BIOACCUMULATION OF PCBS FROM CONTAMINATED SEDIMENTS

IN A

COASTAL MARINE ECOSYSTEM

OF NORTHERN LABRADOR

by

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ABSTRACT

Marine sediments in Saglek Bay, Labrador, contain elevated levels of polychlorinated biphenyls (PCBs) as a result of terrestrial soil contamination at a former military radar station (LAB-2). Concurrent with cleanup of contaminated soil during 1997-1999, this study was conducted to examine the uptake and accumulation of PCBs in the local marine food web. PCB concentrations were examined in several possible receptors including marine invertebrates (bivalves and sea urchins), bottom-feeding fish (shorthorn sculpin, *Myoxocephalus scorpius*), arctic char (*Salvelinus alpinus*), ringed seal (*Phoca hispida*), great black-backed gulls (*Larus marinus*), and black guillemots (*Cepphus grylle*). The transfer of contaminants from sediments to the organisms of this food web is of critical significance because several of the top predators are important in the diets of Labrador Inuit.

Substantial PCB accumulation was discovered in benthic invertebrates, shorthorn sculpin, and black guillemots, indicating efficient transfer of PCBs from sediments to the benthic food web and to predators that feed at the top of this food web. Ringed seal appeared to have an increased concentration of PCBs relative to the other organochlorine contaminants, for which there is no significant local source. This result suggests that Saglek seal PCB burdens may have been affected in a subtle manner by the local sediment contamination. Arctic char were not susceptible to PCB accumulation from the sediment source. Relatively high PCB concentrations were discovered in great black-backed gulls, but similarly high levels in samples from a distant reference area implicate feeding habits as the causal factor.

Sediment-biota PCB transfer was analyzed in detail using shorthorn sculpin data. Although overall biota-sediment accumulation factors (BSAFs) were similar to those measured in temperate systems, low organic carbon content appeared to enhance bioavailability and the efficient transfer of PCBs to the benthic food web. Congener-specific accumulation patterns were complex but appeared to reflect predictable differences in PCB metabolism. The results demonstrate, for the first time, that the bioaccumulation of PCBs from sediments is a significant process affecting the PCB burdens of subarctic coastal marine wildlife.

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I. General Introduction

Polychlorinated biphenyls (PCBs) are industrial chemicals that have become environmental contaminants of concern. The basis for this concern is the persistent and bioaccumulative nature of PCBs, and their well-documented toxic effects on humans and wildlife (Safe 1994). PCBs were produced commercially for more than 40 years and used in large quantities in diverse industrial applications (Tanabe 1988). Restrictions on their production and use were put in place in North America between 1970 and 1980, but the rate of their reduction in the environment is slow, and today they can be detected in virtually every environmental matrix worldwide (Safe 1994; Muir et al. 1999).

PCB contamination is of particular concern in Canada's North, where relatively low-level inputs have resulted in surprisingly high contaminant burdens in marine fish, birds and mammals, some of which are significant in the diets of Inuit (Kinloch *et al.* 1992). PCBs entering northern marine systems are readily incorporated into food webs, and the high lipid content and long, linear structure of these food webs enhances the processes of bioaccumulation and biomagnification (Muir et al. 1997). It has also been suggested that northern food webs are more vulnerable to contaminants than their southern counterparts, as they have little built-in redundancy to buffer disturbances (Shearer and Murray 1997).

While there has been extensive study of top marine predators in the North, very little is known about contaminant levels in lower trophic level biota - especially the benthic community (Bright *et al.* 1995a,b; Landers *et al.* 1995; Muir *et al.* 1997;). Potential pathways of contaminant transfer between environmental compartments like sediments, lower trophic level organisms including benthos, and higher trophic level biota, have been the subject of little, if any, study. Outside the North, it is well documented that sediments serve as both a long-term reservoir for PCBs and a chronic source of contamination to a variety of aquatic species (Tanabe 1988). The factors that affect PCB bioaccumulation from sediments, such as bioavailability, mechanisms of uptake, and metabolism, have also received relatively little study in northern marine systems. These processes may be different in the North than in temperate systems because of differing environmental and biological conditions (Alexander 1995; Macdonald and Bewers 1996).

The present study was conducted to examine the bioaccumulation of PCBs from contaminated sediments in a coastal subarctic marine food web and investigate some of the factors that determine contaminant transfer in this system. These factors potentially include physical and chemical properties of the sediment and the contaminant, and biological or ecological properties of the coastal subarctic food web. The study was conducted in Saglek Bay, northern Labrador, where marine sediments contain elevated levels of PCBs as a result of terrestrial soil contamination at a former military radar station (LAB-2). The Saglek Bay food web, comprised of several benthic invertebrate species, bottom-feeding and pelagic fish, and higher trophic level biota such as seals and seabirds, was examined for evidence of PCB accumulation from the local contaminated sediments. These organisms differ in their trophic level, specific feeding habits, degree of association with sediment, and mobility; thus, their contaminant levels provide insight into the influence of these attributes on PCB accumulation. To investigate uptake and accumulation mechanisms specifically, the concentrations and congener composition of PCBs in shorthorn sculpin, a bottom-feeding fish, and associated sediment, were examined in detail. This analysis used bioaccumulation principles that have been applied in temperate systems to look for differences resulting from the unique physical and biological conditions of the North.

Specifically, the objectives of this thesis were:

I. To determine which components of the Saglek Bay coastal food web are vulnerable to the accumulation of PCBs from contaminated sediments, and to interpret this accumulation in light of the trophic position and specific ecology of organisms.

II. To examine, in detail, sediment-biota PCB transfer using a key indicator species, shorthorn sculpin, for evidence of differences in uptake and accumulation mechanisms, which may be due to the different conditions of the North.

To meet the first of these objectives, PCB concentrations were examined in marine sediments, benthic invertebrates, bottom-feeding fish (shorthorn sculpin, *Myoxocephalus scorpius*), arctic char (*Salvelinus alpinus*), ringed seal (*Phoca hispida*), great black-backed gulls (*Larus marinus*), and black guillemots (*Cepphus grylle*). Tissue PCB residues measured in Saglek Bay biota were compared to residues measured near Nain, Labrador, where there is no known local source of PCBs, and results documented elsewhere in the North, to determine whether they reflected uptake from the local contaminated sediments.

PCB concentrations were also examined in the context of other organochlorine contaminants, where this information was available. These results are discussed in Chapter III of this thesis.

To achieve the second thesis objective, a congener-specific analysis of the PCB residues in sculpin tissues and associated sediment was conducted. Sediment and organism properties that affect bioaccumulation in temperate areas were specifically examined to determine any differences present under northern ecological conditions. These results are presented in Chapter IV of this thesis. In summary, this thesis follows a manuscript format: the relevant literature is reviewed in Chapter II, Chapters III and IV present two manuscripts addressing the above objectives, and Chapter V is a general discussion of conclusions.

Studies to investigate the distribution of PCBs in Saglek Bay sediments and the nature and extent of food web contamination were conducted by the author and other members of the Environmental Sciences Group (ESG) in partnership with the Labrador Inuit Association (LIA), the Geological Survey of Canada Atlantic Region (GSCA), and the Canadian Wildlife Service (CWS). All parties contributed in different ways to sample collection and preparation. The author participated in all sampling, either directly or in a support role (e.g. zodiac operation). SCUBA diving was performed by Sid Pain and Brian Corbin of Nanuk Diving. The design of the biological sampling program and the corresponding analytical program was the responsibility of the author; J. Stow and C. Knowlton provided assistance. The sediment sampling and analytical program was designed and implemented jointly by C. Knowlton, J. Stow, S. Solomon and the author. A portion of the sediment data in this thesis will also be used in a thesis by C. Knowlton. Finally, all analysis and interpretation in this thesis was performed by the author, with the following exceptions:

I. PCB, pesticide, and lipid analysis (performed by Axys Analytical Services Ltd.)

II. Analysis of sediment organic carbon content (conducted by GSCA)

III. Determination of shorthorn sculpin and ringed seal ages (conducted by R. Ennis and I. Stirling, respectively)

IV. Production of a grid map of sediment PCB concentrations in Saglek Bay (conducted jointly by the author and S. Solomon, GSCA)

II. Literature Review

A. Properties of PCBs

PCBs are environmental contaminants of concern because of their persistence, lipophilicity, and toxicity, and their propensity, once released into the environment, to bioaccumulate. These properties also result in PCB biomagnification, a successive increase in concentration as they are passed up a food chain (Macdonald and Bewers 1996). The PCBs are a family of aromatic hydrocarbons that consist of 2 phenyl rings substituted with chlorine atoms at 1-10 positions (Hutzinger *et al.* 1974). The naming convention for these positions is illustrated in Figure II-1. Different patterns of chlorine substitution can theoretically create 209 individual compounds (or congeners) with unique physical, chemical and biological properties (Safe *et al.* 1987). Congeners are usually identified according to their International Union of Pure and Applied Chemistry (IUPAC) number, which ranges from 1 to 209 in order of increasing chlorine substitution.

PCBs were produced commercially beginning in 1929 as complex mixtures of 45 to 118 individual congeners (Safe *et al.* 1987). In North America, the common commercial preparations were Aroclors, which were manufactured by Monsanto; preparations included Aroclor 1221, 1242, 1254, and 1260, where the last two digits refer to the approximate percent chlorine content of the mixture. Commercial PCB mixtures were widely used in diverse industrial applications including coolants and insulating fluids in transformers and capacitors, lubricants, ink solvents, adhesives, and paints (Hutzinger *et al.* 1974).

Due to this widespread and unrestricted use, PCBs were detected in the environment as early as the 1960s (Tanabe 1988). PCBs continue to be detected today, both because of their chemical stability and persistence under ambient environmental conditions (Sawhney 1986), and because there are ongoing sources to the environment, such as open disposal areas (Tanabe 1988). Regulatory controls on the use and disposal of concentrated PCB mixtures were first introduced in North America in 1972 and were formalized by the Toxic Substances Control Act in the United States in 1976 and by the Canadian government's Chlorobiphenyls Regulations in 1977 (Cairns *et al.* 1986; Strachan 1988). PCBs have since been identified as Track 1 substances and slated for virtual elimination by Environment Canada (CCME

1999). Guidelines have been developed for use at contaminated sites to evaluate PCBs in water, soil, and sediments, but they are frequently exceeded in active industrial areas. For instance, several Lake Ontario harbours have sediment PCB levels that exceed the Canadian interim sediment quality guideline for freshwater sediments of 34.1 parts per billion (ppb) (CCME 1999).

Other physical-chemical properties that influence the behaviour of PCBs in the environment are vapour pressure and solubility. PCBs have low vapour pressures compared to other organic contaminants, and these decrease with the addition of each chlorine atom (Sawhney 1986). The solubility of PCBs in water is also low, but spans six orders of magnitude among congeners. As a result, an Aroclor 1260 mixture has an aqueous solubility of 3 ug/L, while Aroclor 1221 has a solubility of 3 500-15 000 ug/L (Mackay *et al.* 1992). Corresponding to their low aqueous solubility, PCBs are highly soluble in organic solvents such as lipids. The potential for PCBs to associate with lipids is often expressed by their octanol-water partition coefficients (K_{ow}) and an analogous coefficient (K_{oc}) has been calculated to describe organic carbon-water partitioning. Both partition coefficients increase with increasing chlorine content; for instance, log K_{ow} values range from 4.46 for congener 1 to 8.18 for congener 209 (Hawker and Connell 1988).

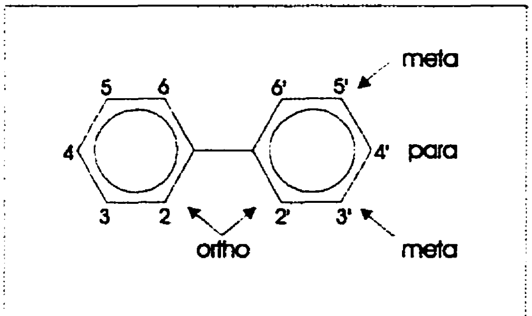

Figure II-1. PCB molecule indicating the ten possible sites of chlorine substitution and the *ortho*, *meta* and *para* positions.

The toxicity of PCBs is also related to their physical-chemical properties. Nevertheless, a congener-specific approach to toxicity studies has only been adopted relatively recently and there are still insufficient data to evaluate the health risks of each congener individually (Expert Panel 1994). Presently, toxicity studies tend to focus on the property of *ortho* substitution as the defining characteristic among PCBs. Non-ortho-substituted (Figure II-1) or 'coplanar' PCB congeners are approximate isostereomers of

2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and resemble this compound in their mode of action and toxic effects (Safe 1984, 1994; Expert Panel 1994). These compounds also tend to have the greatest potency among the PCBs for enzyme induction and possibly for toxic effects (Expert Panel 1994). Toxic Equivalency Factors (TEFs), which estimate the toxicity of a compound relative to 2,3,7,8-TCDD, have been developed for 12 non-*ortho* and mono-*ortho* substituted PCB congeners (van den Berg *et al.* 1998).

While these congener-specific approaches are starting to be widely used, the majority of toxicity studies conducted in the past decade have used PCB mixtures (Kamrin and Ringer 1996). In general, PCB mixtures have relatively little potential for acute toxicity (Safe 1984). Chronic PCB exposure is associated with sublethal effects, which are believed to be the result of alterations to enzyme systems important for normal homeostasis (Expert Panel 1994). Changes in the activity of these enzymes produce multiple secondary effects (e.g. endocrine disruption) which ultimately can bring about changes in body maintenance, immune system functioning, reproduction, growth, and development (Expert Panel 1994; Safe 1994).

A variety of different adverse effects have been associated with PCBs for different species. Mammalian toxicological studies generally conclude that PCBs are not significant mutagens, genotoxins, or carcinogenic inducers (Safe 1994). The most frequently observed effects among mammals relate to body condition (e.g. inhibition of body weight gain or weight loss) or to reproductive or immune system changes. Specifically, common toxic effects include: reduced spleen and thymus weights, pathological changes to reproductive organs, altered levels of circulating sex hormones, decreased fertility, and reduced offspring birth weights and survival (Golub *et al.* 1991; Expert Panel 1994; Kamrin and Ringer 1996). In birds, reproductive impairment is also the most sensitive endpoint, especially manifested as decreased egg hatching success or impaired hatchling health (with symptoms of 'chick edema disease'; Fox 1993; Hoffman *et al.* 1996). Liver porphyria, changes in thyroid function, and disrupted retinol homeostasis are also characteristic of bird PCB exposure (Fox 1993).

Less is known about the effects of PCBs on fish and invertebrate species (Niimi 1996a). In general, the early life stages of fish are believed to be most sensitive to the effects of PCBs, and decreased egg hatching and fry survival have both been observed (Niimi 1996a). Reduced reproductive success, especially as a reduced rate of fertilization, has been found in exposed invertebrates, along with long term reductions in growth and potentially reduced survival (Niimi 1996a).

