs. This observation may be explained by the life histories of each species. First, the spiny dogfish can be highly mobile, migrating up to 7000 km off the west coast of Canada (McFarlane and King, 2003), and are unlikely to have accumulated PCBs solely from False Creek residents. Second, although the migratory patterns could not be found, whitespotted greenling are demersal generalist predators, feeding on worms, crustaceans and small fishes (Hart, 1973), which may account for the levels of PCBs found within this fish. Third, sole (*i.e.*, English Sole and Starry Flounder) are benthic fish and therefore must have been in contact with the highest environmental PCB concentrations (*i.e.*, in the sediment), which may explain the high levels of PCBs detected in these species. Fourth, striped seaperch are omnivorous, feeding on small crustaceans, algae, worms, mussels, and herring eggs (Hart 1973), which may account for their high PCB levels. Fifth, pile perch feed on hard-shelled molluscs, crabs and barnacles and are a demersal species, which may explain the high levels of PCBs (Hart, 1973; Eschmeyer *et al.*, 1983, *in* Froese and Pauly, 2003). Lastly, Dungeness crabs often bury themselves just below the surface of sand or in vegetation (*e.g.* eel grass) (DFO 2003d), which may explain their high levels of PCBs given that sediment concentrations are significantly greater than seawater concentrations. However, the high levels of PCBs may also be explained by the fact that the concentrations represent those of the hepatopancreas and not muscle tissue.

For the log [PCB]-vs-$\delta^{15}N$ relationships, correlations for some PCB congeners may have been weakened by the PCB concentrations in brown algae and surf scoters. For brown algae, lipid-equivalent PCB concentrations were much lower compared to other species at similar $\delta^{15}N$ ratios (*i.e.,* green algae, plankton, blue mussels, manila clams). This may be explained by the life histories of the individual brown algae, *Nereocystis luetkeana* and *Fucus gardneri*. *N. luetkeana* (*a.k.a.* bull kelp) is known for its fast growth during the summer when it grows about 17 cm (or 7″) per day (Druehl, 2000), which may mean that PCB concentrations were not likely at equilibrium at the time of sampling due to growth dilution. *F. gardneri* (= *F. distichus*; *a.k.a.* rockweed) grow in intertidal areas so that they are not continuously covered by seawater, which may also mean that PCB concentrations were not at equilibrium due to decreased exposure. However, brown algae were still included in the regressions since *N. luetkeana* and *F. gardneri* may still be part of the food web. [*N. luetkeana* are grazed upon by green sea urchins, red sea urchins, northern kelp crabs, gastropods, and isopods (Duggins *et al.*, 2001; Pelletreau and Muller-Parker, 2002; DFO, 2003a) and *F. gardneri* are grazed upon by herbivorous gastropods and isopods (Van Alstyne, 1988). These grazers then serve as food for pile perch and striped seaperch (Hart, 1973; Eschmeyer *et al.*, 1983, *in* Froese and Pauly, 2003).] For the surf scoter, concentrations of PCBs 52/73 and 110 were significantly smaller than other organisms with similar $\delta^{15}N$ (Figures F-6 and F-12 in Appendix F, respectively). In addition, concentrations of PCBs 47/75/48, and 101/90 in the surf scoter also appeared to be smaller than other organisms with similar $\delta^{15}N$ although not as significant (Figures F-4 and F-8 in Appendix F). One explanation for the differences in concentrations in surf scoters could be the selective metabolism of those

PCBs by specific isozymes from the cytochrome P450 (CYP) enzyme system, although PCB metabolism has been shown to be slow in sea birds (Walker, 1990) and thus may not entirely explain the above mentioned differences in PCB concentrations. A more plausible explanation is that PCBs could have been assimilated from prey in different areas since surf scoters are migratory birds (ADFG, 2003) and that the prey had lower concentrations of the above mentioned PCBs. In any case, surf scoters were left in the regressions given that concentrations of the remaining PCBs were similar to those in species of similar TP or $\delta^{15}N$.

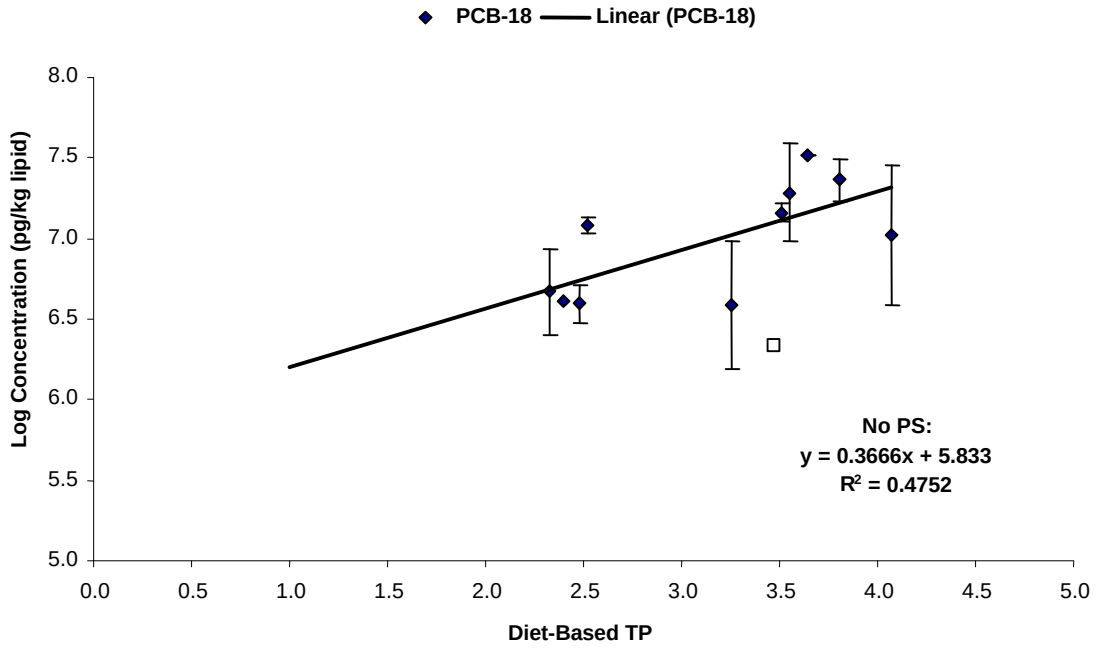

Figure 3-10. Logarithm of PCB-18 Concentration (pg/kg lipid) versus Diet-Based Trophic Position. Each point refers to one Organism. Purple seastars (PS; open square) were omitted from the regression. Solid regression line includes all remaining species. Error bars represent one standard deviation.

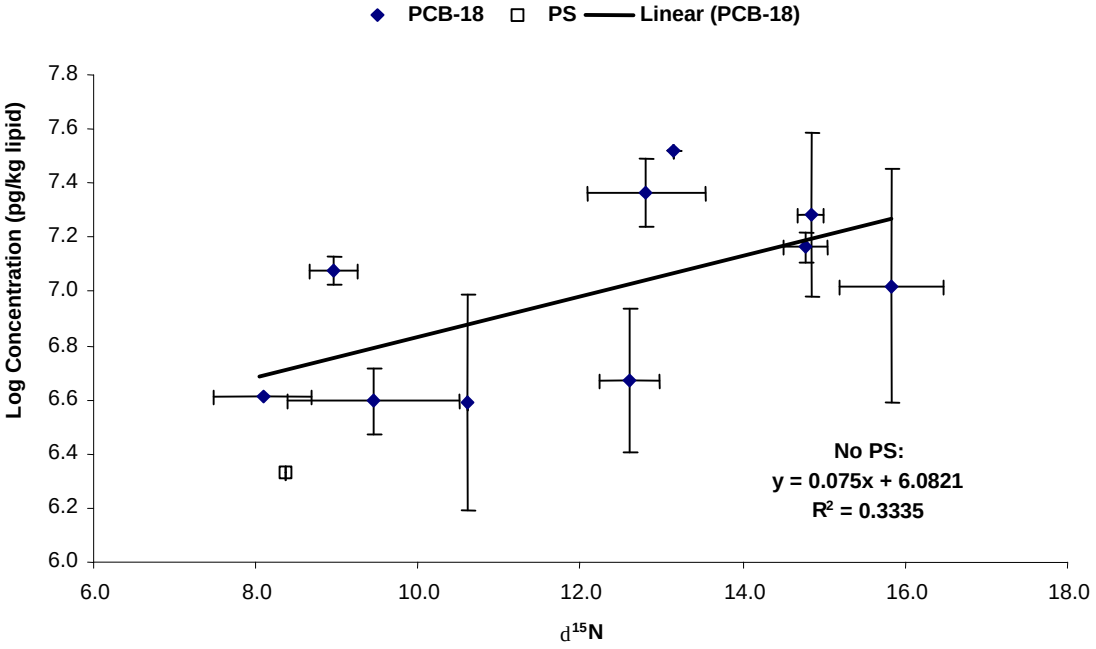

Figure 3-11. Logarithm of PCB-18 Concentration (pg/kg lipid) versus $\delta^{15}N$ (‰). Each point refers to one Organism. Purple seastars (PS; open square) were omitted from the regression. Solid regression line includes all remaining species. Error bars represent one standard deviation. Spiny dogfish liver $\delta^{15}N$ used in place of muscle $\delta^{15}N$ in regressions.

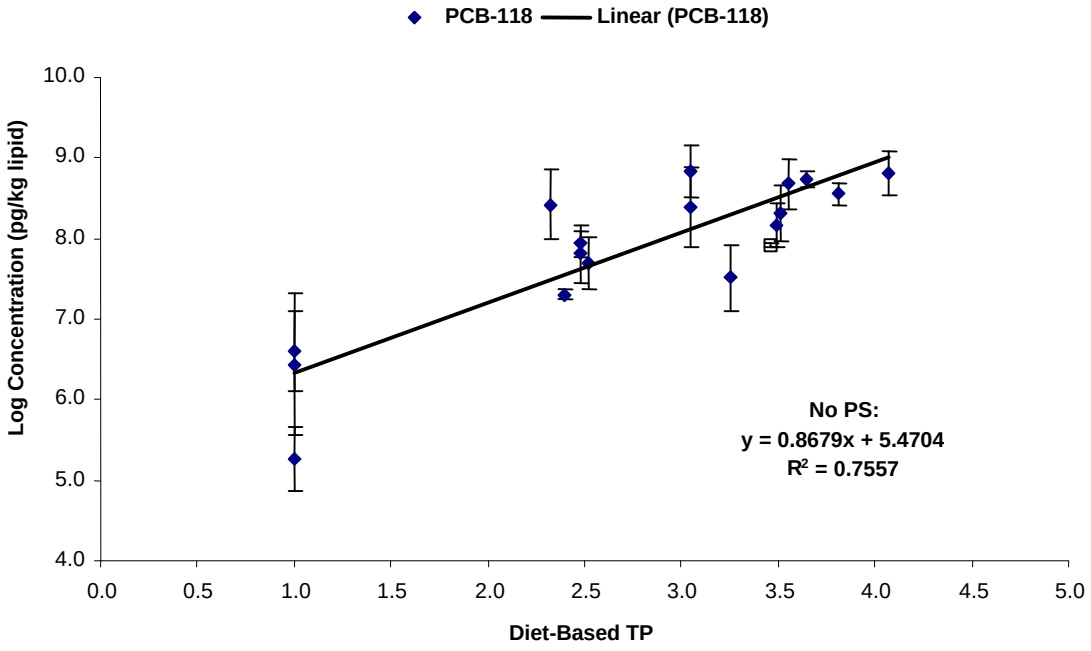

Figure 3-12. Logarithm of PCB-118 Concentration (pg/kg lipid) versus Diet-Based Trophic Position. Each point refers to one Organism. Purple seastars (PS; open square) were omitted from the regression. Solid regression line includes all remaining species. Error bars represent one standard deviation.