B. PCB Contamination in Northern Canada

Although environmental PCB concentrations in the North are typically 10-50 times lower than in temperate systems (Macdonald and Bewers 1996), the presence of contaminants in this system is of particular concern. The North was long considered to be a pristine environment because of its remoteness and sparse population (Shearer and Murray 1997). However, over the last decade, PCBs have been detected in virtually every component of the northern environment including air (Stern *et al.* 1997), soil (Bright *et al.* 1995c); snow, and seawater (Bidleman *et al.* 1989). Surprisingly high concentrations have been measured in fish (Muir *et al.* 1988, 1992), birds (Braune *et al.* 1999), and marine mammals (Muir *et al.* 1992). The tissue burdens of beluga (*Delphinapterus leucas*) and polar bears (*Ursus maritimus*) for example, are frequently in excess of 2 ppm, which is the 'tolerable daily intake' Health Canada has identified for human consumers (Kinloch *et al.* 1992). Because many wildlife species are significant in the diets of Inuit, this contamination represents a critical pathway for the transfer of contaminants to humans (Kinloch *et al.* 1992). While the pathways of contaminant transfer are still not well-understood, it is generally assumed that the primary source of the widespread PCB contamination is long-range transport by air and water currents from multiple distant sources (Oehme 1991). These sources and inputs continue today because PCBs are still in use and/or are being released to the environment from former open disposal areas and contaminated sites (Tanabe 1988; Shearer and Murray 1997). While local sources are known to cause much more significant inputs in some areas of the North (e.g. Bright *et al.* 1995a,b), the overall significance of these sources has not yet been thoroughly evaluated.

Several authors have expressed concern that northern food chains may be more vulnerable to the accumulation and potential adverse effects of these contaminants than their southern counterparts (Muir *et al.* 1992, 1997; Shearer and Murray 1997). Many northern animals maintain a proportionately greater percentage of their body weight as lipids than southern animals do (Macdonald and Bewers 1996), and are therefore more susceptible to the bioaccumulation of lipophilic compounds like PCBs (Shaw and Connell 1986). If these animals undergo a period of starvation, PCBs that were effectively sequestered when fat reserves were high could be mobilized and become toxicologically significant (Muir *et al.* 1997). Several species in the North, including polar bears and seals, can experience large fluctuations in body weight because of the seasonality of productivity and food abundance (Smith 1987). Seasonally reduced productivity in northern marine systems also results in the tendency for poikilotherms (e.g fish) to be relatively slow growing and long lived, providing an opportunity for extensive bioaccumulation (Macdonald and Bewers 1996).

Various properties of food webs in the North tend to promote bioaccumulation and biomagnification, especially in the marine system. Organic carbon is very efficiently recycled, such that organic contaminants, which tend to follow carbon, will also be recycled efficiently (Macdonald and Bewers 1996). The relatively high proportion of lipids in biota results in more energy being transferred between trophic levels in the form of lipids, which facilitates the transfer of PCBs (Muir *et al.* 1997). Northern food webs are generally long and linear, leading to long-lived mammalian predators, which is reflected in high PCB biomagnification factors for these predators (Remmert 1980; Welch *et al.* 1992; Alexander 1995). The marine food web, in particular, has lower species diversity than counterparts in temperate areas or even Antarctica. For instance, eight species of zooplankton comprise 95% of the individuals in surface water communities in the Arctic Ocean but 1500 or more species have been identified throughout the rest of the world's oceans (Remmert 1980). It has been speculated that this lack of built-in redundancy could make the system less equipped to buffer human disturbances, and make the consequences of impacts to even one species relatively more severe (Muir *et al.* 1997). The role of benthos in northern marine food webs is poorly understood; there is some potential that they serve to some extent as a kind of 'buffer' to even out the seasonality of pelagic productivity (Alexander 1995). It is well documented that benthos have a greater relative role in northern marine systems than in temperate systems; for instance, benthic prey species and zooplankton contribute much more equally to the diets of predators in the North than in temperate areas (Petersen and Curtis 1980; Petersen 1989; Alexander 1995). The impact of this benthic food web role in terms of contaminant bioaccumulation potential has not yet been examined (Alexander 1995).

C. PCB Dynamics in Aquatic Systems

1. Physical Behaviour and Fate

Because of the lipophilicity and stability of PCBs, even low-level inputs to aquatic systems have the potential to result in greatly amplified concentrations in aquatic biota (Tanabe 1988). PCBs entering the aquatic system have a tendency to associate with organic-rich particulate material or living organisms (phytoplankton) in the water column (Knezovich *et al.* 1987). In most environments, the bulk of the compounds become adsorbed to suspended particulate matter rather than to phytoplankton because they provide the largest proportion of the available surface area (Jaffe 1991; Hargrave *et al.* 1992). The magnitude of this adsorption also depends upon the concentrations of particulates in the water column, the hydrophobicity of the specific PCB compounds, and the organic carbon content, shape, type, and size of the particulates (Knezovich *et al.* 1987). Once associated with suspended particles, PCBs can enter the food web directly via grazing organisms (Barrie *et al.* 1997), but primarily their transport and fate depends upon sediment transport and deposition processes (Lick 1997). These processes are unique to different environments, but they ultimately result in sedimentation (Bennett 1987; Eisenreich *et al.* 1989). Thus, the majority of PCBs introduced into the aquatic environment are eventually incorporated into sediments (Eisenreich *et al.* 1989).

2. Bioavailability

Because sediments are significant repositories for environmental contaminants, their role as a source of these contaminants to food webs has been relatively well studied. For benthic infauna, there are three possible pathways of contaminant exposure: direct contact with sediment, organic and inorganic sediment ingestion, and contact with interstitial or overlying water (Knezovich *et al.* 1987). Sorption describes the distribution of PCBs between sediment particles and interstitial or overlying water (Landrum and Robbins 1990). The underlying chemistry is still under investigation but is believed to be principally a partitioning process between the sediment organic carbon and aqueous phases (Knezovich *et al.* 1987; Jaffe 1991). Regardless of the specific sediment-water interactions, bioavailability is used as a general term to describe the fraction of the total sediment-associated contaminant (located in interstitial water or on sediment particles) that is available for bioaccumulation (Landrum and Robbins 1990). To date, the theory and chemical measures to predict bioavailability have not been identified, so researchers have evaluated it through a variety of different empirical approaches (Jaffe 1991).

Landrum and Robbins (1990) identified three general factors that interact to affect bioavailability: 1) the characteristics of the contaminant, 2) the characteristics of the sediment, and 3) the ecology and physiology of the organism. Lipophilicity, as represented by K_{ow}, is the most significant contaminant characteristic (Sawhney 1986). Positive K_{ow}-uptake relationships are expected and observed when interstitial or overlying water is the confirmed uptake pathway (Shaw and Connell 1986). However, negative K_{ow}-uptake relationships have been reported in two studies that exposed clams (*Macoma nasuta*) to contaminated sedments in the laboratory (Ferraro *et al.* 1991; Pruell *et al.* 1993) and in field studies of oligochaetes (primarily *Limnodrilus* sp., Ankley *et al.* 1992) and crustaceans (*Gammarus tigrinus*, *Asellus aquaticus* and *Orchestra carimana*, van der Oost *et al.* 1988). Boese *et al.* (1995), who considered a broader array of PCB congeners, found a different and more complex K_{ow}-uptake relationship with *Macoma nasuta*. In this study, congeners with five to seven chlorine atoms (log K_{ow} values 6-7) had greater bioavailability than either lower chlorinated congeners (having 3 or 4 chlorine atoms) or higher chlorinated congeners (having 8 or 9 chlorine atoms) (Boese *et al.*1995). This type of bioavailability pattern has been observed for other infaunal species as well (e.g. the polychaetes *Nereis virens* and *N. incisa*, the bivalves *Yoldia limatula* and *Mercenaria mercenaria*, and the grass shrimp *Palaemonetes pugio*; Lake *et al.* 1990; Pruell *et al.* 1993). To date, the reason for the low bioavailability of very hydrophobic PCBs is unknown (Boese *et al.* 1995). However, it is possible that these congeners are partitioned into fractions of organic carbon that are not readily assimilated, or that the structure of the congeners themselves impedes assimilation (Boese et al. 1995).

Bioavailability can also be affected by the arrangement of the chlorine atoms on the PCB molecule. Shaw and Connell (1984) suggested that non-*ortho* substitution patterns, which allow for a coplanar configuration, promote bioavailability, and developed 'steric effect coefficients' to account for this influence. Willman *et al.* (1997) was able to use these coefficients, along with K_{ow}, to explain observed PCB congener patterns, but the relationships only explained 45-55% of the PCB variability. The significance of this structure relationship is questionable considering evidence for the reduced bioavailability of coplanar congeners has been observed elsewhere (Bright *et al.* 1995b).

The key sediment characteristics that affect the bioavailability of PCBs are organic carbon content and, to a lesser degree, grain size distribution (Landrum and Robbins 1990). Bioavailability is expected to relate in an inverse manner to sediment total organic carbon content (TOC) because of the direct relationship between TOC and the sorption of PCBs by sediments (Knezovich *et al.* 1987; Landrum and Robbins 1990). Several studies have demonstrated this inverse relationship. Lynch and Johnson (1982) found enhanced uptake of a hexachlorobiphenyl (congener 153) by a benthic amphipod (*Gammarus pseudolimnaeus* Bousfield) when organic carbon was removed from sediments. A more minor particle size relationship was also present, such that congener 153 was less bioavailable from the silt-clay particle size fractions than from larger particle sizes (Lynch and Johnson 1982). Rubinstein *et al.* (1983) demonstrated an inverse bioavailability-TOC relationship among polychaetes (*Nereis virens*) in sediments with 6.1%-22.3% TOC. In some studies where no TOC-bioavailability relationships have been evident, authors have suggested that the TOC difference among the test sediments was too small (Oliver 1984).

The relationship between TOC and bioavailability is complicated by the strong tendency for covariance among TOC and sediment contaminant levels (Lake *et al.* 1990; Boese *et al.* 1995). This factor was generally not considered in earlier studies, but during recent years it has become a common practice to normalize sediment contaminant concentrations to sediment TOC (Lee 1992). Using these normalized concentrations, there is still evidence that bioavailability is limited in high organic carbon sediments relative to low organic carbon sediments (Lake *et al.* 1990; van der Oost *et al.* 1996; Means and McElroy 1997). For instance, Means and McElroy (1997) found consistent differences in bioavailability among sediments with varying organic carbon content using two invertebrate species (*Yoldia limatula* and *Nephtys incisa*) and two PCB congeners (IUPAC 47 and 153). Bioavailability also appeared to group according to low (0.7%-2.6%) and high (3.6%-5.2%) sediment TOC content in a study by Lake *et al.* (1990). Alternative explanations for these differential bioavailability results have also been suggested, including contaminant concentration effects, organism-related effects, and effects due to the nature of the organic carbon (Lee 1992; Lake *et al.* 1990; Boese *et al.* 1995). There has been some speculation, for instance, that anthropogenic carbon (e.g manufactured oils, sewage products) may have a higher binding capacity for contaminants than biogenic carbon (e.g. plant material) (Lake *et al.* 1990), or that it may be dominated by non-nutritive carbon (e.g. cellulose), which is selectively rejected or not assimilated by deposit-feeders (Boese *et al.* 1995).

With so many factors potentially affecting bioavailability, tissue PCB residues in benthic infauna are frequently predicted using the equilibrium partitioning model. This model assumes that PCBs obtain a thermodynamic equilibrium among the lipids of infaunal organisms, interstitial water, and sediment organic carbon (Di Toro *et al.* 1991; Lee 1992), so the model's predictions are independent of sediment type and organism exposure pathways. According to this theory, tissue PCB residues can be predicted from the partioning of the compound between organism lipids and sediment organic carbon. This ratio, called an accumulation factor or biota-sediment accumulation factor (BSAF), is calculated by:

$$BSAF = (C_t/L) / (C_s/TOC)$$

where C_t = tissue contaminant concentration (ng/g tissue), L = tissue lipid content (g/g), C_s = sediment contaminant concentration (ng/g sediment), and TOC = total organic carbon in sediment (g/g) (Lee 1992). If a contaminant has equal affinity for lipids and organic carbon, an equilibrium ratio of 1 is predicted. A theoretical BSAF value of 1.7 has been predicted based on the partitioning of neutral organic substances between carbon and lipids (Lee 1992). Thus, this value represents a maximum amount of contaminant uptake that can be explained by partitioning alone (Boese *et al.* 1995).

The success of this model at predicting BSAFs in field and laboratory studies has been mixed. For instance, while Means and McElroy (1997) found good agreement between predicted and observed BSAFs for *Nephtys incisa* and *Yoldia limatula*, Lake *et al.* (1990) found higher than predicted BSAFs in their study of these species. Lee (1992) reviewed multiple studies and concluded that BSAFs for the same species in the same experiment can differ by as much as a factor of four across different sediments. Among PCB congeners with different patterns of chlorine substitution it is not uncommon that BSAFs range from being less than one to exceeding 10 (e.g. van der Oost *et al.* 1988) or even 20 (e.g. Macdonald *et al.* 1993). Varying BSAFs with sediment contaminant level and TOC have also been observed (Lake *et al.* 1990; Means and McElroy 1995). Nevertheless, in comparison to bioaccumulation factors based on wet- or dry weight ratios, BSAFs are a much more reliable approach (Lee 1992). In fact, the equilibrium partitioning approach has been recommended as a tool for the development of sediment quality criteria (Di Toro *et al.* 1991).

3. Bioaccumulation

Bioaccumulation has been described as the net result of uptake and elimination; thus, PCBs are accumulated because uptake rates typically exceed elimination rates (Shaw and Connell 1986). Many field studies have demonstrated that PCBs from contaminated sediments are bioaccumulated; the phenomenon has been observed in the tissues of invertebrates (van der Oost *et al.* 1988; Lake *et al.* 1990), fish (Macdonald *et al.* 1993; van der Oost *et al.* 1996; Liang *et al.* 1999), and fish- or insect eating birds (Ankley *et al.* 1993; Bishop *et al.* 1995; Froese *et al.* 1998). These findings have been supported by laboratory studies on a variety of fish and invertebrate species (Ankley *et al.* 1992; Pruell *et al.* 1993; DiPinto and Coull 1997). Several factors appear to influence the degree of contaminant bioaccumulation in different species. Organism lipid content tends to be positively correlated with bioaccumulation (Pastor *et al.* 1996). Jorgensen *et al.* (1997) observed greater bioaccumulation of octachlorostyrene in fat arctic char (*Salvelinus alpinus*) than in lean arctic char; fat and lean fish were differentiated both by overall size and their levels of triacylglycerols. High levels of PCBs and DDTs in red mullet (*Mullus barbatus*), compared to sea mullet (*Mugil cephalus*) and sea bass (*Dicentrarchus labrax*), have also been attributed to the higher lipid content of that species (Pastor *et al.* 1996). Normalizing tissue contaminant burdens to lipid content has become a standard practice to help reduce this interspecific variability as well as intraspecific variability caused by fish reproductive status or seasonal lipid fluctuations (Pastor *et al.* 1996). Lipid content also tends to vary with trophic level; van der Oost *et al.* (1986) observed lipids increasing from 0.65% in plankton, to 1.74% in molluscs and 0.86% in crustaceans, to 14.9% in eels.

Attributes of different water bodies such as productivity, wave and current dynamics, and depth, may also influence bioaccumulation. Larsson *et al.* (1992) observed increased bioaccumulation in relatively unproductive lakes, which they attributed to lower sedimentation rates (i.e. fewer PCBs sorbed to particulates) and slower fish growth rates. Sediment-associated PCBs would be expected to be more bioavailable from a system with reduced organic carbon (Knezovich *et al.* 1987). However, the findings of Macdonald *et al.* (1993) are somewhat contradictory, in that PCBs appeared to be more bioavailable in shallow, more eutrophic lakes. These authors found a significant negative correlation between biota-sediment accumulation factors (BSAFs) and lake maximum depth (Macdonald *et al.* 1993). It is possible that resuspended sediments or benthic communities play a relatively larger role in the food webs of shallow lakes, thereby facilitating contaminant transfer from sediments (Macdonald *et al.* 1993).

Different feeding habits and food web linkages can create large differences in PCB bioaccumulation. BSAFs tend to be lower in filter-feeding benthic invertebrates than in either deposit-feeding or predatory species (Lee 1992). Bottom-feeding fish tend to accumulate PCBs to higher concentrations than primarily pelagic feeding species (Camanzo *et al.* 1987; Rowan and Rasmussen 1992; Pastor *et al.* 1996). DiPinto and Coull (1997) found that the act of 'grazing' contaminated sediments itself affected PCB bioaccumulation in bottom-feeding fish. Fish (*Leiostomus xanthurus*) accumulated five times the amount of PCB when they fed on copepods in contaminated sediments as opposed to uncontaminated sediments (DiPinto and Coull 1997). Relatively high PCB concentrations accumulated in insect- and fish eating birds have been attributed to their linkages to the benthic- or sediment-based food web (Froese *et al.* 1998). Bishop *et al.* (1995) measured greater bioaccumulation in red-winged blackbirds (*Agelaius phoeniceus*) than in tree swallows (*Tachycineta bicolor*) in the Akwesasne area of the St. Lawrence River, likely due to blackbirds feeding in a cattail marsh and tree swallows foraging in the open waters of the St. Lawrence River. Two species that are primarily piscivorous (Forster's tern, *Sterna forsteri* and common tern, *S. hirundo*) accumulated higher PCB (and dioxin and furan) concentrations than did either tree swallows or blackbirds (Ankley *et al.* 1993).

Trophic position frequently explains much observed variation in contaminant levels among biota, because of the potential for PCBs to biomagnify (Macdonald and Bewers 1996). The process of biomagnification is evident in the well-studied arctic cod (*Boreogadus saida*) – ringed seal (*Phoca hispida*) – polar bear (*Ursus maritimus*) food chain (Muir *et al.* 1988). Concentrations increase by a factor of 61-64 between arctic cod and ringed seal, and by a factor of approximately 7 between ringed seal and polar bears (Muir *et al.* 1997). A similar, but less dramatic, pattern has been observed in more southerly locations. For instance, an approximately threefold increase in PCB concentrations occurs between zooplankton and prey fish (various species) in the Lake St. Clair food web, and a subsequent four- to fivefold increase between prey fish and predators (Haffner *et al.* 1994). Biomagnification, however, does not explain all species differences, as high concentrations were observed in carp (*Cyprinus carpio*), a direct sediment feeder. Higher contaminant concentrations were measured in only one predatory fish, gar pike (*Lepidosteus osseus*), a specialized piscivore (Haffner *et al.* 1994).

Evidently, there are multiple mechanisms involved in the bioaccumulation of PCBs by higher trophic level biota. These mechanisms can include direct uptake from water across gills or epidermis (bioconcentration), direct contact with sediment, and consumption of contaminated food (or sediment) (van der Oost *et al.* 1996). Models of bioaccumulation include some or all of these uptake pathways (Lee 1992). For instance, bioaccumulation in fish has been described as primarily a bioconcentration process using a first-order model, PCB concentrations in tissue and water, and independent uptake and elimination rate constants (Lee 1992). Bioenergetics models add additional detail such as physiological attributes of fish (metabolic rates and growth), feeding rates, and dietary assimilation efficiencies (Lee 1992). Norstrom *et al.* (1976) modelled PCB accumulation in yellow perch (*Perca flavescens*) in the Ottawa River in this manner. Uptake from food was based on prey species' PCB concentrations, metabolic rate- and growth rate-based calorie requirements, as well as the assimilation efficiency of PCBs from diet. Bioconcentration was based on water PCB concentrations, uptake efficiencies from water, and the gill ventilation rates required for respiration (Norstrom *et al.* 1976).

Alternatives to these kinetic approaches are steady-state food web-type models, which assume that contaminant concentrations in biota are unchanging (Morrison *et al.* 1997). Morrison *et al.* (1997) developed this type of model for PCBs in Lake Erie, where relatively detailed information is available about predator-prey relationships. The model includes terms for both water and food uptake and arranges the food uptake term such that it can include multiple prey organisms with different contaminant concentrations. Bioaccumulation predictions for yellow perch, for instance, use diet composition estimates of: 50% zooplankton, 35% zebra mussels, 1% caddisfly larvae, 4% *Gammarus* amphipods, and 5% young-of-year fish, and corresponding contaminant levels for each of these prey species (Morrison *et al.* 1997). While this specificity is a strength of the model it is also the key shortfall; for the majority of aquatic systems, the necessary information concerning predator diets and prey species' contaminant levels is not available (Lee 1992).

In fact, the most common techniques in current use to predict or assess bioaccumulation in higher trophic level biota are empirical ratios between PCB concentrations in different environmental matrices (e.g. Bishop *et al.* 1995; Metcalfe and Metcalfe 1997; Froese *et al.* 1998; Liang *et al.* 1999). BSAFs, calculated in the same manner as they are for benthic invertebrates, are typically used in situations with contaminated sediment. The results of several studies support the use of BSAFs for predicting PCB bioaccumulation in benthically-linked higher trophic level species (Tracey and Hansen 1996; Froese *et al.* 1998). In particular for bottom-feeding fish, researchers have reported remarkably consistent BSAFs across a wide range of species and environments. Ankley *et al.* (1992) documented an average BSAF of 1.91 ± 1.44 (mean ± SD) for black bullhead (*Ameiurus melas*) from six sites in Green Bay, Lake Michigan. More variability was found when BSAFs for bluntnose minnow (*Pimephales notatus* Rafinesque) were compared across six separate freshwater lakes, but the BSAFs grouped into two sets according to lake-depth (Macdonald *et al.* 1993). Considering shallow and deep lakes separately, there was relatively little variability in BSAF values (13.2 and 13.8 in two shallow eutrophic lakes; 1.6-4.3 in four deep lakes). Macdonald *et al.* (1993) suggested several possible reasons for this difference, including greater sediment-water interaction in shallow lakes or possibly a greater role for benthos.

Similar BSAFs have also been reported for several marine species. BSAFs for grey mullet (*Mugil cephalus*) and tilapia (*Oreochromis mossambicus*) were estimated at 1.10-2.37 in a contaminated coastal wetland in Hong Kong. Maruya and Lee (1998) observed slightly higher BSAFs in mullet at a tidal creek site contaminated with Aroclor 1268, an extremely hydrophobic PCB mixture (3.1 ± 1.9, mean ● SD). Sea trout (*Cynoscion nebulosus*), which are an opportunistic rather than benthic feeding species, had an average BSAF value of 0.81 ± 0.47 at this site (Maruya and Lee 1998). Tracey and Hansen (1996) reviewed several other marine and freshwater studies (including unpublished results from environmental monitoring and assessment programs) and identified 10 species they considered 'benthically-coupled'. Among these species, median BSAFs from particular studies ranged from 0.66 to 4.31, and the authors identified an average BSAF for benthically-coupled fish of 2.1 (Tracey and Hansen 1996).

While there is relatively little variability in total PCB BSAFs for bottom-feeding fish, large congener-specific differences are well documented (van der Oost *et al.* 1988, 1996). This phenomenon has been investigated from a variety of different approaches, but primarily it is believed to result from differences in the elimination rates of congeners. PCB congener elimination rates have been investigated directly by several researchers. In general, more highly chlorinated congeners have longer half-lives, varying from months to years or even longer among different fish and invertebrate species (Niimi and Oliver 1983; de Boer *et al.* 1994). For instance, Niimi and Oliver (1983) studied elimination in rainbow trout (*Oncorhynchus mykiss*) and reported half-lives of less than 100 days for dichlorobiphenyls, 100-900 days for eight tetrachlorobiphenyls, and >1000 days for most penta- to decachlorobiphenyls.

The possible pathways of PCB elimination include loss to water via gills, fecal egestion, and metabolic transformation and excretion (Morrison *et al.* 1997). Growth can have a significant 'dilution' effect on tissue PCB concentrations as well and is frequently included as an elimination parameter in bioaccumulation models. In certain species and in certain stages of a life-cycle, observed negative relationships between fish size and contaminant levels have been attributed to this growth dilution effect (Sijm *et al.* 1992; Pastor *et al.* 1996). In the case of female fish, reproduction may also represent a significant elimination pathway (Sijm *et al.* 1992). Decreases in female pike (*Esox lucius*) contaminant levels with age most likely due to reproductive losses were observed in a study by Larsson *et al.* (1992). Sijm *et al.* (1992) incorporated mother-to-young transfer processes into their bioaccumulation model and concluded that the process could result in substantially different adult contaminant levels in males and females.

Significant congener-specific differences in bioaccumulation are usually attributed to differences in metabolism and excretion (Niimi 1996b). The metabolism of PCBs involves enzyme-mediated hydroxylation, which produces reactive arene oxide intermediates, and subsequent reactions to more water-soluble derivatives (Safe 1984). Some of these derivatives (e.g. methyl sulfone PCBs) have been quantified in biological tissues, providing direct evidence for metabolism (Bright *et al.* 1995b).

General structure-related patterns that facilitate PCB metabolism have been identified by various studies. However, to date, no single substitution pattern has been identified that consistently explains observed differences in bioaccumulation (Niimi 1996b). Studies of the metabolism of lower chlorinated PCB congeners have indicated a preference for hydroxylation at the *para*-, possibly the *meta*-, and definitely not the *ortho* positions (Niimi 1996b; Figure II-1). Examining this preference among more highly chlorinated PCB congeners indicates that the presence of adjacent unsubstituted *meta* and *para* carbons enhances metabolism (Niimi 1996b). Many species are capable of metabolizing (at least some) congeners with this substitution pattern (Matthews 1983; Boon *et al.*1989). However, in contrast to these findings, a few studies have found that *ortho* substitution does affect metabolism (Boon *et al.* 1989). Both seals and polar bears show some evidence of the ability to metabolize congeners with adjacent unsubstituted *ortho-meta* carbon atoms in combination with a maximum of one *ortho* substituent (Norstrom *et al.* 1988; Boon *et al.* 1989). Hydroxylation can also occur if congeners are substituted at the *meta-para* positions but have an adjacent unsubstituted *meta* position; in this case, the chlorine atom from the *para* position undergoes a 1,2-shift to the *meta* position and the hydroxyl group is substituted at the *para* position (Niimi 1996b). The difficulty in identifying structure relationships stems from the fact that, in most studies, the substitution patterns of congeners that are selectively bioaccumulated, are also characteristic of some congeners that are depleted (Niimi 1996b).

4. Marine PCB Contamination at Saglek, Labrador

Saglek Bay is located at approximately 58° 23' N, 62° 35' W on the northern Labrador coast (Figure II-2). It is situated on the periphery of the Torngat Mountains and serves as the entrance to a series of deep fjords extending 55 km inland. The headland at the mouth of the Bay was the site of a United States Air Force communication station for a twenty-year period beginning in 1951. The station operated as part of the Pole Vault Line, linking the Distant Early Warning (DEW) Line to the Pine Tree Line, and was the largest installation of its kind on the Labrador coast (Fletcher 1989). The site was abandoned in 1971 and remained largely unused for more than a decade. In 1986, the station was replaced with a North Warning System Long Range Radar facility (LAB-2), which currently operates at the site.

In 1996, a comprehensive assessment of the site identified significant amounts of soil contaminated with PCBs at concentrations exceeding 50 parts per million (ppm). Materials that contain PCBs at concentrations over 50 ppm are regulated under the Canadian Environmental Protection Act (R.S., 1985, c. 16, 4th supp). The contaminated soil was located at three areas of the site, including a sand and boulder beach and beach bench on the shore of Saglek Bay (ESG 1997; Figure II-3). Assessment results indicated that PCBs (in the form of contaminated soil) had migrated from this area into the adjacent marine environment. Tissue PCB concentrations measured in five specimens of a local bottom-dwelling fish, shorthorn sculpin (*Myoxocephalus scorpius*), captured in the immediate nearshore area of the beach, were elevated by several orders of magnitude relative to sculpin elsewhere in northern Canada (ESG 1997). The source of PCBs to the marine system has now been removed; the Canadian Department of National Defence (DND) conducted a cleanup of the contaminated soil over three seasons 1997-1999 (ESG 1998, 1999a, 2000).

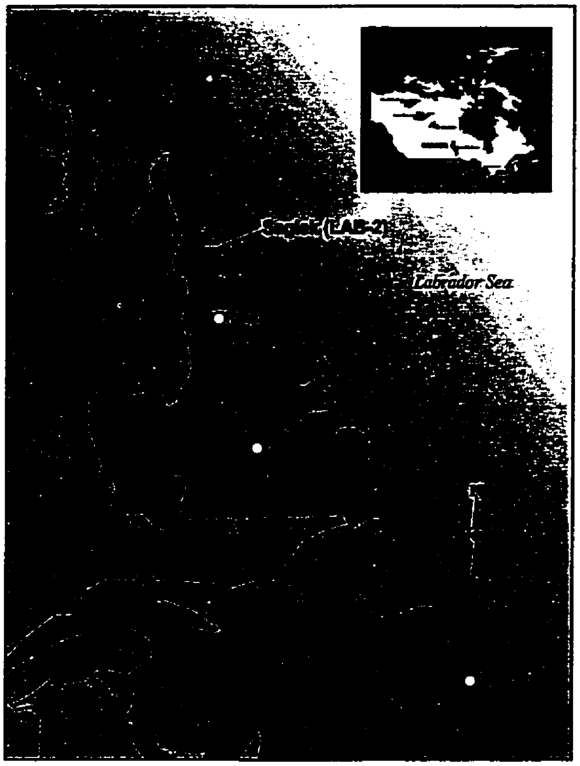

Figure II-1. Location of Saglek Bay, Labrador, and the military installation LAB-2.