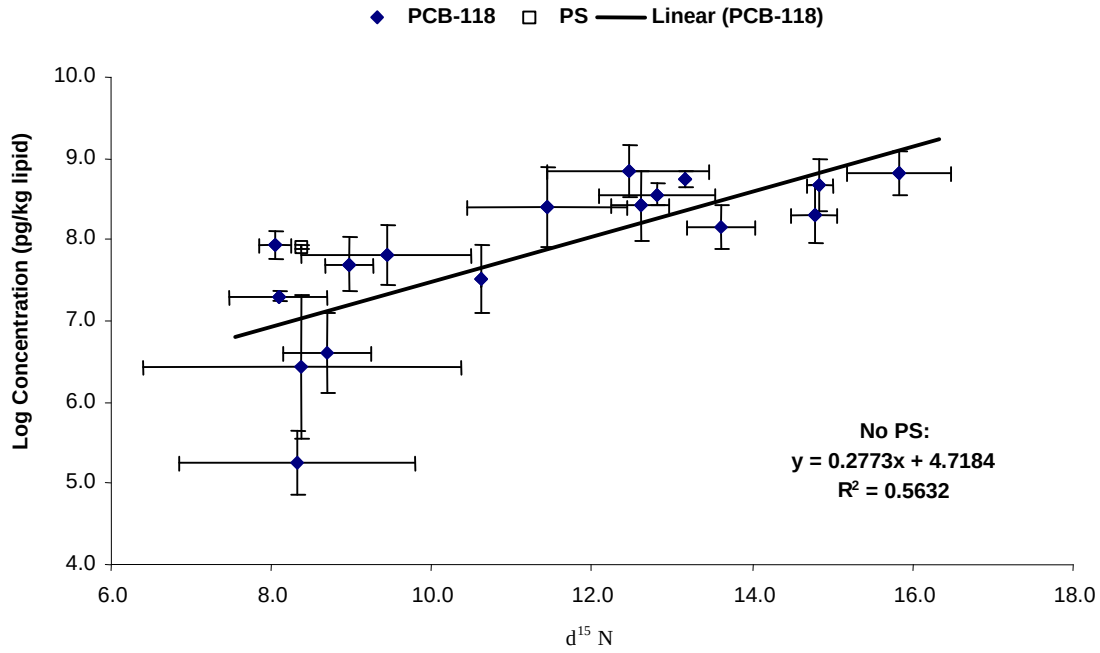

Figure 3-13. Logarithm of PCB-118 Concentration (pg/kg lipid) versus $d^{15}N$ (‰). Each point refers to one organism. Purple seastars (PS; open square) were omitted from the regressions. Solid regression line includes all remaining species. Error bars represent one standard deviation. Spiny dogfish liver $d^{15}N$ used in place of muscle $d^{15}N$ in regressions.

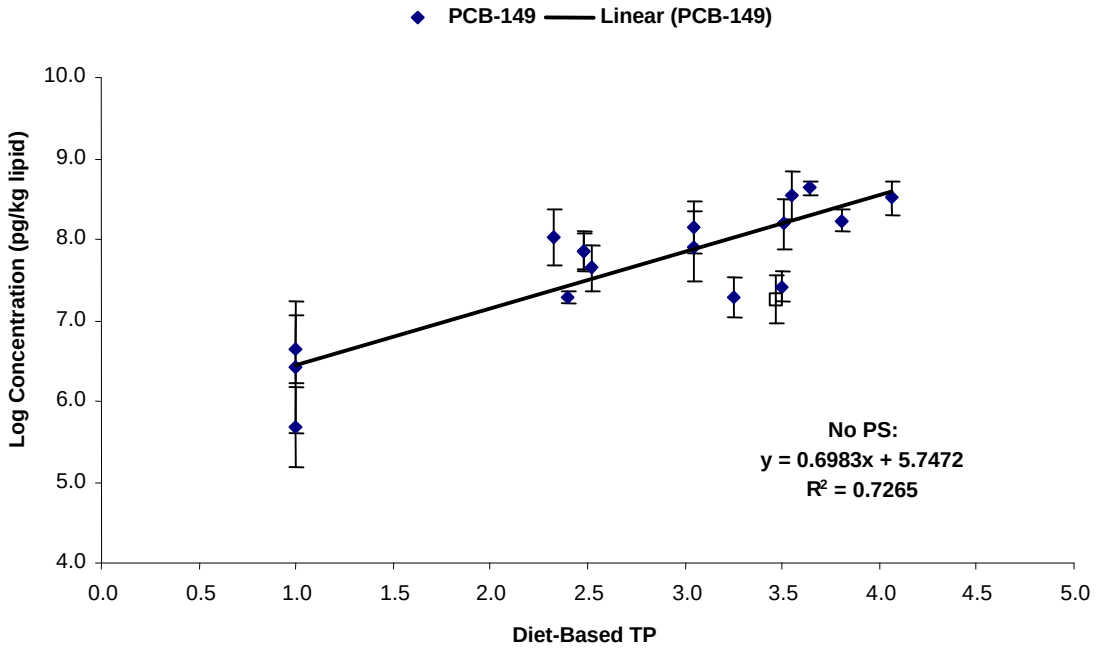

Figure 3-14. Logarithm of PCB-149 Concentration (pg/kg lipid) versus Diet-Based Trophic Position. Each point refers to one Organism. Purple seastars (PS; open square) were omitted from the regression. Solid regression line includes all remaining species. Error bars represent one standard deviation.

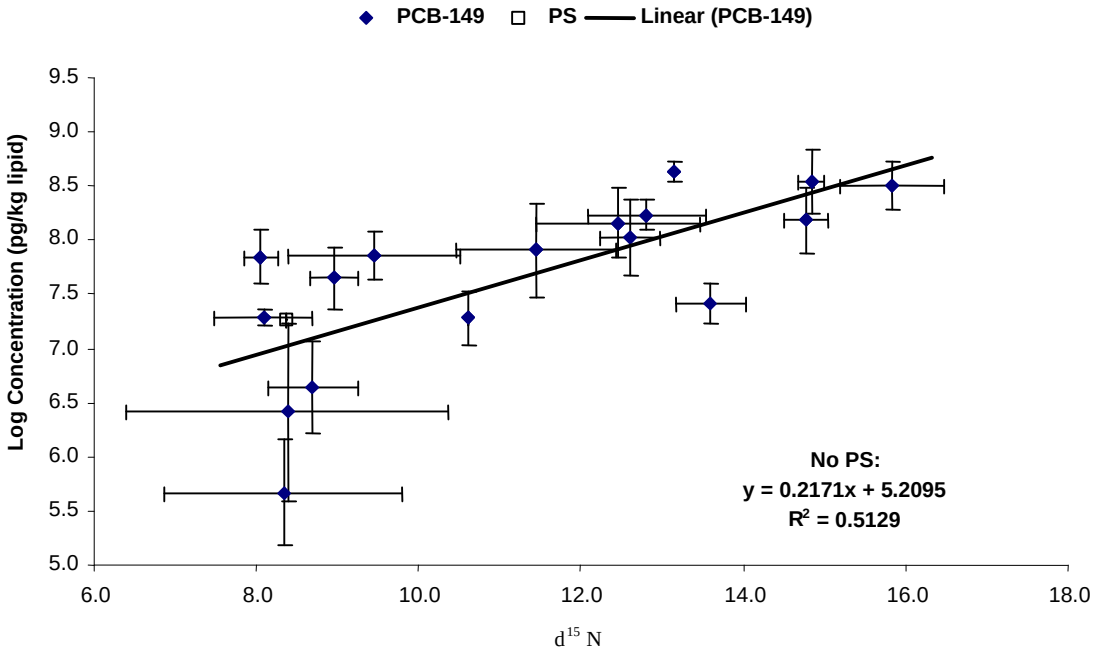

Figure 3-15. Logarithm of PCB-149 Concentration (pg/kg lipid) versus $d^{15}N$ (‰). Each point refers to one organism. Purple seastars (PS; open square) were omitted from the regressions. Solid regression line includes all remaining species. Error bars represent one standard deviation. Spiny dogfish liver $d^{15}N$ used in place of muscle $d^{15}N$ in regressions.

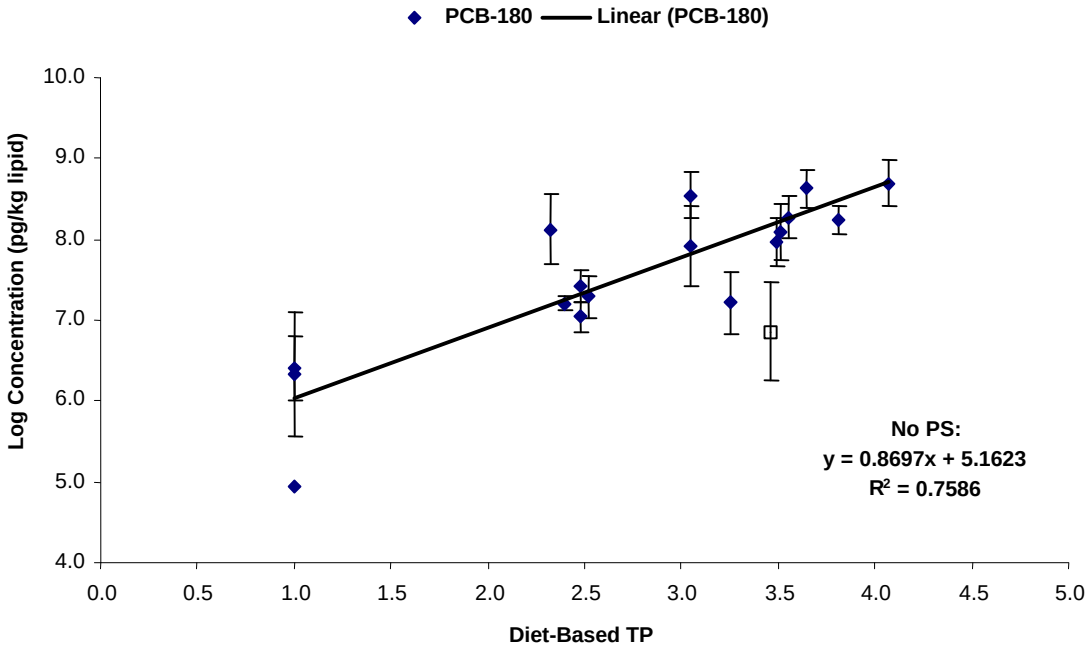

Figure 3-16. Logarithm of PCB-180 Concentration (pg/kg lipid) versus Diet-Based Trophic Position. Each point refers to one Organism. Purple seastars (PS; open square) were omitted from the regression. Solid regression line includes all remaining species. Error bars represent one standard deviation.

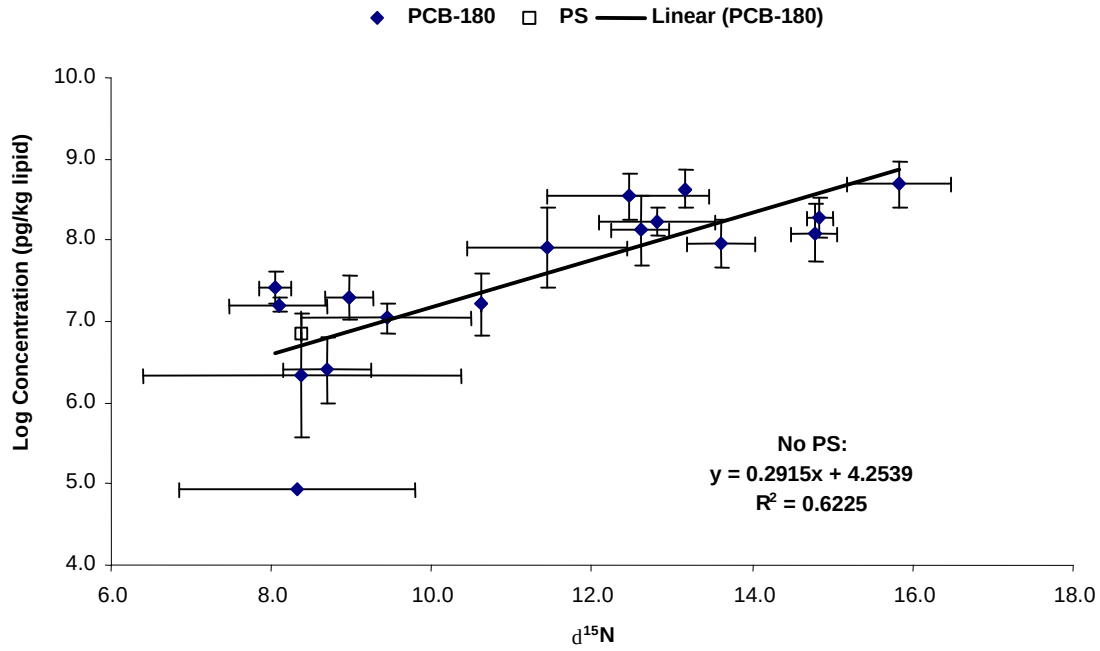

Figure 3-17. Logarithm of PCB-180 Concentration (pg/kg lipid) versus $d^{15}N$ (‰). Each point refers to one organism. Purple seastars (PS; open square) were omitted from the regressions. Solid regression line includes all remaining species. Error bars represent one standard deviation. Spiny dogfish liver $d^{15}N$ used in place of muscle $d^{15}N$ in regressions.