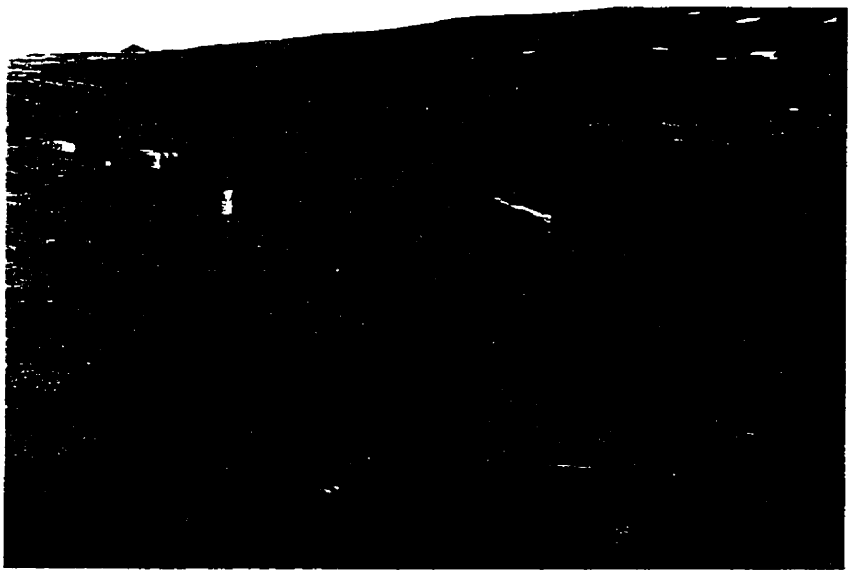

Figure II-2. Aerial photograph of the LAB-2 beach and beach bench area (centre of photo, to right of red tanks) prior to remediation.

III. Bioaccumulation of PCBs from Sediments in a Subarctic Coastal Marine Ecosystem: 1. Multi-trophic Level Survey

A. Introduction

Persistent and potentially toxic organochlorine pesticides and industrial chemicals such as PCBs continue to be contaminants of concern in arctic and subarctic marine ecosystems (Macdonald and Bewers 1996; Shearer and Murray 1997). PCBs have been detected in virtually every environmental compartment of northern Canada (Muir *et al.* 1999) and surprisingly high levels have been found in top marine predators including fish, marine mammals and seabirds (Muir *et al.* 1992). The North is believed to be particularly vulnerable to PCB bioaccumulation and biomagnification because of the long, linear (low diversity) food chains supporting long-lived, lipid-rich top predators (Remmert 1980; Welch *et al.* 1992; Alexander 1995). Human residents of the North are also part of this food chain, and may be similarly susceptible to exposure to these contaminants (Kinloch *et al.* 1992).

To date, a primary focus of research in the North has been identifying the tissue PCB burdens of major species, particularly upper trophic level species and important traditional food items (Kinloch *et al* 1992; Muir *et al.* 1997). Concentrations of PCBs and PCB metabolites in polar bears have been documented at many sites across the North, including the Beaufort Sea, the Arctic Archipelago, Baffin Bay, and Hudson Bay (Norstrom *et al.* 1988). Contaminant levels in beluga whale blubber have also been documented across much of this study area (Muir *et al.* 1997). Ringed seal have been major components of several contaminant-monitoring programs (Muir *et al.* 1999). Good information is now available for most areas where they are part of the traditional Inuit diet, with the exception of Northern Labrador and the Ungava Bay region of northern Quebec (Thomas and Hamilton 1988; Muir *et al.* 1988, 1992, 1997). Analysis has been more limited for other marine mammals, but some information is available for walrus, narwhal, bearded seal, and harp seal (Thomas and Hamilton 1988; Muir *et al.* 1992). Seabirds have also been a subject of study, and limited information about contaminant levels is now available for sites all across the North (Braune *et al.* 1999).

This extensive study of key northern species has provided much valuable data on contaminant levels in the North, and critical information for northerners making informed choices about consuming traditional foods (Shearer and Murray 1997). However, much less information has been gathered about contaminant levels in lower trophic level organisms such as marine fish and invertebrates, and the linkages between these species and higher order predators (Bright *et al.* 1995a; Landers *et al.* 1995; Muir *et al.* 1997). Understanding the dynamics of PCBs within the system is key to predicting their long term fate and likely also to understanding apparent regional anomalies (Muir *et al.* 1997). In particular, very little is currently known about the role of the benthic community in northern marine systems, and potential pathways of contaminant transfer between sediment, this community, and higher trophic level marine biota. Sediments are known 'sinks' for persistent organochlorine contaminants like PCBs, and readily transfer contaminants into benthic invertebrate communities (Landrum and Robbins 1990). The benthic community can be very productive in the North, contributing much more to the overall energy flow of the system than in comparable southern systems (Petersen and Curtis 1980).

This chapter investigates the accumulation of PCBs in a coastal marine food web associated with the input of a local PCB source in Saglek Bay, northern Labrador. The input of a land-based source at a former military installation in Saglek Bay (LAB-2) has resulted in localized marine sediment PCB contamination, several orders of magnitude above the low levels ubiquitous in the North (ESG 1998, 1999a,b). The objective of the study has been to examine the impact of this contamination on the PCB burden of local aquatic biota at different trophic levels and with different linkages to the sediment- or benthic-based food chain. This objective was accomplished by surveying tissue PCB residues in marine invertebrates (clams and sea urchins), fish (arctic char and shorthorn sculpin), ringed seal, and seabirds (great black-backed gulls and black guillemots). The accumulation of PCBs within this system should provide information about sediment-biota PCB transfer that is applicable to other northern systems where the dominant inputs are associated with long-range transport from distant sources. These results also represent some of the first information available regarding the presence of PCBs in northern Labrador marine biota.

B. Materials and Methods

1. Site Description

The study area of Saglek Bay is illustrated in Figure III-1. Briefly, the area lies between the contaminated beach, which is in the Saglek Anchorage area of Saglek Bay, and Big Island to the north.

This area is somewhat isolated from the remainder of Saglek Bay and Saglek Fjord by shallow sills at both its eastern (the mouth of the Bay) and western (between Marker Point and Shuldham Island) reaches (Figure III-1). Between these sills is a complex set of deep basins, reaching depths of more than 165 m.

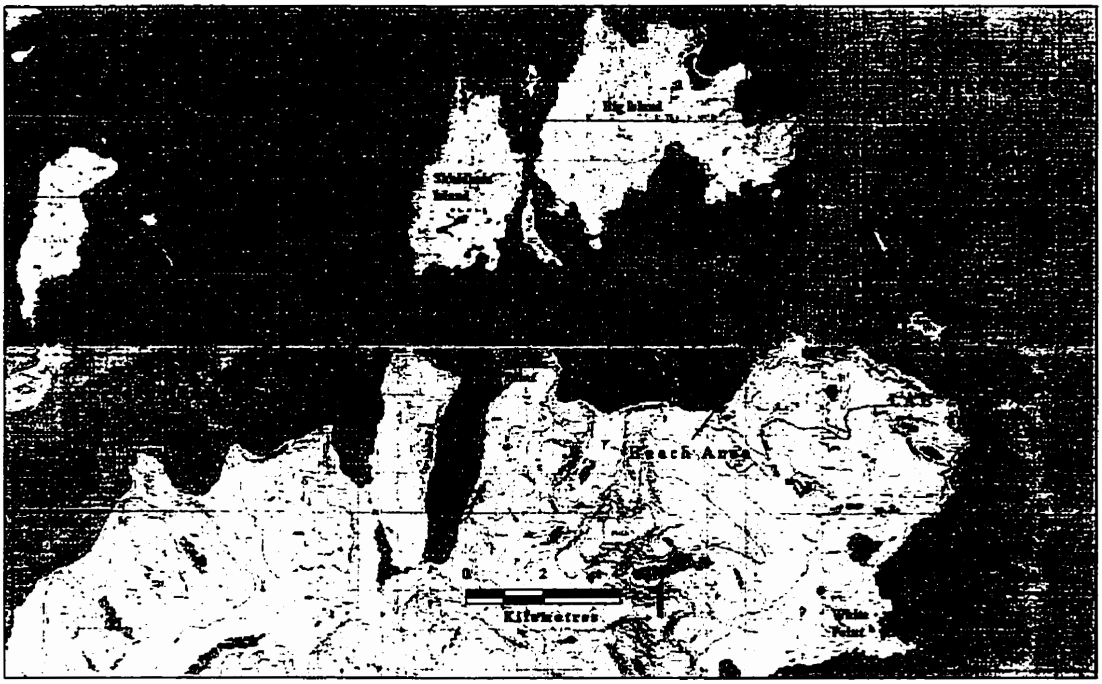

Figure III-1. Map of Saglek Bay, Labrador indicating location of LAB-2.

Two other locations along the Labrador coast were used as reference sites for this study: Cutthroat Island in Okak Bay (57° 30' N, 61° 35' W) and Nain (56° 32' N, 61° 41' W). Okak Bay is remote from any permanent human establishment. Nain is a community with a population of approximately 1500, but no known PCB sources. Shorthorn sculpin were collected from the wharf in Nain Harbour and ringed seal and seabird samples were collected from uninhabited islands away from the community.

2. Sample Collection

Environmental samples were collected over three seasons 1997-1999 and included sediment, invertebrates, bottom-feeding fish, arctic char, ringed seal, and seabirds. The majority of samples were collected in 1997-1998, but additional samples of seabird eggs and adults were obtained in 1999. With the exception of ringed seal from Nain, which were harvested in November-December, all biological sampling was performed during the summer months (June-September).

Several types of sediment sample were obtained and a detailed description is given elsewhere (Knowlton in prep.). Sample locations were determined using an Ashtech Differential Global Positioning System (DGPS). In total, the results for 243 surface sediment samples from Saglek Bay and five background samples (>10 km from the LAB-2 beach) are included in this study. The samples included 62 beach and intertidal sediments, collected with a clean shovel (0-10 cm), and 181 nearshore samples in up to 165 m waterdepth. Nearshore samples were obtained by SCUBA divers (n=42) or a hand-deployed Ponar grab (n=126). In either case, the sample was collected with a clean plastic scoop and represented approximately the top 0-7 cm of the sediment bed. The Ponar grab (surface area 0.05 m^2) was rinsed with water between uses. Additional samples were obtained by vibrocore and split-spoon techniques (n=13, top 1-3 cm). In the vicinity of the contaminated beach, samples were collected in Whirlpak™ bags; elsewhere, sediments were placed in 1 L or 125 mL I-Chem™ amber glass jars fitted with Teflon-lined lids, certified to be free of organic materials. Sediments were frozen within hours of collection and kept frozen until analysis.

All biological tissue samples were packaged in clean aluminium foil and Ziplock™ bags, immediately frozen and kept frozen until analysis. Samples of marine invertebrates were comprised of mussels (*Mytilus* sp., n=2), green sea urchins (*Strongylocentrotus droebachiensis*, n=6), and clams (composites of two genera: *Yoldia* and *Macoma* spp., n=14). Samples were composites of 2-20 individuals. Mussels were collected by hand from intertidal areas in Anchorage Cove, Big Island, and at White Point, south of Saglek Bay (Figure III-2). Sea urchins were collected manually by SCUBA divers from several subtidal areas in Saglek Bay or (in one case) were hand-sorted from a Ponar grab sample. Clams were found exclusively in deepwater sediments and were sieved or hand-sorted from Ponar samples (Figure III-2). All invertebrate samples were thoroughly rinsed with seawater to remove any residual sediment.

Shorthorn sculpin (*Myoxocephalus scorpius*) were collected by jigging at 16 sites in and around Saglek Bay and three additional sites in Saglek Fjord. Similar techniques were used for collections from Okak Bay (n=9) and from the wharf in Nain Harbour (n=6). Sculpin were humanely killed, weighed and measured, and immediately dissected to separate livers and otoliths and describe stomach contents. Sculpin ages, determined from otoliths (Ennis 1970a), ranged from 3- to 9 years; total lengths averaged 23.2 ± 5.46 cm (mean ± SD, n=150). Arctic char (*Salvelinus alpinus*), averaging 55.2 ±7.78 cm in length, were collected at three sites: 1) the mouth of Anchorage Cove, Big Island, near LAB-2 (n=10), 2) the Southwest Arm of Saglek Fjord, approximately 50 km from LAB-2 (n=11), and 3) Okak Bay (n=2). Char were collected by gill net or with a rod and reel and immediately killed. Weight, length, sex, and stomach contents were recorded and otoliths were obtained to allow possible future age determination. Livers were separated from whole-fish samples to allow independent analysis.

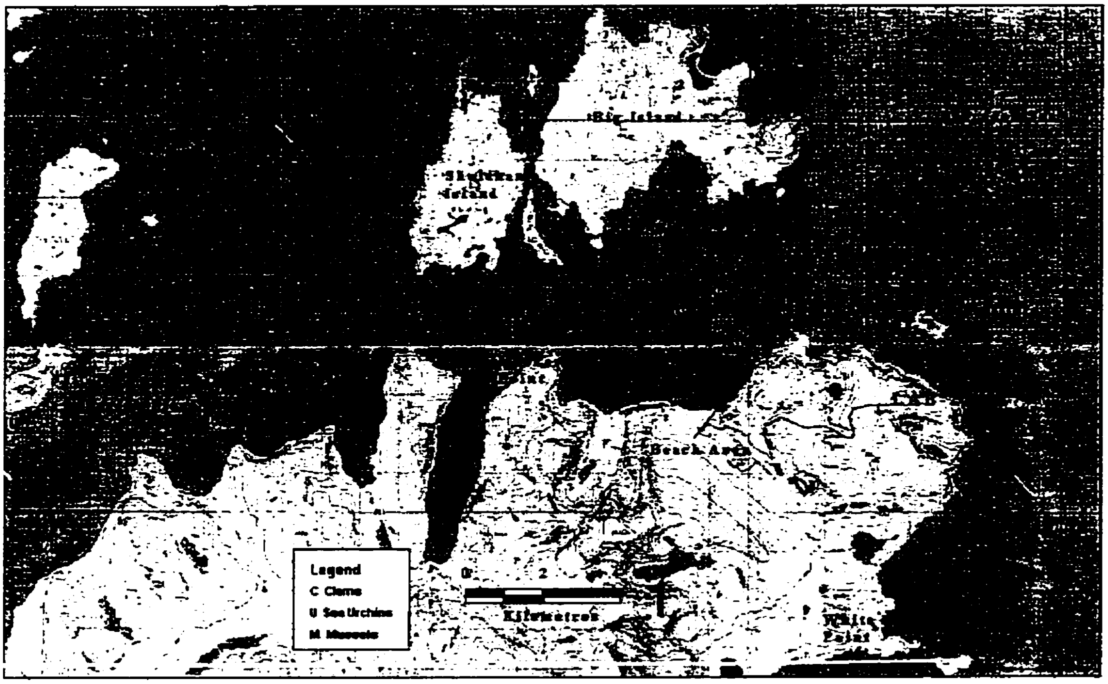

Figure III-1. Locations of marine invertebrate sampling in Saglek Bay.

Ringed seal (*Phoca hispida*) were shot in the head by Labrador Inuit hunters using a 0.22-calibre rifle. Muscle, liver, and blubber samples were obtained from all seals, and the remainders of the animals became the property of the Inuit hunter. Six seals (males aged 1-10 years) were harvested in Saglek Bay during the months of July and August, and four additional seals (males aged 1-24 years) harvested in Two-mile Bay near Nain during November and December. Ages were determined from teeth for six individuals (Smith 1987) and estimated from body size by Inuit hunters for the other four. Substantial differences in body condition (girth) were noted between the summer- and winter harvested seals, consistent with the summertime declines in condition that have been identified elsewhere (Macdonald and Bewers 1996).