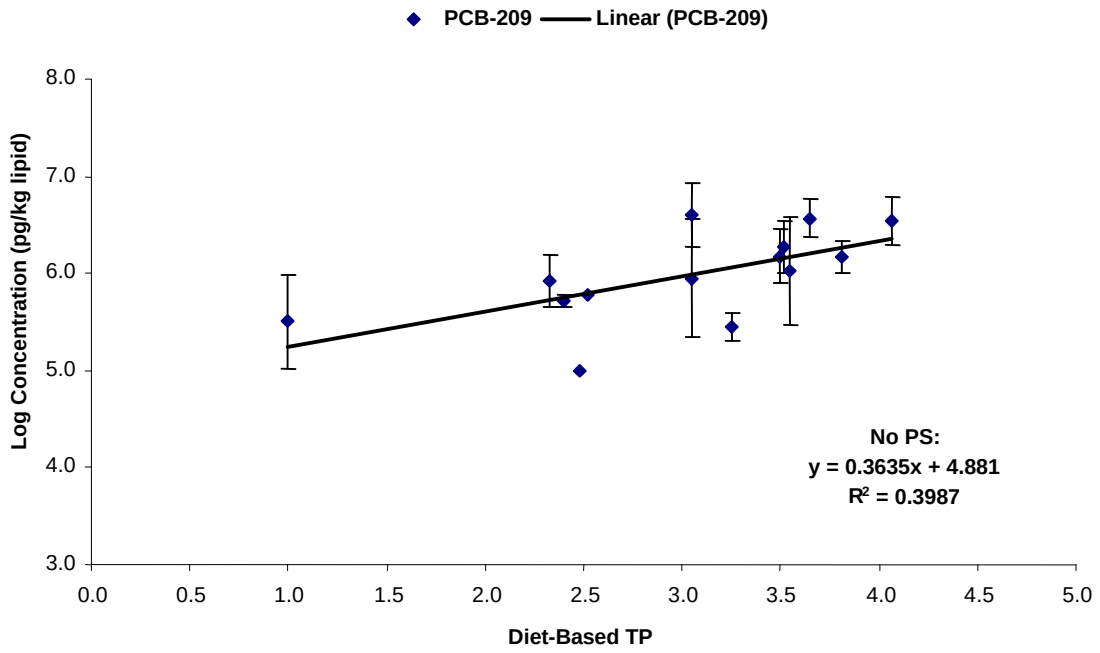

Figure 3-18. Logarithm of PCB-209 Concentration (pg/kg lipid) versus Diet-Based Trophic Position. Each point refers to one Organism. Purple seastars (PS; open square) were omitted from the regression. Solid regression line includes all remaining species. Error bars represent one standard deviation.

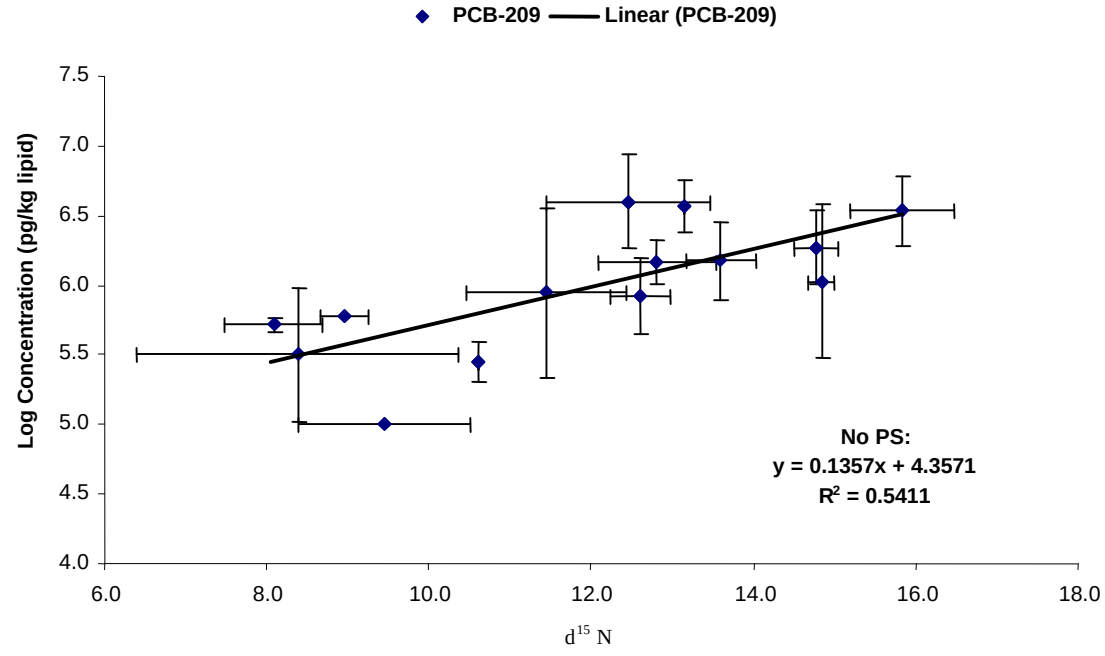

Figure 3-19. Logarithm of PCB-209 Concentration (pg/kg lipid) versus $d^{15}N$ (‰). Each point refers to one organism. Purple seastars (PS; open square) were omitted from the regressions. Solid regression line includes all remaining species. Error bars represent one standard deviation. Spiny dogfish liver $d^{15}N$ used in place of muscle $d^{15}N$ in regressions.

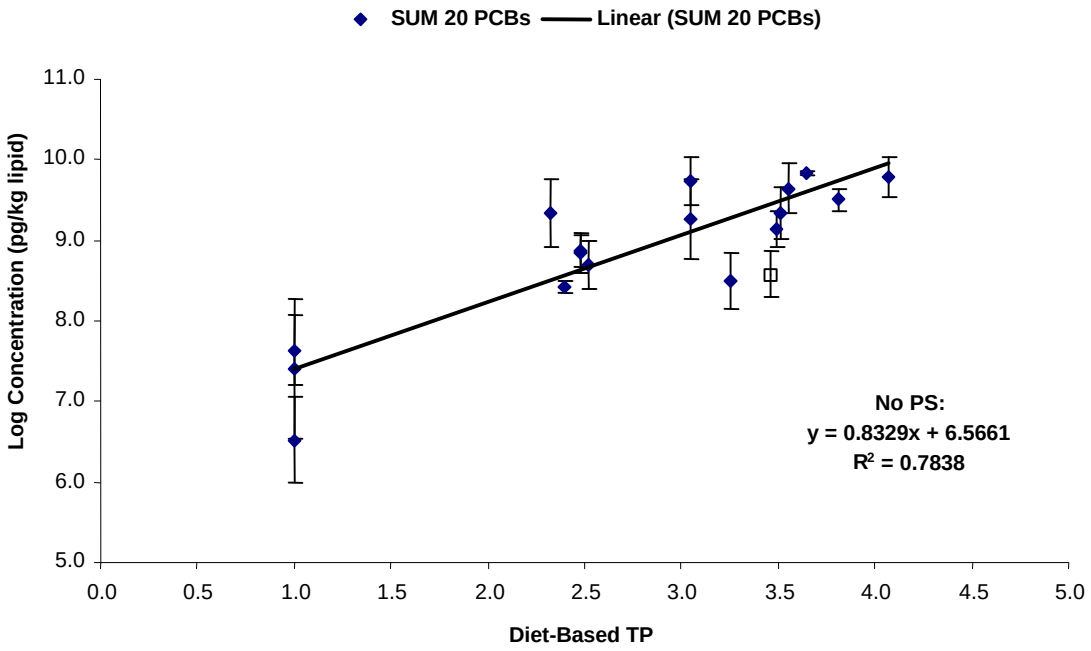

Figure 3-20. Logarithm of 'Sum 20 PCB' Concentration (pg/kg lipid) versus Diet-Based Trophic Position.
Each point refers to one Organism. Purple seastars (PS; open square) were omitted from the regression. Solid regression line includes all remaining species. Error bars represent one standard deviation.

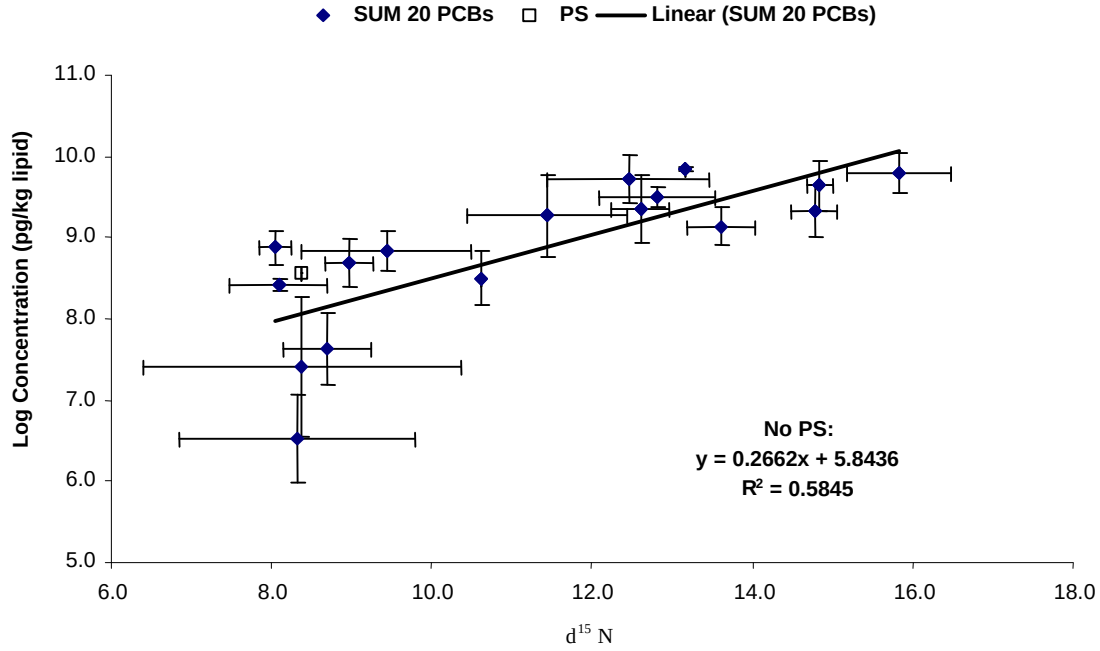

Figure 3-21. Logarithm of 'Sum 20 PCB' Concentration (pg/kg lipid) versus $d^{15}N$ (‰).
Each point refers to one organism. Purple seastars (PS; open square) were omitted from the regressions. Solid regression line includes all remaining species. Error bars represent one standard deviation. Spiny dogfish liver $d^{15}N$ used in place of muscle $d^{15}N$ in regressions.

Table 3-7. Summary of the Results for the Linear Regressions of the Log [PCB] as a Function of Trophic Position and $\delta^{15}N$. Data listed include the Y-Intercept, Slope, R^2, p, and FWMF for each PCB congener analyzed.

PCB Congener	Log K_{ow}[a]	Log [PCB] versus Diet-Based Trophic Position[b]						Log [PCB] versus $\delta^{15}N$[b]					
		n[c]	Y-Int.	Slope	R^2	p[d]	FWMF[e]	n	Y-Int.	Slope	R^2	p	FWMF[f]
18	5.46	10	5.8330	0.3666	0.4752	0.0274	2.3	10	6.0821	0.0750	0.3335	0.0804	1.8
16/32	5.49	13	6.0886	0.3068	0.5295	0.0048	2.0	13	5.7857	0.1026	0.4935	0.0074	2.2
52/73	6.08	17	6.2487	0.4908	0.4253	0.0046	3.1	16	5.4887	0.1969	0.6337	0.0002	4.7[g]
47/75/48	6.06	16	5.8834	0.4928	0.6749	0.0001	3.1	15	5.5042	0.1603	0.6142	0.0005	3.5[g]
101/90	6.64	17	5.7677	0.7478	0.6550	0.0001	5.6	16	4.9471	0.2616	0.5816	0.0006	7.8[g]
99	6.65	17	5.7491	0.7165	0.7430	<0.0001	5.2	17	4.9927	0.2409	0.6133	0.0002	6.6
110	6.74	17	5.8046	0.6882	0.5970	0.0003	4.9	16	5.0340	0.2442	0.5755	0.0007	6.8[g]
118	7.00	17	5.4704	0.8679	0.7557	<0.0001	7.4	17	4.7184	0.2773	0.5632	0.0005	8.8
149	6.95	17	5.7472	0.6983	0.7265	<0.0001	5.0	17	5.2095	0.2171	0.5129	0.0012	5.5
132/153	7.02	17	5.7267	0.8732	0.7711	<0.0001	7.5	17	4.9421	0.2814	0.5849	0.0003	9.1
138/160/163/164	7.22	17	5.7176	0.8634	0.7768	<0.0001	7.3	17	4.9212	0.2801	0.5970	0.0003	9.0
187/182	7.48	17	5.1216	0.8632	0.7360	<0.0001	7.3	17	4.3551	0.2774	0.5551	0.0006	8.8
177	7.38	16	5.2774	0.6616	0.7489	<0.0001	4.6	16	4.7691	0.2086	0.6293	0.0002	5.1
180	7.66	17	5.1623	0.8697	0.7586	<0.0001	7.4	17	4.2539	0.2915	0.6225	0.0002	9.8
200	7.52	16	5.3800	0.4103	0.5547	0.0009	2.6	16	4.7028	0.1609	0.7208	<0.0001	3.5
194	8.12	16	5.0438	0.6022	0.5431	0.0011	4.0	16	4.0247	0.2383	0.7190	<0.0001	6.5
203/196	7.97	16	5.1490	0.5956	0.5207	0.0016	3.9	16	4.1445	0.2354	0.6875	0.0001	6.3
206	8.43	16	4.9241	0.4704	0.4468	0.0046	3.0	16	3.9416	0.2024	0.6992	0.0001	4.9
208	8.05	13	4.9479	0.3414	0.4277	0.0153	2.2	13	4.3089	0.1387	0.6560	0.0008	3.0
209	8.53	14	4.8810	0.3635	0.3987	0.0154	2.3	14	4.3571	0.1357	0.5411	0.0027	2.9
Sum 20 PCBs	-	17	6.5661	0.8329	0.7838	0.0000	6.8	17	5.8436	0.2662	0.5845	0.0004	8.0

[a] Seawater-corrected log K_{ow}; [b] Purple seastars were omitted from all regressions; [c] n = number of species with detectable PCB concentrations;
[d] p = significance of slope greater than zero; [e] FWMF was calculated using Equation 22 (10^{slope}); [f] FWMF was calculated using Equation 23 ($10^{3.4 \times slope}$);
[g] Surf scoters omitted from regression.