Two species of seabird were selected as indicator species principally because of their abundance in the Saglek Bay and Nain areas: great black-backed gulls (*Larus marinus*) and black guillemots (*Cepphus grylle*). For great black-backed gulls, sampling consisted of eight adults and five eggs from Saglek Bay, and eight adults and four eggs from Nain. For black guillemots, 10 adults and 25 eggs were collected at Saglek, and eight adults and five eggs were collected at Nain. The egg collections in Saglek Bay were made at various distances from LAB-2 : <2 km, 5 km east, 6 km northwest, and 16-18 km west. Adult birds were shot by CWS biologists or Inuit hunters using rifles of various calibres.

3. Analytical Techniques

PCB and pesticide analyses were carried out by AXYS Analytical Services Ltd. located in Sydney, BC. Sediments were homogenized, subsampled for determination of wet weight-dry weight ratios, spiked with surrogate standard, and then 10-15 g were extracted on a shaker table. The extraction was done with 1:1 dichloromethane/methanol followed by dichloromethane. The two extracts were combined, washed with solvent-extracted water, dried over anhydrous sodium sulphate and concentrated.

Biological tissue samples were homogenized and subsampled for determination of wet weight-dry weight ratios. Then, wet tissue (5-10 g) was combined with anhydrous sodium sulphate and surrogate standard and ground with a glass mortar and pestle to a free-flowing powder. This powder was eluted with dichloromethane on a glass chromatographic column. A portion of the eluent was used for lipid analysis. The remainder was concentrated and transferred to a calibrated Biobead SX-3 gel permeation column and eluted with 1:1 dichloromethane/hexane. The 150-300 mL fraction was collected and evaporated to a small volume.

Cleanup of both sediment and tissue samples was conducted on a Florasil column. For samples being analyzed by gas chromatography/mass spectrometry (GC/MS), the column was eluted with hexane followed by 15:85 dichloromethane/hexane to produce Fraction 1 (used for PCB analysis), and then subsequently eluted with 1:1 dichloromethane/hexane to produce Fraction 2 (used for polar chlorinated pesticides). These fractions were concentrated, transferred to a microvial, and spiked with recovery standard (^{13}C-PCB 153).

The majority of PCB and pesticide analyses were conducted using a Finnigan INCOS 50 mass spectrometer equipped with a Varian 3400 GC, a CTC autosampler and a ProLab Envirolink for MS control and data acquisition. Pesticides were separated using a DB-5 column (60 m, 0.25 mm i.d. and 0.10 μm film thickness). The mass spectrometer was operated in the electron impact (EI) mode at unit mass resolution and in the multiple ion detection (MID) mode acquiring two characteristic ions for each target analyte and surrogate standard. A few samples that required very low PCB detection limits were analyzed using a VG 70 SE mass spectrometer equipped with a Hewlett Packard 5890 GC, a DB-5 column (60 m, 0.25 mm i.d. and 0.10 μm film thickness), and a CTC autosampler.

For analysis using gas chromatography with electron capture detection (GC/ECD), the Florasil column was also eluted with three solvents but three fractions were separated: hexane (Fraction 1), 15:85 dichloromethane/hexane (Fraction 2) and 50:50 dichloromethane/hexane (Fraction 3). In this case Fraction 1 was used for PCBs and mildly polar chlorinated pesticides and Fractions 2 and 3 for the moderately and most polar chlorinated pesticides, respectively. Surrogate standard was added to Fraction 2 because the original standard eluted into Fractions 1 and 3. After concentration and transfer to a microvial, Fractions 1 and 2 were spiked with 4,4'-dibromooctafluorobiphenyl and PCB 204 as recovery standards; Fraction 3 received an aliquot of ^{13}C-PCB 153.

GC/ECD analysis was conducted using an HP 5890 Series II Plus gas chromatograph equipped with a ^{63}Ni electron capture detector (GC/ECD), a SPB™-1 fused silica capillary column (30 m, 0.25 mm ID x 0.25 μm film thickness) and HPChem station software. Helium was used as a carrier gas with a flow rate of 2 mL/min. Nitrogen was used as a makeup gas for the ECD. Reported pesticides included alpha hexachlorocyclohexane (α-HCH), β-HCH, γ-HCH, dichlorodiphenyltrichloroethane (o,p'-DDT and p,p'-DDT), dichlorodiphenyldichloroethane (o,p'-DDD and p,p'-DDD), dichlorodiphenyldichloroethene (o,p'-DDE and p,p'-DDE), hexachlorobenzene (HCB), heptachlor, aldrin, oxychlordane, trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor, mirex, heptachlor epoxide, alpha-endosulphan, dieldrin, endrin, and methoxychlor. PCBs were quantified as individual congeners by calibrating the GC/ECD with four well-characterized mixtures of 51 congeners obtained from the National Research Council (NRC). Aroclor mixtures of known composition were used for congeners not present in the NRC mixture. A total of 84 individual or co-eluting congeners were coded in the samples. Limits of detection were calculated on a sample-specific basis by measuring the mean noise level of the chromatogram, converting this to an area using the area/height ratio of a large peak and calculating a concentration based on three times this 'noise area'. Quality control data are provided in Appendix A.

The carbon content of sediment samples was analyzed by the Geological Survey of Canada Atlantic Region. Total carbon (organic + inorganic) was determined in 0.5 g of dried sediment using a Leco WR-112 carbon combustion furnace analyzer. Organic carbon was determined with the same equipment after the sample was treated with 1 M hydrochloric acid to release inorganic carbon (carbonate) as carbon dioxide. Precision for the method is assessed at +/- 0.03% carbon, based on 5 replicate analyses of calibration standards.

4. Computational Methods and Statistical Analyses

a. General

PCBs were quantified as congeners for all biological tissue samples, because the quantification of PCBs as Aroclor equivalents, rather than individual congeners, can be erroneous if the congener composition of PCBs in the samples is significantly different from technical Aroclor mixtures (Duinker *et al.* 1988). Sediment PCB analyses were conducted using both Aroclor equivalent and congener-specific techniques (n=184 and 63, respectively) because the congener composition of Saglek Bay sediments strongly resembles the composition of Aroclor 1260, the commercial mixture used at the LAB-2 (Schulz *et al.* 1989; ESG 1998). Among 30 samples analyzed by both techniques, the variation between Aroclor determinations and ΣPCB was consistently low (average CV=0.13). Remote samples were significantly different from Aroclor 1260 and only congener information was used for these samples.

Of the 84 congeners reported by Axys Analytical Services Ltd., 29 were detected in less than half of all samples, so total PCB concentrations (ΣPCB) were calculated based on the sum of the remaining 55 congeners. Results less than the detection limit were replaced with a random number between the detection limit and one-half the detection limit. Unless otherwise stated, all PCB and pesticide results are reported on a dry weight basis for sediment samples and on a wet weight basis for tissue samples.

b. Distribution of PCBs in Saglek Bay Sediments

The distribution of PCBs in Saglek Bay sediments around the former contaminated beach was estimated from the 243 surface sample results for this area. In order to visualize the PCB distribution and trends and to relate them to biota, the point data must be interpolated to create a continuous PCB concentration surface. This was done in two stages using MapInfo™ GIS and the Vertical Mapper™ application which works within it. First, two independent human observers examined sample PCB results in light of seabed characteristics (e.g. sediment grain size) and bathymetry, and visually interpreted concentration isopleths (2, 5, 10, 25, 50, 100, 500, 1 000, 5 000, 10 000 ng/g dry wt.). The isopleths were converted to artificial concentration points at each node and combined with the original measured concentration data from samples and core tops. Second, a concentration grid was produced from the original sample data and the artificial points using a natural-neighbour method as implemented in Vertical Mapper™. This method calculates values for each grid area using the weighted-average of all data surrounding it; the method is very effective where data is linear and highly clustered. Grid spacing was set at 20 m in order to capture the rapid decrease in concentration that occurs within the first kilometre from the contaminated beach. Concentrations were more spatially homogeneous and sampling correspondingly less dense at greater distances from the beach. The distribution map is illustrated in Figure III-2.

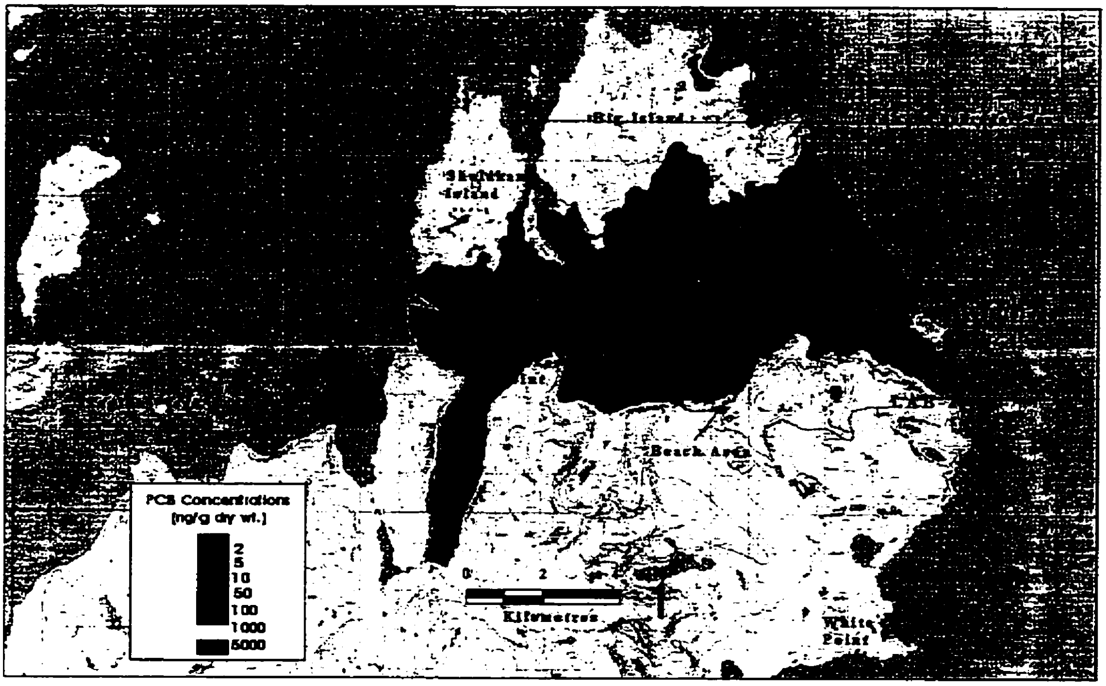

Figure III-1. Estimated distribution of PCBs (ng/g dry wt.) in Saglek Bay sediments.

C. Results and Discussion

1. Source: Marine Sediment PCB Contamination

PCB concentrations in the marine sediment of Saglek Bay have been strongly influenced by the terrestrial contamination at the LAB-2 beach (Figure III-3). While organochlorine contaminants are typically expected to be associated with organic matter and fine particles and 'focused' in quiescent, depositional basins (Eisenreich *et al.* 1989), the distribution of PCBs in Saglek sediments (during the period 1997-1999) was largely a function of distance from the LAB-2 beach. The relationship between nearshore sediment PCB concentrations and distance was described by: PCB concentration in ng/g dry wt. = 90.6*(distance in km)^(-1.6) (n=191, R^2=0.7, p<0.001). In the intertidal and subtidal areas near the beach where concentrations are highest, sediments are primarily well-sorted sands with few fine particles (generally <1%) and little organic matter (generally <0.05%). PCB concentrations as high as 130 000 ng/g (dry wt.) were observed in the intertidal area in 1997, at the outset of terrestrial cleanup, and concentrations in the subtidal area and throughout much of Saglek Anchorage were in excess of 1 000 ng/g.

The most likely explanation for the unusual PCB distribution pattern in Saglek Bay is that PCB inputs from the terrestrial source occurred recently, and sampling was conducted when there had been relatively little opportunity for redistribution. The fact that some redistribution had occurred is evident from the above-background PCB levels detected throughout the Bay, and likely the contaminated sediments will undergo further redistribution in the future. Sediment transport, in fact, is likely to be extensive since the contaminated beach lies along a stretch of coastline exposed to the mouth of the Bay and the Labrador Sea (Solomon 1999).

At the time of this study, there was a steep declining PCB concentration gradient with distance away from the beach source. Within a distance of 800 m east and north, PCB concentrations fell below 100 ng/g; a similar decline occurred over a distance of approximately 2.5 km to the west. Concentrations continue a noticeable decline to a distance of at least 6-8 km from the beach (Figure III-3). No distinct spatial pattern in PCB concentrations was observed among samples collected outside this area; concentrations in five samples from distances of 10-25 km varied between 0.23 and 0.80 ng/g (dry wt.).

These concentrations for remote Saglek Bay sediments are similar but slightly higher than other reported sediment PCB levels in northern Canada (DND and EC 1994; Bright *et al.* 1995a,b; DND *et al.* 1995). There is no published information about sediment PCB concentrations for northern Labrador specifically, but limited study has been conducted in the central and eastern Canadian Arctic. Concentrations attributable to long-range oceanic and atmospheric transport (herein called 'background' concentrations) were documented at 0.052-0.44 ng/g in Queen Maud Gulf (n=2, Bright *et al.* 1995b). Similar PCB concentrations were measured in the eastern Arctic marine system, as well (0.023-0.65 ng/g, n=13, DND *et al.* 1995). The sites examined in this second study share similar longitudes and ocean current influences with Saglek, but are much further removed from industrial areas of Atlantic Canada (Thompson and Aggett 1981; DND *et al.* 1995). Minimum sediment PCB concentrations of approximately 1 ng/g have been reported for relatively pristine regions of temperate Atlantic Canada (EC 1985).

Concentrations of organochlorine (OC) pesticides were also examined in Saglek Bay sediments to verify that no other significant local contamination has occurred. The results confirm that LAB-2 has only been a very low-level source of OC pesticides, with the inputs being almost negligible in comparison to the input of PCBs. The OC pesticide results for two high-PCB sediment samples from close to the source area are presented in Table III-1, along with documented concentrations of these contaminants in sediments of the eastern Arctic (DND *et al.* 1995). In general, the Saglek OC pesticide levels are an order of magnitude higher than the upper levels measured at these remote Arctic sites. However, ΣDDT concentrations in Frobisher Bay sediments (near the community of Iqaluit; DND *et al.* 1995) are quite similar to the Saglek ΣDDT results, suggesting that the ΣDDT inputs of LAB-2 and this community may be of a similar magnitude.

Table III-1. Sediment organochlorine contaminant concentrations (ng/g dry wt.).