3.4.3. Food Web Magnification Factors (FWMF)

FWMFs from this study were similar to previously reported values from other marine studies (Tables 3-7 and 3-8). FWMFs ranged from 2.0 (PCB-16/-32) to 7.5 (PCB-132/-153) for the log [PCB]-vs-TP correlation and from 1.8 (PCB-18) to 9.8 (PCB-180) for the log [PCB]-vs-$\delta^{15}N$ relationships (Table 3-7). For 'Sum 20 PCBs', FWMFs were 6.8 and 8.0 for the log [PCB]-vs-TP and the log [PCB]-vs-$\delta^{15}N$ regressions, respectively, which were higher than those reported for ΣPCBs by Hoekstra *et al.* (2003) and Fisk *et al.* (2001) (3.26 and 4.6, respectively), but more comparable to the value of 6.2 reported by Ruus *et al.* (2002). (Table 3-8). However, the use of ΣPCBs for reporting values (*e.g.,* FWMFs, concentrations, BAFs) may not be appropriate since individual congeners show much variation. In this case, FWMFs varied between congeners and, therefore, a comparison of FWMFs for ΣPCBs depends on the congeners that make up ΣPCBs.

In addition, comparison of FWMFs, in general, depends on the components of each food web. For example, Fisk *et al.* (2001) stated "FWMFs determined for food webs that include only zooplankton and fish tend to be lower than those that include seabirds and/or mammals". As support, Hop *et al.* (2002) found that FWMFs for ectotherms were lower than those for endotherms. Reasons for differences in FWMFs between endothermic and ectothermic food webs include (Fisk *et al.,* 2001; Hop *et al.,* 2002): (1) endotherms have higher energy requirements (and hence greater feeding rates); (2) endotherms have higher trophic positions; (3) endotherms have longer life-spans; (4) marine mammals and seabirds have negligible exchange of contaminants with seawater across respiratory surfaces; and, (5) endotherms have greater potential for

metabolism of contaminants. Therefore, a comparison of FWMFs between studies must take into account the components of each food web. From the studies reported in Table 3-8, the ectothermic food web from the Barents Sea in Hop *et al.* (2002) should be most comparable to the False Creek food web since the only endotherm in the False Creek food web was the surf scoter. False Creek FWMFs were generally 1 to 2 times greater than Barents Sea FWMFs. However, the Barents Sea ectothermic food web was comprised of only two fish, polar cod and Atlantic cod, (as well as, zooplankton, krill, a pelagic amphipod, an ice amphipod, and spider crabs), whereas the False Creek food web was comprised of seven fish. Thus, False Creek FWMFs may be greater than Barents Sea FWMFs because of the greater number of predatory and forage fish in the False Creek food web.

The use of FWMFs in identifying biomagnifying substances is limited then by the following points. First, the use of FWMFs is relatively new, making comparisons between studies somewhat limited. Broman *et al.* (1992) was the first to calculate similar factors [as far as this author knows], which they termed 'biomagnification power'. Since then, only a handful of studies have calculated FWMFs. Second, FMWFs can vary greatly depending on the composition of the food web. Food webs comprised of solely ectotherms have lower FWMFs than those including endotherms. Lastly, FWMFs require a contaminant to already be in the environment and so are not useful for predicting biomagnifiable substances.

An analysis of the relationship between FWMFs of individual congeners and their hydrophobicity (*i.e.*, log K_{ow}) for the log [PCB]-vs-TP and log [PCB]-vs-$\delta^{15}N$ relationships was performed and can be seen in Figures 3-22 and 3-23, respectively.

FWMFs increased with log K_{ow} and peaked at a seawater-corrected log K_{ow} of 7 to 7.6 and then declined above a log K_{ow} of 7.6. The figures suggest that biomagnification is greatest within the log K_{ow} range of 7 to 7.6. For both the log [PCB]-vs-TP and the log [PCB]-vs-$\delta^{15}N$ relationships, FWMFs, and therefore biomagnification, was greatest for PCBs 118, 132/153, 138/160/163/164, 187/182, and 180 (Figures 3-22 and 3-23, respectively). This supports previous observations in which the highest FWMFs or biomagnification factors (BMFs) or bioaccumulation factors (BAFs) were found to be highest for hexa-chlorinated (*i.e.,* PCBs 132/153 and 138/160/163/164) and hepta-chlorinated biphenyls (*e.g.,* PCBs 187/182, and 180) (Fisk *et al.,* 2001). The parabolic shape of the trendline in Figures 3-22 and 3-23 appeared to contradict observations from previous studies (Fisk *et al.*, 2001; Kidd *et al.,* 1998a) in that the relationship between FWMF and log K_{ow} was not linear. However, Fisk *et al.* (2001) only reported FWMFs for congeners with up to seven chlorines (PCBs 180 and 170/190 had the highest FWMFs) and Kidd *et al.* (1998a) based their conclusions on two PCBs (PCBs 52 and 153), whereas this study included FWMFs for higher chlorinated PCBs (PCBs 200, 194, 203/196, 206, 208, PCB-209). Interestingly, the parabolic curves from this study mirror those frequently reported for the relationship between log BCF and log K_{ow} (Bintein *et al.,* 1993; Meylan *et al.,* 1999; Crimmins *et al.,* 2002). Since the curvilinear relationship between log BAF and log K_{ow} has often been attributed to decreased bioavailability and/or increased time to reach equilibrium between water and lipids for super hydrophobic compounds (*i.e.,* log K_{ow} > 7.5), why would the same curvilinear relationship be observed between FWMFs (and BMFs) and log K_{ow} if, by definition, FWMFs and BMFs are independent of water concentrations? This question remains to

be investigated and this is critical for a more complete understanding of the processes of biomagnification and bioconcentration for chemicals with log K_{ow}'s greater than 4.

Table 3-8. Comparison of Food Web Magnification Factors (FWMFs) from This Study with those from Other Studies of Marine Food Webs[a].

PCB	Hop et al. (2002)[b]		Hoekstra et al. (2003)	Fisk et al. (2001)	Ruus et al. (2002)	Jarman et al. (1996)	This Study	
	Ectotherms	Endotherms					Log [PCB]-vs-TP	Log [PCB]-vs-$d^{15}N$
18							2.3	1.8
16/32							2.0	2.2
28	5.4	5.4	1.29	2.1				
31	3.5	3.5						
47	2.8	14.5						
47/48				2.5				
47/75/48							3.1	3.5
52			2.62					
52/73							3.1	4.7
56/60				2.4				
64				2.5				
74				6.2				
70/76				1.8				
95/66			3.75	2.2				
97				1.7				
99	3.1	28.4	5.94	7.5			5.2	6.6
101			3.89	3.6				
101/90							5.6	7.8
105	3.4	21.4	5.79	6.1				
110				2.5			4.9	6.8
118	3.9	26.2	3.77	5.1			7.4	8.8
128				6.9				
130/176				4				
138	3.7	27.8	4.72	8.8				

[a] LOCATION OF STUDIES: Hop *et al.* (2002): Barents Sea; Hoekstra *et al.* (2003): Beaufort-Chukchi Seas; Fisk *et al.* (2001): Northwater (NOW) Polynya in northern Baffin Bay; Ruus *et al.* (2002): Southeastern Norway; Jarman *et al.* (1996): Gulf of the Farallones.

[b] Hop *et al.* (2002) refer to ectotherms and endotherms as 'poikilotherms' and 'homeotherms', respectively.

Table 3-8 (Continued). Comparison of Food Web Magnification Factors (FWMFs) from This Study with those from Other Studies of Marine Food Webs[a].

PCB	Hop et al. (2002)[b]		Hoekstra et al. (2003)	Fisk et al. (2001)	Ruus et al. (2002)	Jarman et al. (1996)	This Study	
	Ectotherms	Endotherms					Log [PCB]-vs-TP	Log [PCB]-vs-$d^{15}N$
138/160/163/164							7.3	9.0
141				2.7				
149	3.4	14.3		2.3			5.0	5.5
153	4.1	26.3	6.69	9.7				
132/153							7.5	9.1
156				9				
158				7.4				
177							4.6	5.1
178				6.6				
170/190				10.1				
180			6.52	10.7			7.4	9.8
183				7.4				
187				7.3				
187/182							7.3	8.8
194							4.0	6.5
200							2.6	3.5
203/196							3.9	6.3
206							3.0	4.9
208							2.2	3.0
209							2.3	2.9
SUM PCB			**3.26**	**4.6**	**6.2**	**9.2**	**6.8**	**8.0**

[a] LOCATION OF STUDIES: Hop *et al.* (2002): Barents Sea; Hoekstra *et al.* (2003): Beaufort-Chukchi Seas; Fisk *et al.* (2001): Northwater (NOW) Polynya in northern Baffin Bay; Ruus *et al.* (2002): Southeastern Norway; Jarman *et al.* (1996): Gulf of the Farallones.

[b] Hop et al. (2002) refer to ectotherms and endotherms as 'poikilotherms' and 'homeotherms', respectively.

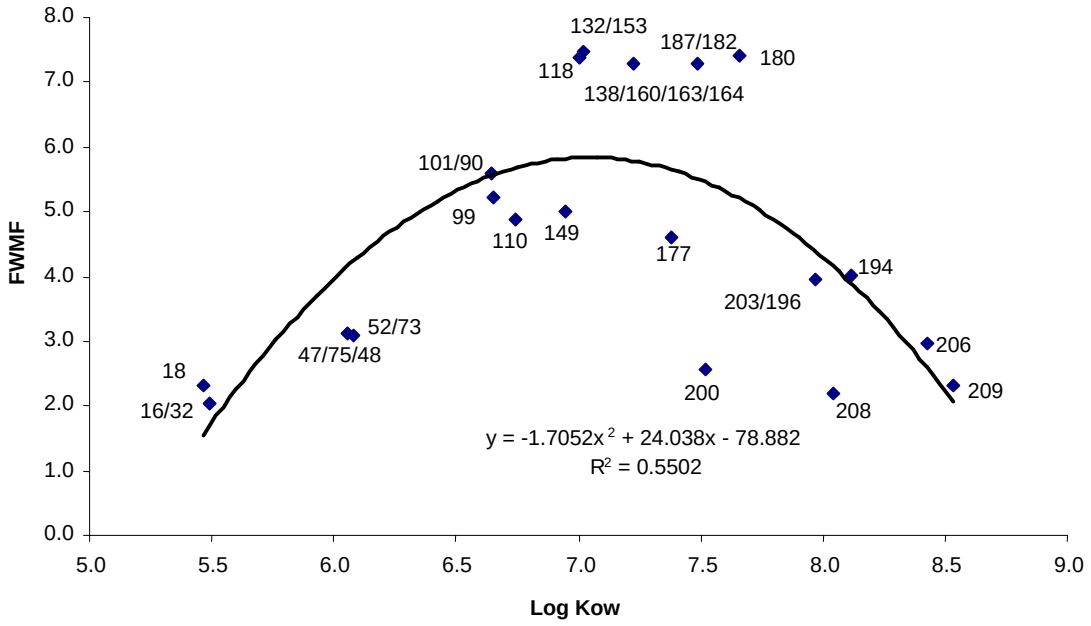

Figure 3-22. Relationship between FWMFs and the log Kow of each PCB congener. The FWMFs were Calculated from the Regression Line of Log PCB Concentration versus Diet-Based Trophic Position.
FWMFs were derived from regressions omitting the purple seastar.

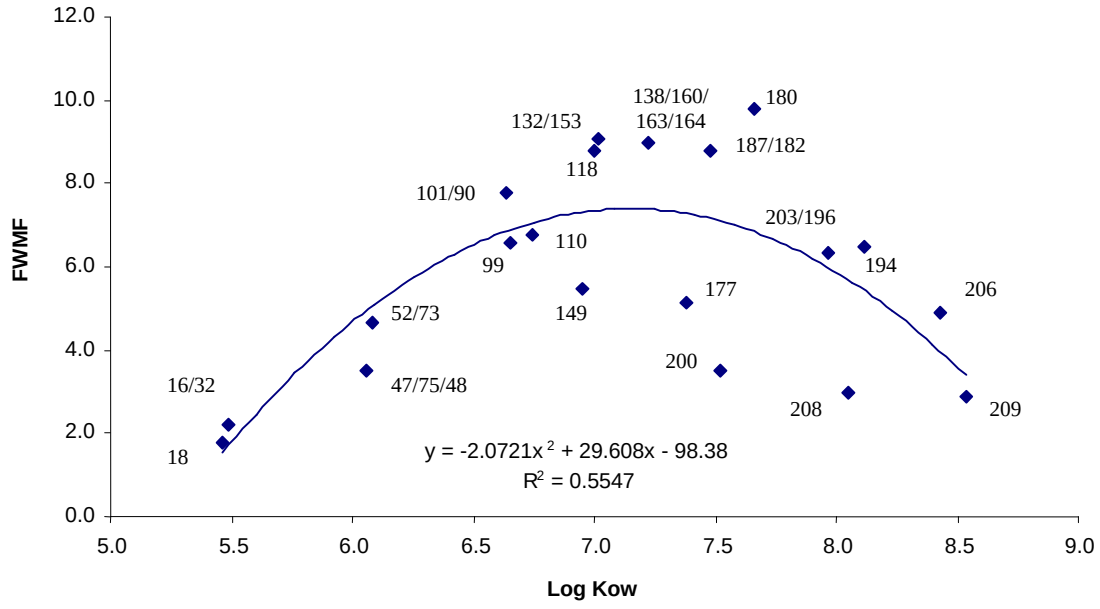

Figure 3-23. Relationship between FWMFs and the log Kow of each PCB congener. The FWMFs were Calculated from the Regression Line of Log PCB Concentration versus d^{15}N Ratio.
FWMFs were derived from regressions omitting the purple seastar. As well, FWMFs for PCBs 52/73, 47/75/48, 101/90, and 110 were derived from regressions that omitted surf scoters.

3.4.4. Biota-Sediment Accumulation Factors ($BSAF_L$)

Bioaccumulation has often been quantified using biota-sediment accumulation factors (BSAFs), which represent the ratio of the concentrations in an organism to that in sediment. BSAFs (and lipid-normalized, organic carbon-normalized $BSAF_L$s) are more practical since contaminant concentrations in sediment are easier to measure than freely-dissolved concentrations. BSAFs and $BSAF_L$s were calculated for each False Creek organism using the geometric means of biota and sediment concentrations and their logarithms (and standard deviations) are reported in Table H-1 in Appendix H. Figures 3-24 to 3-27 show the relationships between log $BSAF_L$ and seawater-corrected log K_{ow} for 17 marine organisms (surf scoters were excluded) and their comparison to predicted log $BSAF_L$s (see Section 2.6.6.8.). Observed mean log $BSAF_L$s were below the predicted lower limit log $BSAF_L$s over the full range of PCB K_{ow}'s for plankton and algae (Figure 3-24), bivalves (Figure 3-25), and purple seastars and forage fish (Figure 3-26). For small forage fish, striped seaperch, and pile perch (Figure 3-26) and for sculpin, crabs, sole, greenlings, and dogfish (Figure 3-27), observed mean log $BSAF_L$s were above the predicted lower limit for PCBs with seawater-corrected log K_{ow}'s ranging from 6 to 7.5, while PCBs outside of this range (*i.e.*, PCBs 18, 194, 203/196, 206, 208, and 209) were below the predicted lower limit. Thus, for PCB congeners with observed BSAFLs below the predicted lower limit, a degree of disequilibrium between the marine organism and sediment exists.

Biota-sediment disequilibrium was somewhat unexpected for the bivalves. Since geoduck and manila clams bury into sediment or mud (DFO, 2003b, 2003c) and pacific oysters live on firm mud, sand, gravel, or rocks (PSMFC, 2003), it was expected that

direct contact with sediment would result in $BSAF_L$s approaching predicted values. This result may be explained by several factors. Firstly, although some bivalves have been shown to possess mixed-function enzymes (Sole *et al.*, 1994), their capacity for biotransforming PCBs is generally considered insignificant compared to fish (Porte and Albaigés, 1993). The degree of disequilibrium may, therefore, be likely due to abiotic factors. A relatively sudden increase in PCB inputs to the sediment in False Creek (through perhaps increased storm runoff after a rainfall) could have increased concentrations above equilibrium levels. Such an increase would take time to be transferred to the bivalves, since uptake from sediment in bivalves is slow with steady-state achieved after 42 days through a first-order process (Boese *et al.*, 1997). Sediment concentrations may also be elevated in part due to organic carbon decomposition which is thought to increase the fugacity (and hence concentration) of settling particles with respect to water (Gobas and Maclean, 2003). Alternatively, the measured PCB concentrations in the sediment may have overestimated the fraction of chemical which is available for uptake by bivalves. PCB concentrations represent those from 'aged' sediments, which have been described as consisting of rapid-desorbing, slow-desorbing, and very-slowly-desorbing compartments (Cornelissen *et al.*, 1997) and which have been shown to decrease bioavailability of hydrophobic organic contaminants (Landrum, 1989). The true reason for the observed disequilibrium between sediment and benthos is likely due to a combination of the above factors.

For benthic fish and crabs (Figures 3-26 and 3-27), PCB levels were likely due to contact with contaminated sediment and ingestion of contaminated prey. As with the bivalves, some fraction of PCBs within the aged sediments was likely unavailable for

uptake by these species and so PCB levels within these organisms must have been due to ingestion of contaminated prey. For pelagic fish, observed $BSAF_L$s within predicted levels would indicate that PCB concentrations in equilibrium between biota and sediment. However, since contact with the sediment is not as pronounced as more benthic organisms, this apparent equilibrium must be an artifact of the biomagnification of PCBs in the predatory fish.

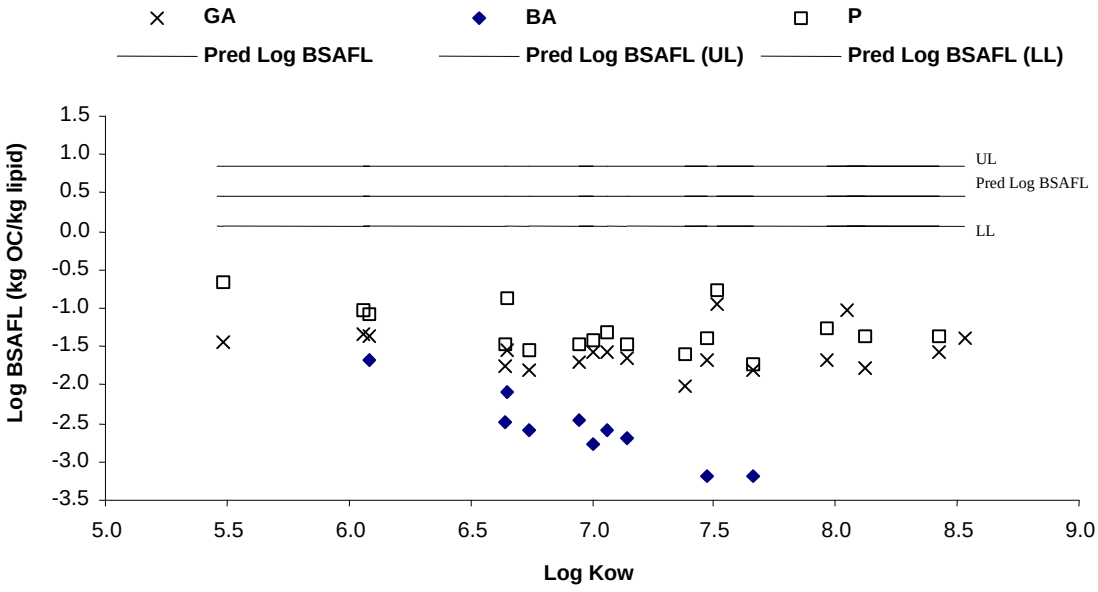

Figure 3-24. Observed Log $BSAF_L$ versus Log Kow for Green Algae (GA), Brown Algae (BA), and Plankton (P) and Predicted Log $BSAF_L$ (with Upper and Lower Limits).

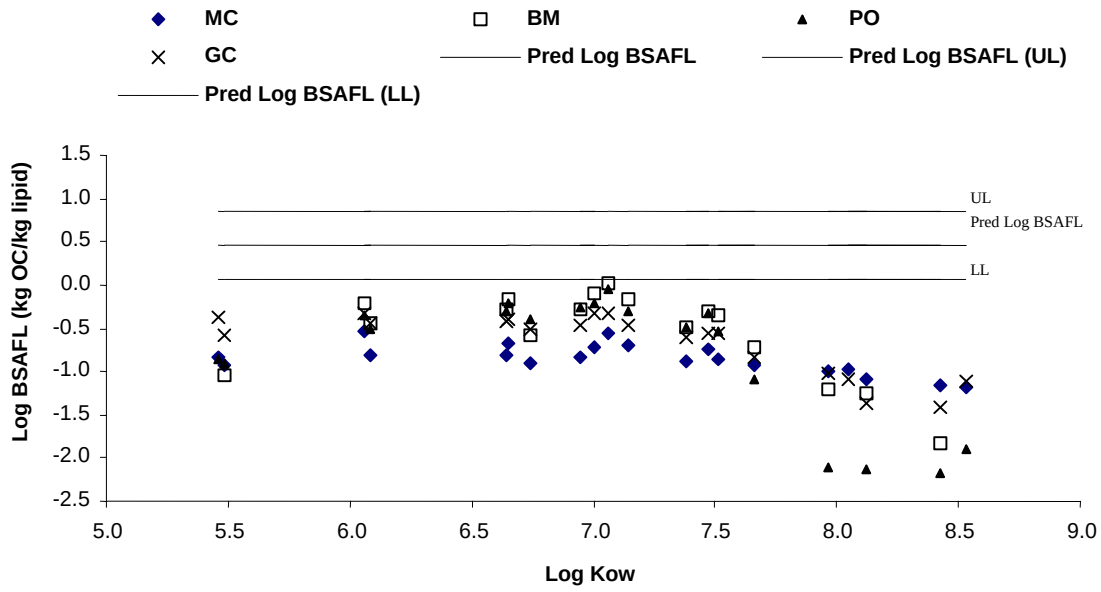

Figure 3-25. Log $BSAF_L$ versus Log Kow for Manila Clams (MC), Blue Mussels (BM), Pacific Oysters (PO), and Geoduck Clams (GC) and Predicted Log $BSAF_L$ (with Upper and Lower Limits).

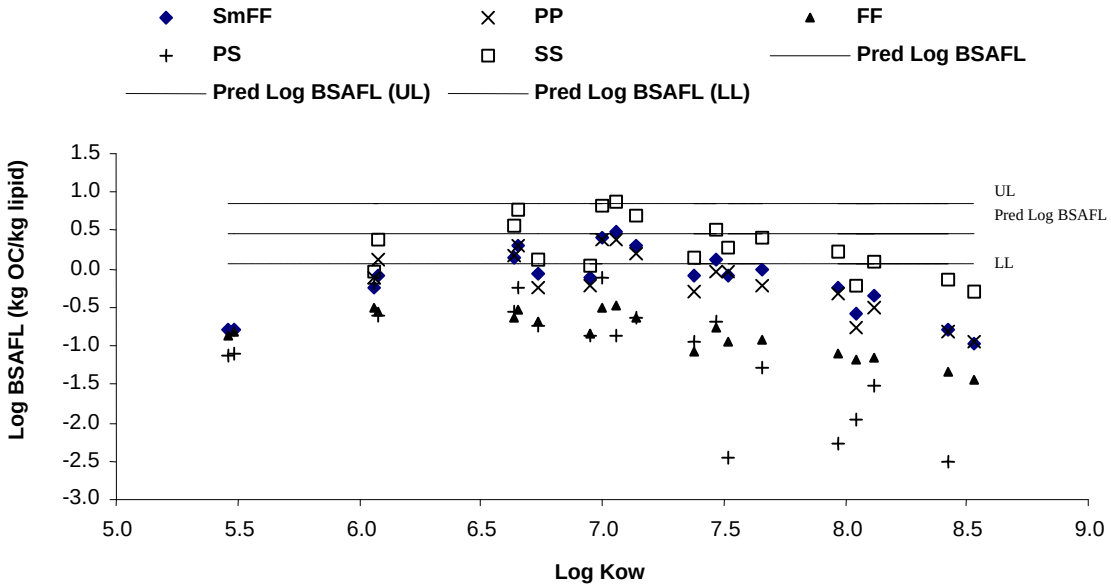

Figure 3-26. Log $BSAF_L$ versus Log Kow for Small Forage Fish (SmFF), Pile Perch (PP), Forage Fish (FF), Purple Seastar (PS), and Striped Seaperch (SS) and Predicted Log $BSAF_L$ (with Upper and Lower Limits).