Region	Area	N	ΣPCB	HCB	ΣHCH	ΣChl	ΣDDT	Dieldrin	%TOC	Reference
Saglek Bay, Labrador	LAB-2 Subtidal	2	3470	0.58	<6.2	4.6	1.89	<0.01	0.03-0.64[1]	This study
Baffin Island, Eastern Arctic	Remote Sites	13	0.023-0.65	0.006-0.07	0.01-0.16	0.008-0.1	0.02-0.69	0.05-0.31	0.06-2.09	DND *et al.* 1995
Baffin Island, Eastern Arctic	Iqaluit Area	6	0.1-120[2]				0.2-7.7			DND *et al.* 1995

[1]Range for 25 sediment samples from region
[2]Total Aroclor equivalents
ΣHCH=α–HCH+β–HCH+γ–HCH
ΣChl=heptachlor + oxychlordane + cis-chlordane + trans-chlordane + cis-nonachlor + trans-nonachlor + heptachlor epoxide + methoxychlor
ΣDDT=DDT isomers + DDD isomers + DDE isomers
%TOC=percent total organic carbon

2. Marine Invertebrates

Benthic invertebrates have been used extensively as an environmental monitoring tool because they readily accumulate contaminants from sediment and transfer this contamination to higher trophic level biota (Landrum and Robbins 1990). In the North, benthic invertebrates form the basis of the coastal food web, supporting demersal fish, diving seabirds, walrus, bearded seal, narwhal, and beluga (Muir *et al.* 1997). Other species, commonly considered part of the pelagic system, also spend at least a portion of their lifetimes in coastal areas feeding on benthos (Smith 1987; Bright *et al.* 1995a). To date, relatively few benthic invertebrate groups have been analysed for organic contaminants in the North. However, limited reference data are available for offshore and nearshore amphipods (Hargrave *et al.* 1992; Bright *et al.* 1995b), bivalves (Cameron and Weis 1993; Bright *et al.* 1995b; Muir *et al.* 1997), and sea urchins (Bright *et al.* 1995b). PCB results from this study for green sea urchins (*Strongylocentrotus droebachiensis*), mussels (*Mytilus* sp.), and clams (*Macoma* and *Yoldia* spp.), and their associated sediment samples are presented in Table III-2.

Sea urchins were common in the rocky, kelp-dominated subtidal areas of Saglek Bay and samples were obtained from Saglek Anchorage as well as sites located 2.8 to 25 km away. PCB concentrations in the Anchorage area (5 190 ng/g wet wt.) were surprisingly high for an herbivorous species that feeds primarily on macroalgae. This result may suggest that they have a closer association with sediment and include detritus in their diets, as has been suggested elsewhere (Bright *et al.* 1995a). Concentrations from other nearby subtidal areas (2.8-6 km from the LAB-2 beach) are dramatically lower (16-79 ng/g), but still elevated relative to concentrations at a distance of 25 km away (3.3 ng/g). Sea urchin tissue PCB concentrations measured near the community of Cambridge Bay in the central Arctic were more than eightfold higher than this level (24-26 ng/g, Bright *et al.* 1995b). No contaminants information is available for sea urchins from truly remote northern locations.

Mussels are relatively uncommon in the Saglek Bay area and samples were obtained from only one site within the Bay (Anchorage Cove, Big Island) and one site outside the Bay, near White Point (Figure III-2). White Point is quite remote from LAB-2 in terms of marine circulation systems, but it lies within the surface water drainage area for much of the headland on which LAB-2 is situated. Aerially, it is approximately 7 km southeast of the LAB-2 beach. Concentrations were similar at the two sites, but elevated substantially above the concentration that has been reported for one background sample of mussels collected in the central arctic (0.99 ng/g, Bright *et al.* 1995b). This comparison suggests that White Point has received low-level inputs from the contamination at LAB-2. Whether these inputs occurred via aerial redistribution, terrestrial run-off, marine circulation, or some combination, is unknown.

Yoldia and *Macoma* clams are among the most abundant infauna in the depostional basins of Saglek Bay. They were typically associated with fine-sized and relatively organic-rich sediments (mean total organic carbon = 0.77% ± 0.33% SD) and were present in 72% of grab samples from 30 m or greater water depth (n=50).

In total, 14 composite samples (including both genera) were analyzed for PCBs. Thirteen samples were collected within Saglek Bay at distances of 1.5 to 5.3 km from LAB-2; PCB concentrations for these samples ranged from 46 to 285 ng/g. The highest tissue residues were not in clam samples from the deepest (most-depositional) areas, where contamination would be expected to be most focused (Eisenreich *et al.* 1989), but instead were in clams close to the beach. These results are consistent with observations about the distribution of contaminated sediments.

The most distant site of clam sampling was approximately 11 km northwest of LAB-2, just north of Big Island (Figure III-2). Tissue PCB concentrations at this site (12.6 ng/g) are elevated several times above bivalve PCB levels found at other northern locations, suggesting that some PCB contaminated sediment from the beach source has been redistributed to this area. Cameron and Weis (1993) measured much lower PCB concentrations in clam tissue in samples from southeast Hudson Bay (1.1 ng/g). Similarly low concentrations (0.89-2.2 ng/g) were reported by Bright *et al.* (1995b) for *Mya truncata* samples (n=4) near the central Arctic community of Cambridge Bay and levels were below detection limit in a sample from their reference site (<0.62 ng/g).

Table III-2. PCB Concentrations (ng/g) in marine invertebrates and associated sediments.

Species	N	Marine Invertebrate Data		Associated Sediment Data	
		ΣPCB (wet wt.) Range	% Lipid Mean (SD)	ΣPCB (dry wt.) Range	%TOC Mean (SD)
Green Sea Urchins (*Strongylocentrotus droebachiensis*)	6	3.3 - 5190	0.97 (0.37)	0.52 - 1005	0.20 (0.15)
Clams (*Macoma* and *Yoldia spp.*)	14	12.6 - 285	2.36 (0.35)	0.80 - 49.4	0.77 (0.33)
Mussels (*Mytilus* sp.)	2	7.3 - 11.2	1.45	-	

3. Shorthorn Sculpin

Shorthorn sculpin (*Myoxocephalus scorpius*) are abundant benthic fish that feed primarily on polychaetes, amphipods, gastropods, small sea urchins, and other fish (Scott and Scott 1988) and provide food for arctic char, seals, seabirds, and occasionally people (Bradstreet and Brown 1985; Smith 1987). Because of their link to sediment and limited movement (Ennis 1970b; Pepper 1974), they are an excellent indicator species for localized marine contamination (Bright *et al.* 1995a,b; Muir *et al.* 1997).

At Saglek, sculpin were used as a primary monitoring species and were sampled at distances of up to 25 km from the beach remediation site. Figure III-4 illustrates the spatial pattern of sculpin (whole minus liver) PCB concentrations (mean ± SD, n=4-13) at these sampling sites. PCB concentrations ranged over three orders of magnitude, generally decreasing with increasing distance from the beach. At the sites closest to the beach, concentrations were extremely variable (CV=0.82) and a few sculpin had PCB loads in excess of 10 000 ng/g wet wt. The mean PCB concentration in this area (4 390 ± 3 470 ng/g, n=9) was similar to that observed in sea urchins in spite of the differing trophic levels. Elsewhere, sculpin PCB levels were 2-35 times higher than sea urchin levels (n=7). This finding suggests that PCB transfer within the food web at the beach area is reduced or delayed, perhaps due to PCB inputs having occurred recently.

To identify background PCB levels for sculpin in northern Labrador, samples were also collected from the harbour near the community of Nain, Labrador (n=6), and a remote site, Okak Bay, between the community and Saglek (n=9). In spite of the community presence at Nain, PCB concentrations were not significantly different between the sites (ANOVA, $p>0.05$), and the results suggest an average background concentration of 5.9 ± 3.9 ng/g wet wt. (mean ± SD) for northern Labrador sculpin. This level is consistent with sculpin PCB concentrations at four of the Saglek sites, those at distances of 14-25 km from LAB-2. It is also very similar to the average sculpin tissue PCB concentration reported at remote eastern Arctic sites (7.2 ± 4.3 ng/g, n=5, DND *et al.* 1995).

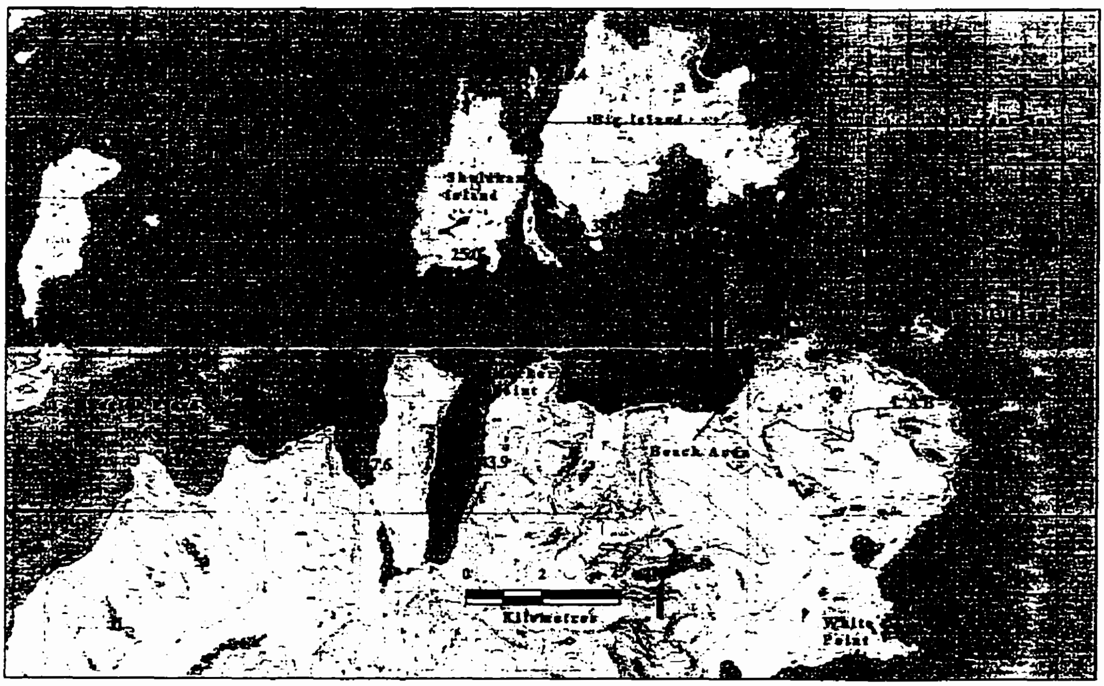

Figure III-1. Mean tissue PCB concentrations in shorthorn sculpin at sampling sites around LAB-2. Bars and numbers reflect PCB concentrations in whole fish minus liver (ng/g wet wt.).

4. Arctic Char

Arctic char (*Salvelinus alpinus*) are anadromous fish that feed heavily while in the sea, consuming a variety of both invertebrates and fish. Common dietary items include both pelagic species such as copepods (*Calanus* spp.), euphausids (*Meganyctiphanes norvegica*), capelin (*Mallotus villosus*), and Arctic cod (*Boreogadus saida*), and bottom-dwellers such as gammaridean amphipods, sculpin, sandlance, (*Ammodytes* spp.), and snailfish (*Liparis* spp.) (Scott and Scott 1988). Although char are occasionally consumed by seals and whales, their most significant link in northern food webs is to humans, as they are an important traditional food and commercial resource all across the North (Scott and Scott 1988). Because of this significance, arctic char PCB levels have been monitored in many areas of the North with the exception of Labrador (Bowes and Jonkel 1975; Thomas and Hamilton 1988; Muir *et al.* 1992, 1997).

PCB concentrations measured in whole (minus liver) char in this study and a summary of levels documented elsewhere are presented in Table III-3. Sampling sites in Saglek Bay included Anchorage Cove, Big Island, and two background sites where char have been fished commercially (Southwest Arm of Saglek Fjord, 50 km inland, and Okak Bay). While arctic char samples could not be obtained nearer to the contaminated beach itself, whole-body PCB residues at the above sites show no evidence of a local PCB source influence (Table III-3). Concentrations in tissues at the Big Island site are equivalent to concentrations at the reference site on both a wet- and lipid weight basis (ANOVA, $p>0.05$, $df=21$). Liver lipid fractions are significantly higher among the char closest to LAB-2, and create an apparent concentration difference at this site if concentrations are compared solely on a wet weight basis (ANOVA, $p<0.001$, $df=11$). Lipid normalizing helps account for the fact that PCB distribution within organisms is positively correlated with the location of lipids (Jorgensen *et al.* 1997). The reason for different lipid distributions among the samples is unknown, but Okak Bay and the Southwest Arm are considerably closer to freshwater than the LAB-2 area, and may have different abundant prey species. Half of the char from the LAB-2 area had fish among their stomach contents, while at the reference sites, stomachs contained invertebrates or nothing at all. Substantial changes in the body condition of arctic char during their summer seawater residence have also been observed (Jorgensen *et al.* 1997).

The PCB levels measured in this study are comparable to levels documented for arctic char from Ungava Bay, but slightly higher than most levels reported elsewhere (Table III-3). This result may reflect a broad geographic trend towards slightly higher PCB concentrations in Hudson Bay and eastern arctic/subarctic areas, compared to west and central areas. Spatial patterns of this nature have been observed among both ringed seal and polar bear contaminant levels (Muir *et al.* 1997).

Table III-3. PCB concentrations (ng/g wet wt.) in arctic char from this study and documented elsewhere.

Location	N	Tissue	ΣPCB Mean (SD)	Lipid (%) Mean (SD)	Reference
Northern Labrador – Okak Bay	2	Whole	36.5	3.4	This study
	2	Liver	36.6	5.8	
Saglek Fjord – 50 km from LAB-2	11	Whole	28.2 (12.3)	7.4 (2.0)	
	5	Liver	26.1 (10.8)	6.3 (2.2)	
Saglek Bay – Near Big Island	10	Whole	37.6 (10.1)	8.2 (1.9)	
	4	Liver	90.2 (42.4)	22.8 (3.9)	
Eastern Baffin Island	3	Liver	10 (9.1)	-	Bowes and Jonkel 1975
Arctic Archipelago	1	Whole	15	-	
	4	Liver	5.2 (4.2)	-	
	3	Muscle	8.0 (9.5)	-	
North Baffin Island – Arctic Bay	1	Liver	25	-	Thomas and Hamilton 1988
East Baffin Island – Pangnirtung	6	Liver	34 (7)	-	
East Baffin Island – Pangnirtung	10	Whole	10 (1)	-	Muir *et al.* 1992
West Hudson Bay	10	Whole	14 (3)	-	
Central Arctic – Queen Maud Gulf	10	Whole	16 (4)	-	
South Beaufort Sea	9	Whole	4 (1)	-	
South Hudson Bay – Sanikiluaq	8	Filet*	23.6 (17.0)	4.9 (3.2)	Muir *et al.* 1997
Hudson Strait – Kangiqsujuaq	9	Filet*	24.0 (9.63)	8.6 (2.0)	Muir *et al.* 1997
Ungava Bay – Kangiqsualujjuaq	4	Filet*	53.8 (31.6)	10.2 (6.1)	Muir *et al.* 1997

*Muscle and skin

5. Ringed Seal

Ringed seals (*Phoca hispida*) are the most abundant and widely distributed marine mammals in the North and are key components of coastal food webs (Smith 1987). While the linear Arctic cod – ringed seal – polar bear system has been most studied, their actual food linkages can be quite complex and involve a variety of other prey species, including benthos (Smith 1987). A study examining the stomach contents of 519 ringed seals in the Beaufort Sea found that 36 prey species were present, including a wide variety of pelagic (*Parathemisto libellula*, *Thysanoessa raschii*) and benthic (*Mysis oculata*) crustaceans (Smith 1987). The benthic mysids were consistently a dominant prey species, appearing in 55% of all seal stomachs from all areas (Smith 1987). Of the fish identified in the stomach contents, Arctic cod were most important, but sculpin (*Myoxocephalus* sp.) were present in significant proportions (16% occurrence) in some areas and some of the time (Smith 1987).