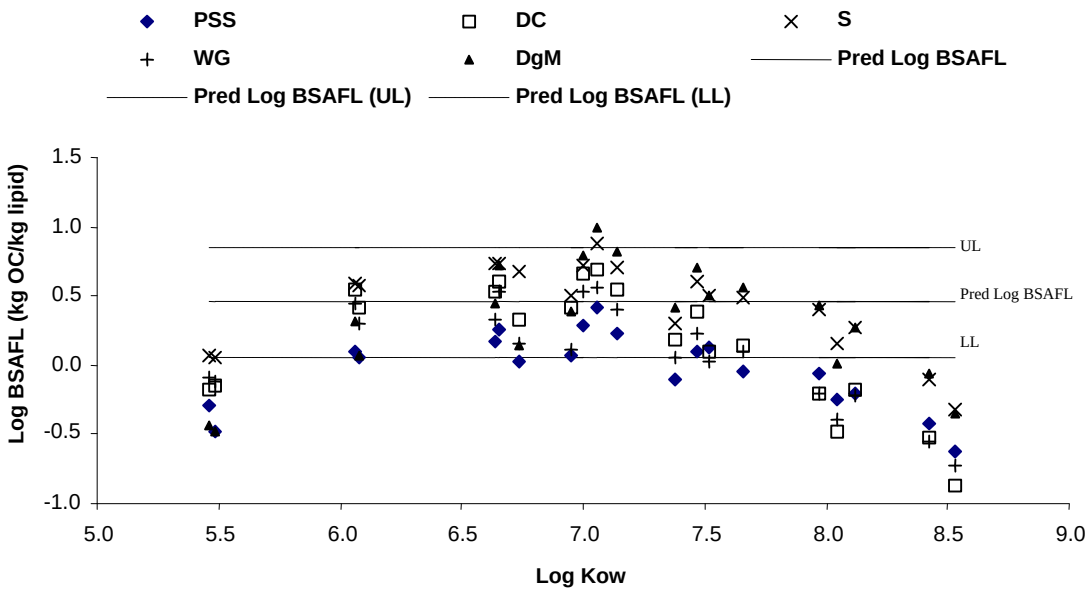

Figure 3-27. Log $BSAF_L$ versus Log Kow for Pacific Staghorn Sculpin (PSS), Dungeness Crab (DC), Sole (S), Whitespotted Greenling (WG), and Spiny Dogfish (DgM) and Predicted Log $BSAF_L$ (with Upper and Lower Limits).

3.4.5. Bioaccumulation Factors (BAF_L)

Lipid-normalized bioaccumulation factors (BAF_Ls) based on total water (BAFL-TOT), C_{18} (BAFL-C18) and model-estimated freely-dissolved concentrations (BAFL-FD) for eighteen marine organisms are reported in Table G-1 of Appendix G. In general, BAF_Ls were 1.4 to 1.7 orders of magnitude greater than wet weight BAFs (data not shown). No BAF_Ls could be calculated for highly chlorinated PCBs (*i.e.*, PCBs 200, 203/196, 206, 208, and 209) due to non-detectable water concentrations. For all species, BAFL-TOT and BAFL-C18 (Figure 3-28) showed a parabolic relationship with log K_{ow} which peaked at a log K_{ow} between 6.6 and 7.0. In general for BAFL-TOT and BAFL-C18, PCBs with intermediate-to-high hydrophobicities had log BAF_L's above predicted levels, while PCBs to either extreme of log K_{ow} had log BAF_Ls below predicted levels. BAFL-FD showed a more logarithmic relationship with log K_{ow} where BAF_L plateaued

above a log K_{ow} of 6.6 for all species (Figure 3-29). For BAFL-FD, log BAFL's were above predicted levels for all PCBs except PCB-18.

The parabolic relationship for BAFL-TOT-vs-Log K_{ow} and BAFL-C18-vs-Log K_{ow} has frequently been observed for bioconcentration factors (BCFs) (Bintein *et al.,* 1993; Meylan *et al.,* 1999; Crimmins *et al.,* 2002). In bioconcentration studies, the drop in BCF for chemicals with log K_{ow} greater than 7 has previously been attributed to a variety of factors, including "steric effects in membrane permeation, a large barrier in water diffusivity at the membrane/water interface, exceptionally long times to reach steady-state partitioning (via small depuration rate constants) or metabolism" (Crimmins *et al.,* 2002). For PCBs, metabolism is not a probable factor for the observed decline, since these super-hydrophobic PCB congeners are the most recalcitrant (James, 2001). However, the remaining factors could explain the observed parabolic relationship for BAFL-TOT-vs-Log K_{ow} and BAFL-C18-vs-Log K_{ow} in this study. For BAFL-FD, the familiar parabolic shape was absent because model predicted freely dissolved concentrations dropped exponentially with log K_{ow}. This suggests that the drop in BAF_L's for congeners with seawater-corrected log K_{ow}'s greater than 7 was due, at least in part, to overestimated freely-dissolved concentrations with increasing log K_{ow}. Above a log K_{ow} of 7, model predictions state that freely-dissolved concentrations decrease exponentially (see Figure 3-5 in Section 3.2.2.).

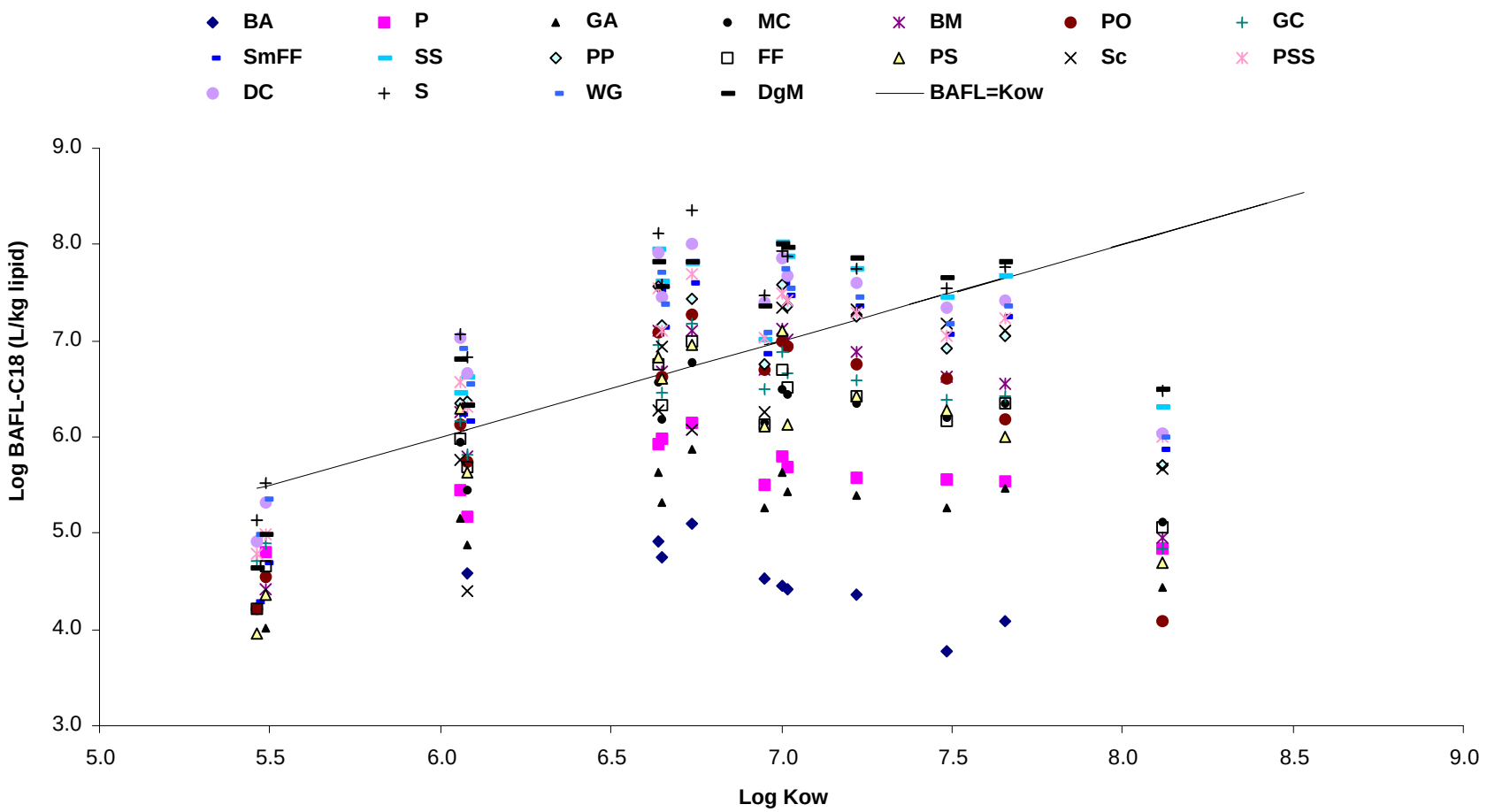

Figure 3-28. Logarithm of Lipid-Normalized Bioaccumulation Factors for 18 Marine Organisms Based on PCB Concentrations on C18 Extraction Disks (Log BAFL-C18) versus the Log Kow of 20 PCB Congeners/Coeluters. Solid line: Log BAFL = Log K_{ow}.
Abbrev.: Brown Algae (BA), Plankton (P), Green Algae (GA), Manila Clams (MC), Blue Mussels (BM), Pacific Oysters (PO), Geoduck Clams (GC), Small Forage Fish (SmFF), Striped Seaperch (SS), Pile Perch (PP), Forage Fish (FF), Purple Seastar (PS), Surf Scoter (Sc), Pacific Staghorn Sculpin (PSS), Dungeness Crab (DC), Sole (S), Whitespotted Greenling (WG), and Spiny Dogfish (DgM).

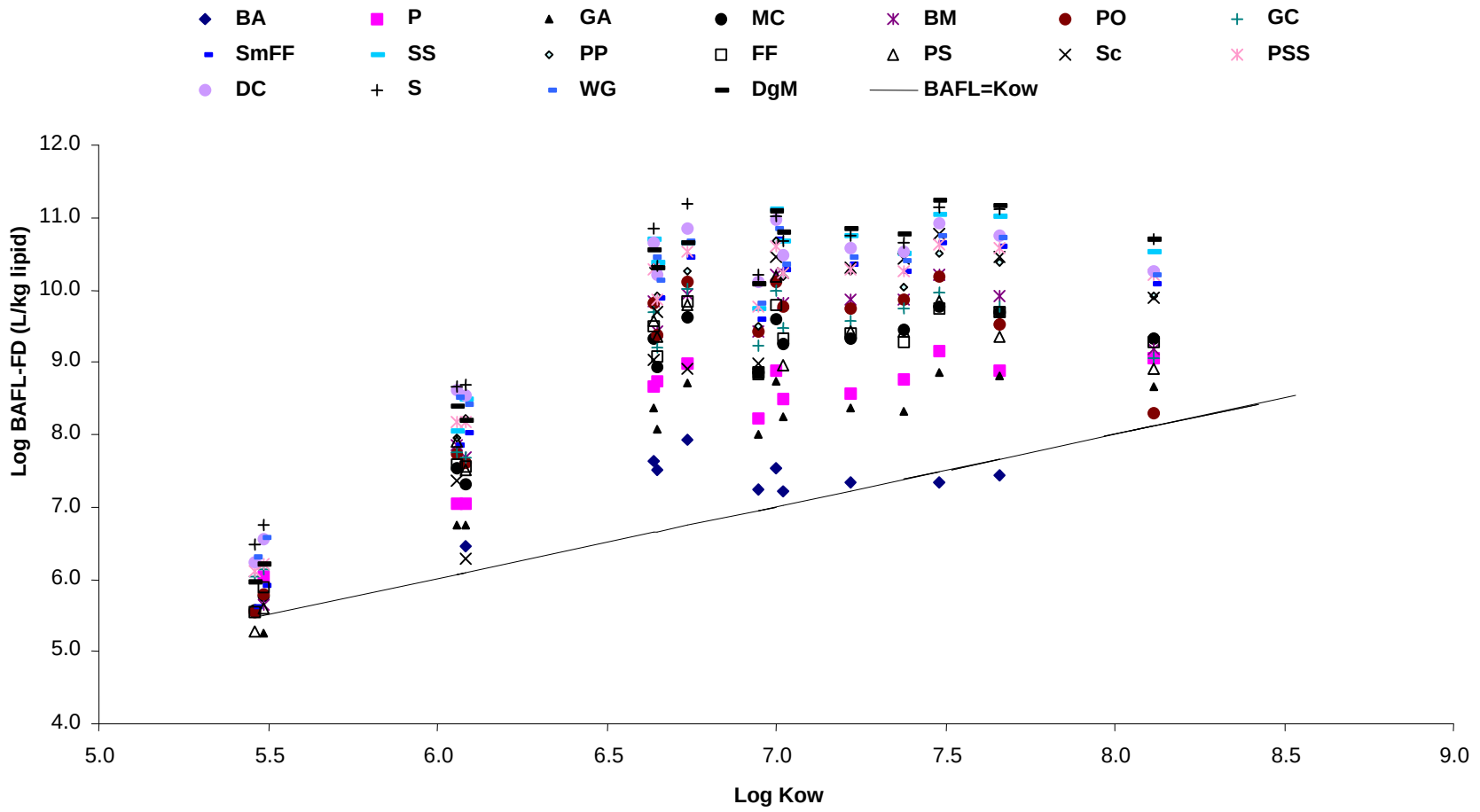

Figure 3-29. Logarithm of Lipid-Normalized Bioaccumulation Factors for 18 Marine Organisms Based on Model-Derived Freely-Dissolved PCB Concentrations (Log BAFL-FD) versus the Log Kow of 20 PCB Congeners/Coeluters. Solid line: Log BAFL = Log K_{ow}.
Abbrev.: Brown Algae (BA), Plankton (P), Green Algae (GA), Manila Clams (MC), Blue Mussels (BM), Pacific Oysters (PO), Geoduck Clams (GC), Small Forage Fish (SmFF), Striped Seaperch (SS), Pile Perch (PP), Forage Fish (FF), Purple Seastar (PS), Surf Scoter (Sc), Pacific Staghorn Sculpin (PSS), Dungeness Crab (DC), Sole (S), Whitespotted Greenling (WG), and Spiny Dogfish (DgM).

Figures 3-30 and 3-31 illustrate the difference between bioaccumulation factors calculated with total water, operationally-defined 'freely-dissolved' (*i.e.,* C_{18}), and model-derived freely-dissolved concentrations for green algae and spiny dogfish, respectively. In general, BAFL-C18 was 2 to 3 times greater than BAFL-TOT, which was expected since the C_{18} fractions of the total water concentrations were approximately 50% (Section 3.2.2). More notably, BAFL-FD were 1 to 4 orders of magnitude greater than BAFL-TOT. This demonstrates the potential for tremendous underestimation of bioaccumulation factors when based on total water concentrations. If total water concentrations are used, true BAFs are underestimated, since the truly bioavailable water concentration would be overestimated. The use of the operationally-defined dissolved concentrations (*i.e.,* C_{18} in this study) would be a better alternate for estimating true BAFs, although the truly bioavailable water concentration would still be overestimated given that the truly bioavailable fraction of chemical fraction is heavily influenced by the presence of dissolved organic matter and colloids. Thus, this emphasizes the need for developing a standard method for estimating operationally-defined freely-dissolved concentrations so that BAFs can be compared between studies. Perhaps, the use of ultrafiltration, which uses filters of consecutively smaller pore size (including pore sizes below 0.45 μm), could be used to provide a better measure of freely-dissolved concentrations and hence BAFs.

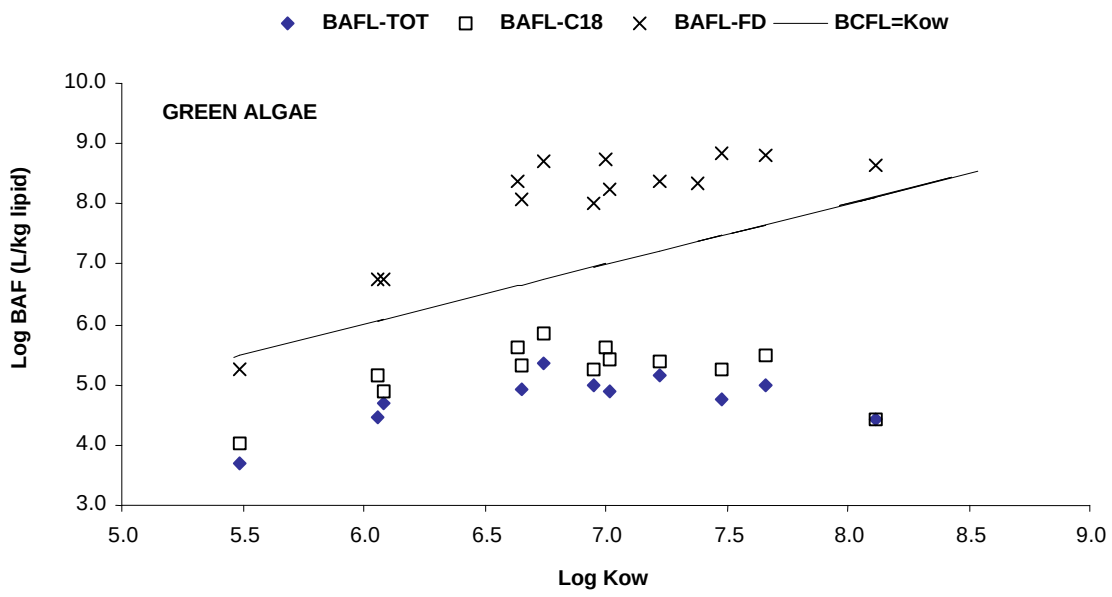

Figure 3-30. Observed Log BAFL-TOT, BAFL-C18, BAFL-FD, and Predicted Log BCF_L (L/kg lipid) versus Log K_{ow} for Green Algae.

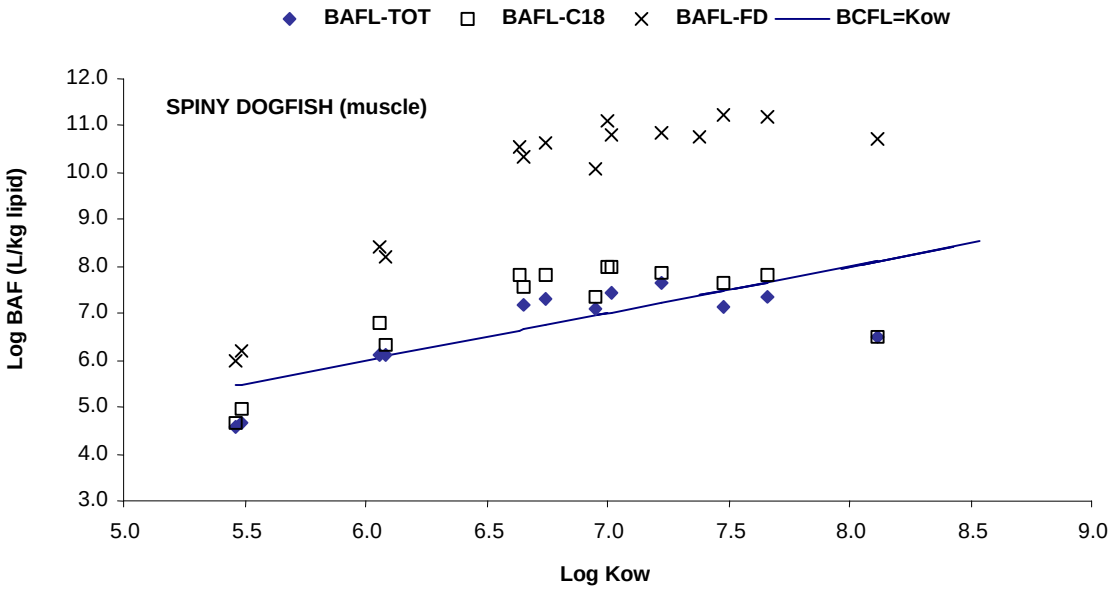

Figure 3-31. Observed Log BAFL-TOT, BAFL-C18, BAFL-FD, and Predicted Log BCF_L (L/kg lipid) versus Log K_{ow} for Spiny Dogfish.

A theoretical method for determining whether biomagnification is occurring is to compare observed BAF_Ls with predicted bioconcentration factors (BCF_Ls). Since predicted BCF_Ls are based on partitioning between lipids and seawater, the difference between observed BAF_Ls and predicted BCF_Ls provide evidence for dietary uptake or biomagnification when BAF_Ls are greater than BCF_Ls. In green algae (Figure 3-30), BAFL-TOT and BAFL-C18 were below predicted BCF_Ls over the whole range of log K_{ow}'s by up to 3.7 orders of magnitude. This implies that equilibrium between lipid and organic carbon compartments (or lipid-equivalents) in algal cells and seawater had not been reached. This may not be unexpected since green algae were sampled from the intertidal zone and were thus not always in contact with seawater. Assuming that green algae were in fact at equilibrium with seawater, observed BAFL-FD should not have been significantly different from predicted BCF_Ls. However, BAFL-FD was found to be greater than predicted BCF_Ls by up to 2 orders of magnitude for all congener/coeluters except PCB-16/32, suggesting biomagnification. This would imply that pinocytosis of nutrients, in combination with DOC-bound contaminants, contribute to the overall bioaccumulation of PCBs in algal cells. Alternatively, it is possible that model-derived freely dissolved concentrations were underestimated by 1 to 2 orders of magnitude. This discrepancy requires further testing to understand the processes involved in PCB bioaccumulation in algal cells and to validate the calculation of freely-dissolved concentrations using a three-phase aqueous model.

In spiny dogfish (Figure 3-31), as an example, evidence for biomagnification exists in that observed BAFL-TOT and BAFL-C18 for the penta- and hexa-chlorinated biphenyls (*i.e.*, PCBs 101/90, 99, 110, 118, 149, 132/153, and 160/163/164/138) were

above predicted BCF_Ls by up to 0.5 and 1 order of magnitude, respectively. The seawater-corrected log K_{ow} range of these chlorination classes, *i.e.,* between 6.0 and 7.5, are among the most bioaccumulative congeners (*e.g.,* Metcalfe and Metcalfe, 1997). BAFL-FD was found to be 0.5 to 4 orders of magnitude greater than predicted BCF_Ls. Therefore, the spiny dogfish provides evidence that dietary uptake is driving PCB concentrations in organisms above those achievable by water alone. Similar observations were noted for all fish, except forage fish.

3.4.6. FWMF versus BAF_L for Classifying Bioaccumulative Substances

According to the Canadian Environmental Protection Act (CEPA, 1999), substances are considered bioaccumulative if they have a wet weight BAF (or BCF) equal to or greater than 5000 or a lipid-normalized BAF equal to or greater than 100000 (log $BAF_L \geq 5$). In this study, this criteria would not be able to classify the bioaccumulative potential of PCBs 177, 200, 203/196, 206, 208, and 209, since water concentrations of these congeners were below MRLs. If one were to simply look at brown algae in this study, PCBs 18, 16/32, 47/75/48, and 194 would also not be classifiable with respect to bioaccumulative potential since these congeners were below MRLs in the organisms. For striped seaperch and pile perch, BAFs could not be calculated for PCBs 18 and 16/32 for the same reason. Thus, perhaps a better method for quantifying the bioaccumulative potential of ubiquitous contaminants, such as PCBs, would be to use FWMFs.

Figures 3-32 to 3-34 compare FWMF (from the linear regressions for log [PCB]-vs-TP) and log BAFL-TOT, for spiny dogfish muscle, spiny dogfish liver, and sole,

respectively[3], and their relationships to log K_{ow}. Observed log BAF_Ls were compared to the CEPA 1999 criteria for bioaccumulation (*i.e.*, log $BAF_L \geq 5$; dotted straight line), which also represents the line above which FWMFs indicate biomagnification. (Recall that FWMF is equal to 10^{slope}, so a slope of zero from the linear regressions results in a FWMF of 1 and indicates that bioconcentration is dominating the food web, with little or no biomagnification.) Figures 3-32 (spiny dogfish muscle) and 3-33 (spiny dogfish liver) show that observed log BAF_Ls for PCBs 18 (seawater log K_{ow} = 5.46) and 16/32 (seawater log K_{ow} = 5.49) were below the line, indicating little or no potential for bioaccumulation according to CEPA (1999), but above the line for FWMFs, indicating biomagnification of these congeners. Figure 3-34 shows that observed log BAF_Ls for sole were above the line for all congeners, indicating bioaccumulative potential according to CEPA (1999) and biomagnification according to FWMFs. Thus, these figures provide evidence that the CEPA (1999) criteria (log $BAF_L \geq 5$) could possibly designate chemicals as non-bioaccumulative, when they are indeed biomagnifying in the environment. In addition, designation of a chemical as bioaccumulative would depend on the species selected for the application of the CEPA (1999) criteria. Finally, this analysis suggests that FWMFs would be more inclusive in the designation of a chemical as 'biomagnifiable', since FWMFs do not depend on water concentrations, which are difficult to measure for superhydrophobic chemicals.