Much of the concern about ringed seal contaminant levels relates to their significance to Inuit, both directly, as a food source, and indirectly, via the dependence of polar bears on seal skin and blubber (Kinloch *et al.* 1992; Gilman *et al.* 1997). Because of the link to human consumers, the contaminant levels of ringed seal are probably the best studied of any northern species and have been documented throughout much of the North (Muir *et al.* 1988, 1997; Cameron and Weis 1993). However, the results of the present study provide some of the first information for northern Labrador.

To assess contaminant levels in Saglek Bay ringed seal, samples were obtained from both Saglek and Nain. Because samples were obtained opportunistically, courtesy of Labrador Inuit hunters, Saglek collections were made in July-August and Nain collections in November-December. Blubber PCB concentrations (n=6 and 4, respectively) and concentrations of OC pesticides for the two sites (n= 5 and 3, respectively) are presented in Table III-4, along with blubber contaminant levels that have been documented elsewhere. PCB concentrations span a surprisingly large range among the Saglek samples (CV=1.37), with extremely high concentrations measured in one individual (9380 ng/g wet wt.). The results for this seal (for muscle and liver as well as blubber) exceed any other Saglek results by factor of 4.5-6, and appear to be much higher than results reported for any other site in the North (Table III-4). If the results for this individual are excluded, the variance within the Saglek sample set is much reduced

(CV=0.35). In addition, a mean PCB concentration calculated for the Saglek Bay seals without this individual (1100 ng/g wet wt.) is comparable to that reported for other northern areas (Muir *et al.* 1988, 1997; Cameron and Weis 1993).

PCB concentrations in the Nain sample set are approximately a factor of 2 lower than this adjusted Saglek average (i.e. excluding the exceptionally high result), and among the lowest reported for ringed seal to date (Table III-4). The low levels are surprising if considered in the context of the spatial trends for ringed seal contaminant levels across the North; these trends generally indicate that seal organochlorine levels increase west to east, and from arctic to subarctic areas (Muir *et al.* 1997). A possible explanation for the low concentrations in this sample set is the time of year of sampling, because it coincided with seals having gained thick layers of blubber and effectively 'diluted' their PCB loads. Typical sample collection periods in spring-summer would find thinner blubber and correspondingly elevated contaminant concentrations (Smith 1987; Macdonald and Bewers 1996). The effect of seasonal changes in body condition on ringed seal contaminant levels has not been explicitly evaluated, but significant seasonal changes in contaminant concentration have been identified for other species such as polar bears (Muir *et al.* 1997). Restricted feeding studies with fish have also demonstrated the potential for increased contaminant concentrations in at least some tissues following a loss of lipids (Jorgensen *et al.* 1997).

OC pesticides, for which LAB-2 is only a minor source, were also analysed as a means of exploring whether PCB levels are elevated in seals from Saglek Bay compared to seals elsewhere. Chlordane and DDT-related compounds (DDT) are the most prominent OC pesticides at both Saglek and Nain (Table III-4). As with PCB concentrations, the Nain pesticide levels are among the lowest that have been reported. Among the Saglek samples, the seal with unusually high PCB concentrations is also an exception with respect to the other organochlorine contaminants, in particular chlordane and DDT (3 410 ng/g and 1 320 ng/g, respectively). With this sample excluded, the average pesticide concentrations for Saglek are within the ranges that have been reported elsewhere (Muir *et al.* 1988, 1997; Cameron and Weis 1993).

The presence of subtle PCB differences among Saglek ringed seal were also investigated by examining the relationships of PCB and pesticide concentrations at Nain and other reference areas, and comparing them to observed and predicted results for Saglek. To this end, regression relationships were derived for PCB and pesticide concentrations in Nain samples (n=3) and data that have been reported for other northern locations (n=6 mean values, as presented in Table III-4; Muir *et al.* 1988,1997; Cameron and Weis 1993). The relationships between PCBs and each of DDT, chlordane, and dieldrin are illustrated in Figure III-5. The strongest PCB-pesticide relationship existed with DDT (log PCB = 0.49[log DDT] + 1.54, R^2=0.74, p<0.003), but all three relationships were significant. These results suggest that the relative abundance of OC contaminants varies in a consistent manner across these sites; this result is not surprising in light of the fact that the primary input, in all cases, is long-range transport from distant sources (Muir *et al.* 1997).

To see if the relative abundance of these contaminants follows a similar pattern at Saglek, seal tissue PCB concentrations were predicted from the above equations and the measured levels of DDT, chlordane, and dieldrin in the Saglek samples. If PCB inputs from the local source have increased the relative abundance of PCBs in Saglek seals, the observed PCB concentrations would be expected to deviate from the predicted concentrations. Figure III-6 illustrates both the predicted and observed PCB values for Saglek seal. For all three regression relationships, the predicted PCB concentrations are lower than those observed for four of the five Saglek samples. In the case of both the strongest regression relationship (DDT), and the relationship based on dieldrin, these observed concentrations also fall outside the 95% confidence limits for the predicted values. While these data are exploratory and not conclusive, they do suggest that there are subtle differences in the abundance of PCBs, relative to the other OC contaminants, in seals from Saglek and that PCB concentrations in at least some individuals are locally elevated. A more thorough analysis of the impact of the contaminated sediments on Saglek Bay seal PCB levels would likely require more information about ringed seal contaminant levels both in Saglek Bay and elsewhere in Labrador.

Table III-4. Mean (SD) concentrations (ng/g wet wt.) of organochlorine contaminants in ringed seal blubber.

Region	N	ΣPCB	ΣHCH	ΣChl	ΣDDT	Dieldrin	% Lipid	Reference
Saglek, Labrador	5	2480 (3397)[1]	299 (194)	1028 (1348)	575 (450)	81 (90)	90 (7.5)	This study
Saglek, Labrador (Excluding 1 Sample)	4	1100 (385)[2]	221 (99)	431 (230)	389 (200)	42 (20)	92 (8.7)	
Nain, Labrador	3	480 (116)[3]	135 (33)	91 (48)	228 (105)	23.5 (9.5)	100 (3.3)	
North Baffin Island - Admiralty Inlet	10	794 (879)	227 (141)	463 (306)	1334 (1500)	74 (50)	90	Muir *et al.* 1988
Barrow Strait	19	568 (287)	274 (105)	457 (212)	714 (401)	96 (59)	90	
South Hudson Bay - Sanikiluaq	3	1283 (323)	434 (175)	214 (96.7)	1652 (700)	187 (112)	87.2	Cameron and Weis 1993
West Hudson Bay - Arviat	30	2066 (1390)	336 (127)	1596 (1119)	1662 (1103)	107 (72.5)	92.4 (3.4)	Muir *et al.* 1997
East Hudson Bay- Inukjuaq	4	1234 (636)	275 (123)	708 (453)	1143 (681)	86.6 (102)	94.7 (2.0)	
North Baffin Island - Arctic Bay	10	1435 (1203)	250 (98.6)	1272 (978)	1542 (1905)	115 (61.9)	91.2 (3)	

[1] N=6, [2] N=5, [3] N=4

HCB=hexachlorobenzene

ΣChl=chlordane related compounds

ΣDDT=dichlorodiphenyltrichloroethane related compounds

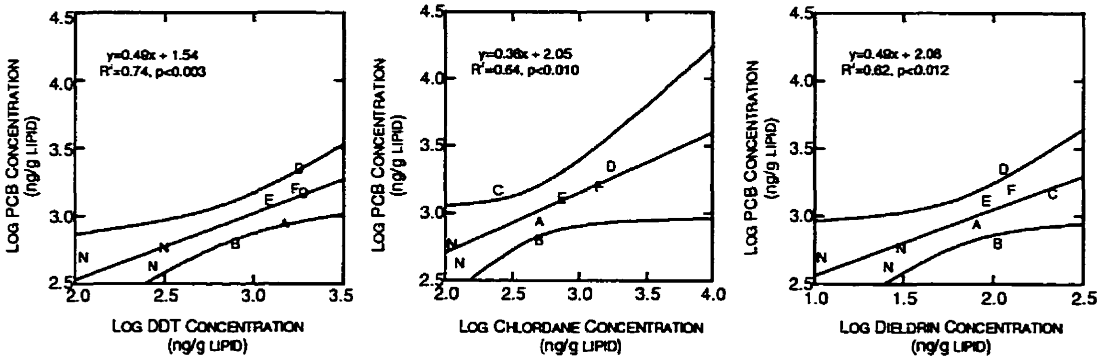

Figure III-1. Regression relationships (and 95% confidence limits) between (log_{10} transformed) concentrations of PCBs and organochlorine pesticides in ringed seal blubber based on results for three seals from Nain, Labrador (N), and results documented elsewhere. Legend: A-Admiralty Inlet, B-Barrow Strait (Muir *et al.* 1988), C-Sanikiluaq (Cameron and Weis 1993), D-Arviat, E-Inukjuak, F-Arctic Bay (Muir *et al.* 1997). Additional information for these sites is provided in Table III-4.

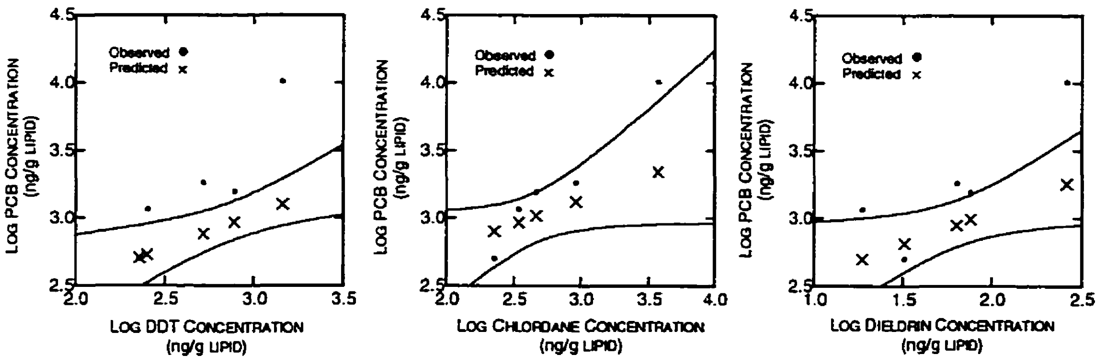

Figure III-2. Concentrations of PCBs and pesticides (log_{10} transformed) measured in ringed seal blubber from Saglek Bay, Labrador (=observed), and PCB concentrations predicted from the measured pesticide levels and the regression equations provided in Figure III-5 (=predicted).

6. Seabirds

Organochlorine contaminant levels in northern seabirds have been monitored since the mid-1970s (Muir *et al.* 1997). Inuit harvest both eggs and adult birds of several species including seaducks, gulls, murres, and guillemots (Gilman *et al.* 1997). The feeding habits of species vary, but several feed at a high trophic level in the marine food web and can be subject to correspondingly high contaminant biomagnification (Muir *et al.* 1997). Two species were assessed for elevated PCB levels in association with the contaminated sediments at Saglek: great black-backed gulls (*Larus marinus*) and black guillemots (*Cepphus grylle*).

a. Great Black-backed Gulls

Great black-backed gulls are predators and opportunistic scavengers, which may feed on invertebrates, fish, small mammals, other seabirds, and carrion (Good 1998). Their breeding range in the North is limited to northern Labrador and Quebec, where they are relatively abundant. They are considered to be partial migrants, moving somewhat farther south along the coast in the winter, but not undergoing long migrations (Good 1998).

Samples for this study consisted of eggs and adults from Saglek Bay and Nain. In Saglek Bay, the closest observed nest to LAB-2 was located on a small island approximately 9 km away. However, adults have been observed feeding along sections of the shoreline much closer to the site. PCB concentrations for both eggs and adult breast muscle are presented in Table III-5, along with PCB data for glaucous gulls (*Larus hyperboreus*) and herring gulls (*Larus argentatus*) elsewhere in the North. Comparable contaminant data for great black-backed gulls are not available. Glaucous and herring gulls have generalist diets similar to great black-backed gulls (invertebrates, fish, rodents, and eggs of other birds), but are smaller, and unable to prey upon adult birds and other large organisms (Good 1998).

PCB concentrations in great black-backed gull eggs varied from 3340 ng/g, in the single egg from 9 km north of LAB-2, to 805-1350 ng/g for eggs from islands at a distance of 16-18 km from LAB-2 (n=4). These concentrations (as a group) are not significantly elevated relative to the concentrations detected at Nain (ANOVA, $p>0.05$, $df=7$). In comparison to the glaucous and herring gull monitoring results, the results would suggest that Saglek levels are not locally elevated. Similar and higher concentrations to those at Saglek have been reported for a glaucous gull colony in the Arctic Archipelago (Muir *et al.* 1997). Concentrations measured by Braune *et al.* (1999) in Ungava Bay herring gulls are also higher than the Saglek results.

Concentrations in great black-backed gull pectoral muscle are also consistent between Saglek and Nain (ANOVA, $p>0.05$, df=14). PCB concentrations at both sites were highly variable, with coefficients of variation exceeding 1.0 (1.8 and 1.3 for Saglek and Nain, respectively). Four birds, two from each location, had PCB concentrations in the range of 5 000 to 20 000 ng/g, concentrations that are uncommonly high for northern animals with the exception of polar bears (Norstrom *et al.* 1988). There was also one extremely high concentration (54 500 ng/g) among the pectoral muscle samples from Saglek. These results are higher than pectoral muscle results reported for either glaucous or herring gulls in other studies (Langlois and Langis 1995; Braune *et al.* 1999).

Different dietary preferences among individual great black-backed gulls may be responsible for at least some of this variation. Muir *et al.* (1997) attributed substantial differences in contaminant levels among gull colonies to dietary differences (Muir *et al.* 1997). While many great black-backed gulls become specialized predators on seabirds, some individuals consume almost entirely fish and invertebrates, and others consume high proportions of terrestrial species (Good 1998). Terrestrial wildlife in the North typically have much lower PCB concentrations than do marine wildlife, so this latter diet would likely result in substantially lower PCB burdens than a diet dominated by seabirds (Thomas *et al.* 1992; Muir *et al.* 1997). Similarly, biomagnification is reduced for predators consuming at a lower trophic level (Muir et al. 1997). Foraging behaviour is also influenced by age, sex, and the nutritional requirements of different life stages (e.g. egg formation, Good 1998). These parameters were not documented in this study, but may also be contributing to the variation in the data.

Table III-5. Mean (SD) PCB concentrations (ng/g wet wt.) in gull eggs and pectoral muscle for Saglek Bay and elsewhere in northern Canada.