[3] Spiny dogfish were included in this analysis since they are the top predators of the False Creek food web. In addition, both muscle and liver BAF_Ls were compared to FWMFs, since lipid-normalized PCB concentrations in liver were significantly greater than those for muscle tissue and since liver tissue was significantly fattier than muscle tissue (66% vs. 8%, respectively). Sole was included in the analysis to provide an example of the analysis for another fish species.

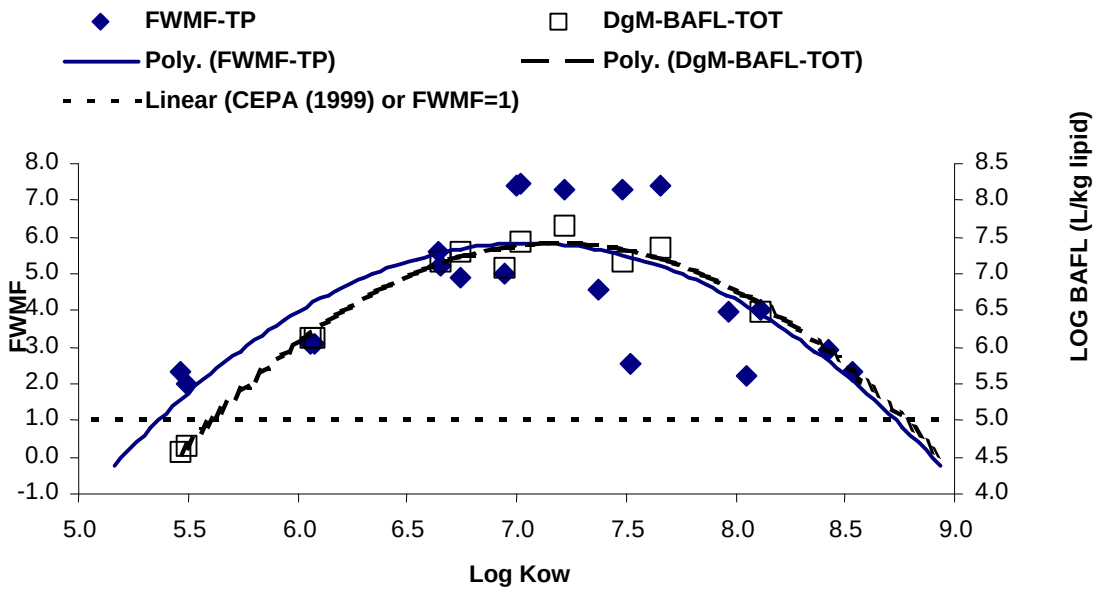

Figure 3-32. A Comparison of the Relationship between Food Web Magnification Factors (FWMF) and Log BAFL-TOT (for Spiny Dogfish Muscle) and Log Kow.
Log BAF_L values for spiny dogfish (open squares) are based on total water concentrations. FWMFs are from the Linear Regressions for Log [PCB]-vs-TP. Points above the dotted straight line indicate congeners that are bioaccumuating according to CEPA (1999) (*i.e.*, Log BAF_L > 5) and biomagnifying according to FWMFs (FWMF > 1).

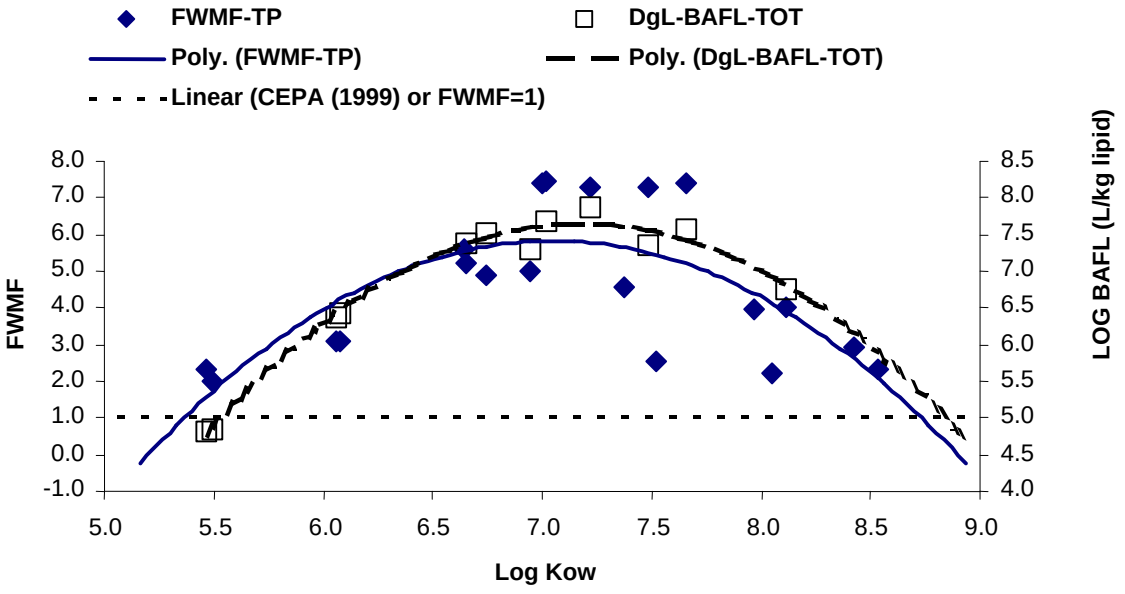

Figure 3-33. A Comparison of the Relationship between Food Web Magnification Factors (FWMF) and Log BAFL-TOT (for Spiny Dogfish Liver) and Log Kow.
Log BAF_L values for spiny dogfish (open squares) are based on total water concentrations. FWMFs are from the Linear Regressions for Log [PCB]-vs-TP. Points above the dotted straight line indicate congeners that are bioaccumuating according to CEPA (1999) (*i.e.*, Log BAF_L > 5) and biomagnifying according to FWMFs (FWMF > 1).

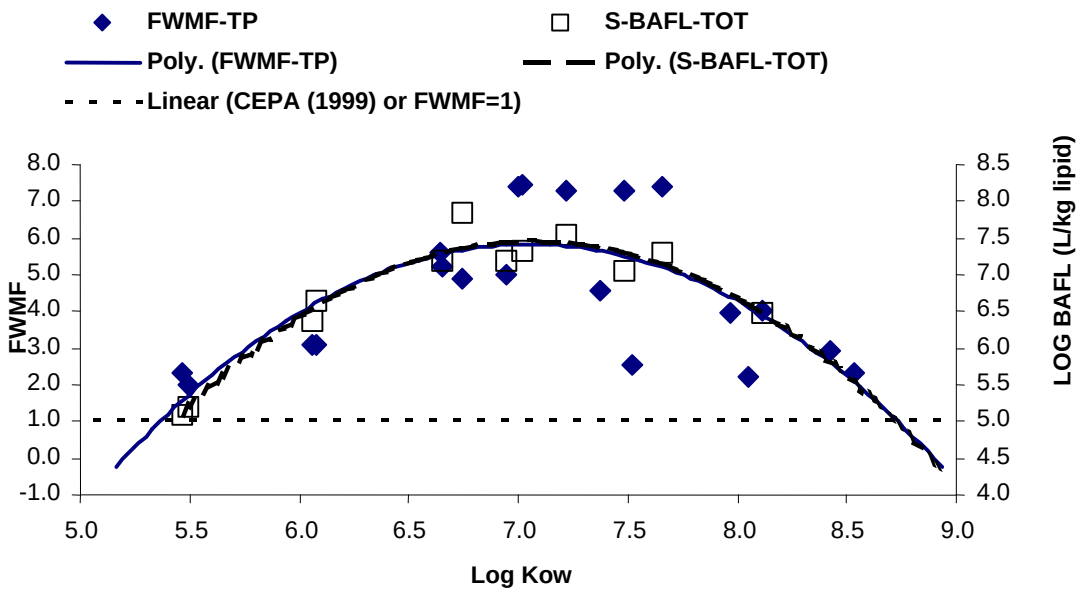

Figure 3-34. A Comparison of the Relationship between Food Web Magnification Factors (FWMF) and Log BAFL-TOT (for Sole) and Log Kow.
Log BAF_L values for sole (open squares) are based on total water concentrations. FWMFs are from the Linear Regressions for Log [PCB]-vs-TP. Points above the dotted straight line indicate congeners that are bioaccumuating according to CEPA (1999) (*i.e.*, Log BAF_L > 5) and biomagnifying according to FWMFs (FWMF > 1).

4. CONCLUSIONS

This study provided evidence for the biomagnification of polychlorinated biphenyls (PCBs) in a marine food web. Lipid-normalized PCB concentrations increased significantly ($p << 0.05$) with diet-based trophic position and with stable nitrogen isotope ratios for all PCB congeners with the exception of PCB-18 ($p > 0.05$). Food Web Magnification Factors (FWMFs) ranged from 2.03 (for PCB-16/32) to 7.47 (for PCB-132/153) and from 1.69 (for PCB-18) to 7.87 (for PCB-187/182) for the log [PCB]-vs-TP and log [PCB]-vs-$\delta^{15}N$ relationships, respectively. These FWMFs were slightly elevated compared to those reported for PCBs in studies of arctic marine food webs that also confirmed the occurrence of biomagnification.

The degree of biomagnification of each PCB congener depended on its lipophilicity (log K_{ow}). FWMFs showed a curvilinear relationship with log K_{ow}, where FWMFs were greatest for PCB congeners with seawater-corrected log K_{ow} between 7 and 7.7 (or freshwater log K_{ow} between 6.7 and 7.4). Thus, PCBs 118, 132/153, 160/163/164/138, 187/182, and 180 showed the greatest biomagnification.

Evidence for biomagnification was also obtained from comparisons between observed BAF_Ls and predicted BCF_Ls. In general, all fish except for the forage fish (*i.e.*, Pacific Herring, Surf Smelt, and Northern Anchovy) showed some degree of biomagnification for congeners with seawater-corrected log K_{ow} between 6.6 and 7 (PCBs 101/90, 99, 110, 118, and 132/153). For all fish, PCB-149 were found to have mean BAF_Ls in fish which were similar to, or less than, predicted BCF_Ls, suggesting

biotransformation. In bivalves, only PCBs 101/90 and 110 showed evidence of biomagnification.

Observed BAF_Ls showed a curvilinear relationship with log K_{ow}, providing evidence for differences in bioaccumulation between congeners. The decline in BAF_Ls for super-hydrophobic compounds (*i.e.,* seawater-corrected log K_{ow} > 7.5) could be a result of the same factors reported for the drop in BCFs for super-hydrophobic compounds: steric effects in membrane permeation, a large barrier in water diffusivity at the membrane/water interface, and exceptionally long times to reach steady-state partitioning (via small depuration rate constants).

Bioaccumulation factors varied considerably depending on the method of calculation. Although use of lipid-normalized (BAF_L), as opposed to wet weight, concentrations in biota significantly elevated bioaccumulation factors, the method of determining concentrations in water was also very important. BAF_Ls were found to vary by up to 3 orders of magnitude depending whether total water, operationally-defined freely-dissolved (*i.e.,* concentrations detected on the C_{18} filters), or model-derived freely-dissolved water concentrations were used in the calculations. This emphasizes the need for specifying the water concentration when reporting bioaccumulation factors, in order to be able to compare values across studies.

Biota-Sediment Accumulation Factors (log $BSAF_L$s) showed a similar relationship with log K_{ow} as BAF_Ls. $BSAF_L$s were greatest for PCBs with seawater-corrected log K_{ow} between 6.6 and 7.2 (*i.e.,* PCBs 101/90, 99, 110, 118, 149, 132/153, and 160/163/164/138). However, observed $BSAF_L$s were also found to be lower than

predicted for plankton, algae, and bivalves, suggesting a disequilibrium between sediment and these organisms.

The curvilinear relationship between FWMF and log K_{ow} was found to be similar to the relationship between BAF_L and log K_{ow}, making comparisons interesting. BAF_Ls could only be compared to the CEPA (1999) criterion for bioaccumulation (*i.e.,* $BAF_L > 10^5$), while FWMFs could be compared to the theoretical line for bioconcentration (*i.e.,* FWMF = 1). This analysis showed that there was the potential for misidentification of compounds as non-bioaccumulative based on the CEPA (1999) criteria, when FWMFs provided evidence of biomagnification. Thus, it is suggested that FWMFs are better suited for identifying biomagnifying substances rather than BAF_Ls.

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6. APPENDICES