Species	Region	N[1]	ΣPCB	% Lipid	Reference
A. Eggs					
Great Black-backed Gull	Labrador – Saglek Bay	5	1180 (513)	7.6 (2.2)	This study
	Labrador – Nain	4	965 (537)	8.0 (0.87)	
Glaucous Gull	Arctic Archipelago – Browne Island	5 (2)	1262	8.4	Muir *et al.* 1997
	Arctic Archipelago – Prince Leopold Island	5 (2)	3330	8.9	
	South Beaufort Sea – Anderson River Delta	5 (2-3)	316	8.4	
	Central/Western Arctic – Coppermine	5 (3)	462	8.6	
Herring Gull	Ungava Bay – Kangiqsualujjuaq	1 (5)	2665	10.2	Braune *et al.* 1999
	Southeast Hudson Bay – Great Whale Area	2 (7)	2372	-	Langlois and Langis 1995
B. Pectoral Muscle					
Great Black-backed Gull	Labrador – Saglek Bay	8	10090 (18285)	4.1 (0.67)	This study
	Labrador – Nain	8	4120 (5484)	3.8 (0.92)	
Glaucous Gull	East Hudson Bay-Inukjuaq	1 (3)	782	6.61	Braune *et al.* 1999
	Southeast Hudson Bay – Kuujjuarapik	1 (2)	2224	4.91	
	Northeast Hudson Bay – Salluit/Ivujivik	1 (3)	1666	7.07	
Herring Gull	East Hudson Bay-Inukjuaq	1 (2)	1230	6.17	
	Southeast Hudson Bay – Kuujjuarapik	1 (3)	2369	2.88	
	Southeast Hudson Bay – Great Whale Area	1 (6)	1988	-	Langlois and Langis 1995

[1] Number of samples analyzed individually, or number of pools (number of samples per pool)

b. Black Guillemots

Black guillemots are diving alcids that inhabit coastal arctic and subarctic waters year round (Muir *et al.* 1997). Their diets consist of fish and invertebrates found on or near the sea bottom such as marine worms, shellfish, amphipods, copepods, mysids, arctic cod, sandlance, eelpout, and sculpin (Cairns 1981, 1987; Bradstreet and Brown 1985). In Saglek Bay, black guillemots nest in small numbers along the steep bedrock shoreline east and west of the beach remediation site. Greater numbers nest on small islands, the nearest of which are located near Bluebell Island and near the southeast tip of Big Island. Eggs were obtained from each of these nesting sites relatively close to LAB-2, and from islands deeper in Saglek Bay, at a distance of 16-18 km from LAB-2. For reference purposes, eggs were also collected from islands near Nain. Adult guillemots were collected from flocks in both regions, so the specific locations of their nests are not known. PCB concentrations for both eggs and adult pectoral muscle are presented in Table III-6.

PCB concentrations in eggs differ significantly among the four Saglek Bay sites, with concentrations near LAB-2 substantially elevated relative to the more distant island sites (ANOVA, $p<0.002$, $df=21$). Concentrations decrease along a strong spatial gradient away from LAB-2, declining by more than a factor of 40 between the nearest shoreline nests (mean 18 300 ng/g wet wt.) and the furthest island sites (435 ng/g) (Table III-6). This spatial pattern corresponds to the distribution of PCBs in marine sediments and benthic species such as clams and shorthorn sculpin, which suggests that there is a significant PCB transfer pathway up this food web to guillemots. Benthic prey such as marine worms, crustaceans, shellfish, sandlance, and sculpin, have been noted elsewhere in black guillemot diets (Cairns 1981, 1987; Bradstreet and Brown 1985). Black guillemot egg PCB residues are approximately 5-10 times higher than the corresponding residues in shorthorn sculpin, consistent with food web biomagnification (Macdonald and Bewers 1996). It also appears that uptake and accumulation patterns are site-specific and localized, consistent with black guillemots foraging very close to their individual nests. Foraging distances of 1.5 km, 4 km, 7 km, and 15-20 km have all been reported in other studies (Bradstreet and Brown 1985). Behaviour consistent with the lowest of these records may account for the distinct concentration differences among the nest sites in Saglek Bay.

PCB concentrations in the pectoral muscle of adult black guillemots were also significantly elevated in Saglek Bay, exceeding concentrations in Nain birds by more than an order of magnitude (ANOVA, $p<0.007$, $df=16$). The maximum concentration measured in pectoral muscle samples was lower than the maximum for eggs, even after accounting for the differences in lipid content (Table III-6). Relatively little information is available concerning pectoral muscle PCB levels in other areas of the North. However, the results for pooled samples from east Hudson Bay and Ungava Bay reported by Braune *et al.* (1999) appear to be lower than the results for both Saglek and Nain in this study. It is impossible to say with the current information whether this disparity reflects variation due to age, diet, or season of collection, or whether it may reflect regional contaminant differences between Labrador and these areas. The egg PCB concentration measured in an Ungava Bay pool was also lower than the corresponding Nain results of this study, so regional trends may warrant further investigation.

Table III-6. Mean (SD) PCB concentrations (ng/g wet wt.) in black guillemot eggs and pectoral muscle in Saglek Bay and elsewhere in northern Canada.

Region	N[1]	ΣPCB	% Lipid	Reference
A. Eggs				
Northern Labrador - Saglek Bay				
-1-2 km from LAB-2	8	18300 (17773)	8.3 (2.5)	This study
-Island 5 km E of LAB-2	3	2870 (1785)	11.7 (0.58)	
-Island 6 km NW of LAB-2	8	799 (337)	11.8 (1.88)	
-Islands 16-18 km W of LAB-2	6	435 (176)	10.6 (1.00)	
-Northern Labrador - Nain	5	600 (235)	10.9 (1.78)	
Ungava Bay - Kangiqsualujjuaq	1 (5)	252	11.4	Braune *et al.* 1999
Northern Labrador - Nain	1 (2)	425	7.8	
North Hudson Bay - Nuvuk Island	4 (3)	577	9.4	Muir *et al.* 1997
North Hudson Bay - Walrus Island	5 (3)	300	11.7	
Arctic Archipelago - Prince Leopold Island	4 (3)	318	10.1	
B. Pectoral Muscle				
Northern Labrador - Saglek Bay	10	2570 (2230)	2.0 (0.20)	This study
Northern Labrador - Nain	8	120 (35.2)	1.9 (0.34)	
East Hudson Bay- Inukjuaq	1 (5)	53	2.81	Braune *et al.* 1999
Ungava Bay - Kangiqsualujjuaq	1 (5)	44	2.61	

[1] Number of samples analyzed individually, or number of pools (number of samples per pool)

D. Conclusions

Overall, the presence of PCB contaminated sediments in Saglek Bay, Labrador, has resulted in locally elevated PCB concentrations in biota at several different trophic levels of the coastal food web. As expected, tissue PCB concentrations were elevated in benthic invertebrates, particularly infaunal species that contact sediment directly. Consistent with biomagnification theory, shorthorn sculpin had accumulated more substantial PCB burdens; levels were clearly elevated even at sites where sediment PCB concentrations were almost indistinguishable from background.

The PCB loads of black guillemots have also been affected by the Saglek Bay contamination. Both eggs and adult birds had higher PCB concentrations than sediments and benthic species, illustrating the effectiveness of PCB transfer through the food web. Limited mobility and strong linkages to the benthic food web are clearly key factors in promoting this accumulation. Great black-backed gulls had widely varying PCB loads, likely reflecting dietary preferences ranging from terrestrial mammals to invertebrates to other adult seabirds. However, large variation in the PCB loads of seals was an unusual finding, and it is possible that this variation reflects an effect of the local contamination on a small number of individuals. Extremely high PCB concentrations were measured in the tissues of one ringed seal and one great black-backed gull. An increase in the abundance of PCBs relative to the other OC contaminants suggests that, in general, Saglek seal PCB burdens may have been affected in a subtle manner by the local contamination.

In summary, the study results clearly demonstrate that coastal marine sediments and benthic species can be significant pathways for contaminant transfer to multiple higher trophic level consumers. Tissue PCB burdens in shorthorn sculpin, ringed seals, gulls, and black guillemots are surprisingly high, exceeding the Health Canada tolerable daily intake level of 2 ppm (2 000 ng/g). This guideline is based on dietary assumptions not applicable to the North, so is of limited significance, but it does provide a benchmark for comparing the Saglek results to results elsewhere (Kinloch *et al.* 1992). A more meaningful interpretation benchmark may simply be the fact that the levels in Saglek sculpin and guillemots, and the levels in a subgroup of ringed seals and great black-backed gulls, are among the highest ever reported for these species in northern Canada. This fact emphasizes the potential significance of contaminated sediments in the North.

IV. Bioaccumulation of PCBs from Sediments in a Subarctic Marine Ecosystem. 2. Bottom-feeding Fish (Shorthorn Sculpin)

A. Introduction

The potential for contaminated sediments to serve as a source of PCBs to aquatic food webs has been well documented. Elevated tissue PCB concentrations have been measured in benthic invertebrates and demersal fish in association with contaminated sediments under field (Mudroch *et al.* 1989; Lake *et al.* 1990; Connolly 1992, van Bavel *et al.* 1995) and laboratory (Ankley *et al.* 1992; Pruell *et al.* 1993) conditions. Sediments can also be a source of PCBs to non-benthic species such as zooplankton (van der Oost *et al.* 1988; Willman *et al.* 1997) and pelagic fish (Macdonald *et al.* 1993; Haffner *et al.* 1994), and to fish- and insect-eating birds (Ankley *et al.* 1993; Bishop *et al.* 1995; Froese *et al.* 1998).

The transfer of PCBs from contaminated sediments to aquatic biota is a function of both the contaminant bioavailability and the degree of biological uptake and accumulation. Bioavailability depends upon the hydrophobicity of the compound, which is represented by its octanol-water partition coefficient (K_{ow}), and the compound's specific structure (Shaw and Connell 1984). Bioavailability is also affected by characteristics of the sediment, including organic carbon content and particle size (Knezovich *et al.* 1987).

Uptake and accumulation of PCBs depends on a variety of different mechanisms. For benthic infauna, accumulation is usually described as an equilibrium partitioning process in which the distribution of contaminant between organisms and sediment (at equilibrium) is controlled solely by chemical partitioning between organism lipids and sediment organic carbon (Lake *et al.* 1990; Di Toro *et al.* 1991). Thus, the ratio of the lipid-normalized contaminant concentration in an organism to the organic carbon-normalized contaminant concentration in sediment (or biota-sediment accumulation factor – BSAF) is predicted to be constant regardless of the specific properties of the organisms or sediment involved (Morrison *et al.* 1996). However, measured BSAFs are higher than the predicted maximum (1.7) (Lake *et al.* 1990; Boese *et al.* 1995; Tracey and Hansen 1996), and several studies have found variability among species (Lake *et al.* 1990; Pruell *et al.* 1993) and among sediment types (Oliver 1984; Means and McElroy 1997).

Among higher trophic level consumers, the significant modes of contaminant uptake are complex. Direct uptake from water (bioconcentration) can be significant when a contaminant is relatively water soluble (Haffner *et al.* 1994); however, most PCB congeners have very low water solubility (Spacie and Hamelink 1982). Direct uptake from contaminated particulate matter is also a possible pathway (DiPinto and Coull 1997), but few studies have examined its significance. Contaminated food or ingested sediments is by far the most significant uptake pathway for higher trophic level biota (Thomann 1989; Haffner *et al.*1994; van der Oost *et al.* 1996). It has been suggested that dietary sources contribute almost the entire PCB body burden of top predators like lake trout (Thomann and Connolly 1984). Feeding mode, in addition to trophic level, governs the extent of bioaccumulation (Haffner *et al.* 1994; Metcalfe and Metcalfe 1997). Because sediments are a reservoir for PCBs, linkages to benthic- or sediment-based food webs tend to promote PCB accumulation (Ankley *et al.* 1993; Bishop *et al.* 1995; Froese *et al.* 1998).

For complex mixtures of chemicals such as PCBs, the different physical and chemical properties of congeners also affect bioaccumulation (Safe 1994). These properties influence rates of sediment-water partitioning, water-lipid partitioning, dietary assimilation, metabolism, and excretion, such that some PCB congeners are selectively accumulated in aquatic food webs, and others diminished (Shaw and Connell 1984, 1986; Knezovich *et al.* 1987; Niimi 1996b). PCB metabolism has a significant impact on the patterns of PCB accumulation that are observed; the number and position of substituted chlorine atoms both influence the degree to which a congener is metabolized (Boon *et al.* 1989; Niimi 1996b). Because congeners have different toxic potencies, congener-specific bioaccumulation patterns are very significant (Safe 1994).

The present study examines the transfer of PCBs from sediments to bottom-feeding fish in the subarctic coastal marine ecosystem of Saglek Bay, Labrador. Sediment-biota PCB transfer in northern marine systems has received relatively little study, despite significant differences between northern systems and their southern counterparts (Pederson 1989; Alexander 1995), and significant concerns about the presence of PCBs in the North (Muir *et al.* 1992, 1999). Northern marine systems, and particularly the coastal systems, typically have low levels of sediment organic carbon and high levels of organism lipids (Muir *et al.* 1997), which may significantly modify bioaccumulation trends. Benthos also play a relatively more important role in northern marine food webs, and the implications of this role for contaminant transfer have not yet been evaluated (Alexander 1995).

As indicated in Chapter III of this thesis, contaminated sediments in Saglek Bay have resulted in substantial PCB accumulation in shorthorn sculpin (*Myoxocephalus scorpius*), common bottom-feeding fish. This Chapter presents a detailed and congener-specific characterization of the sediment-sculpin PCB transfer using data from monitoring sites at distances of up to 25 km from the PCB source. The data provide insights as to the possible influence of subarctic environmental conditions (e.g. low sediment organic carbon), varying contaminant concentrations, and specific organism attributes, on PCB bioaccumulation.

B. Materials and Methods

1. Sample Collection

Major collections of marine sediment and shorthorn sculpin samples were made during the period 1997-1998, with a few additional sediment samples also taken in 1999. The details of sample collection and preparation are provided in Chapter III.

2. Analytical Techniques

PCB analysis, conducted by Axys Analytical Services Ltd., and organic carbon analysis by the Geological Survey of Canada Atlantic Region, are described in detail in Chapter III. Quality control information is provided in Appendix A.

3. Computational Methods and Statistical Analyses

a. General

PCB analyses were conducted on a congener-specific basis for sculpin samples and on either a congener-specific or Aroclor-equivalent basis for sediments. A detailed explanation of these approaches is provided in Chapter III.

b. Distribution of PCBs in Saglek Bay Sediments

The distribution of PCBs in Saglek Bay sediments was estimated by interpolating the results for 243 surface sediment samples, as described in detail in Chapter III. The map was extended to cover an area approximately 5.5 x 12.5 km to correspond to 12 sculpin collection sites. The location of these sites with respect to the estimated distribution of PCBs in sediments is presented in Figure IV-1. Sites are numbered according to their proximity to LAB-2, which is stated in Table IV-1. A single sediment PCB concentration estimate was generated for each of these sites using the mean grid map value in the 500 m by 500 m area around the site of sculpin capture. While there is little quantitative information about shorthorn sculpin distribution patterns, this area is consistent with sculpin movement observations made by Pepper (1974) and Ennis (1970b). The sediment PCB concentration associated with sculpin from background sites (>13 km from the beach - outside the area of the grid map) was calculated from the average (mean) of five background sediment samples (0.4 ng/g dry wt.). The organic carbon content of sediment from all sculpin areas was estimated at 0.3% based on the average water depths in these areas and the observed linear relationship between sediment organic carbon content and depth (% organic carbon = 0.006*water depth in metres + 0.11, R^2=0.65, p<0.001). The variety of other computational methods and statistics that are employed in this Chapter are described as they arise.

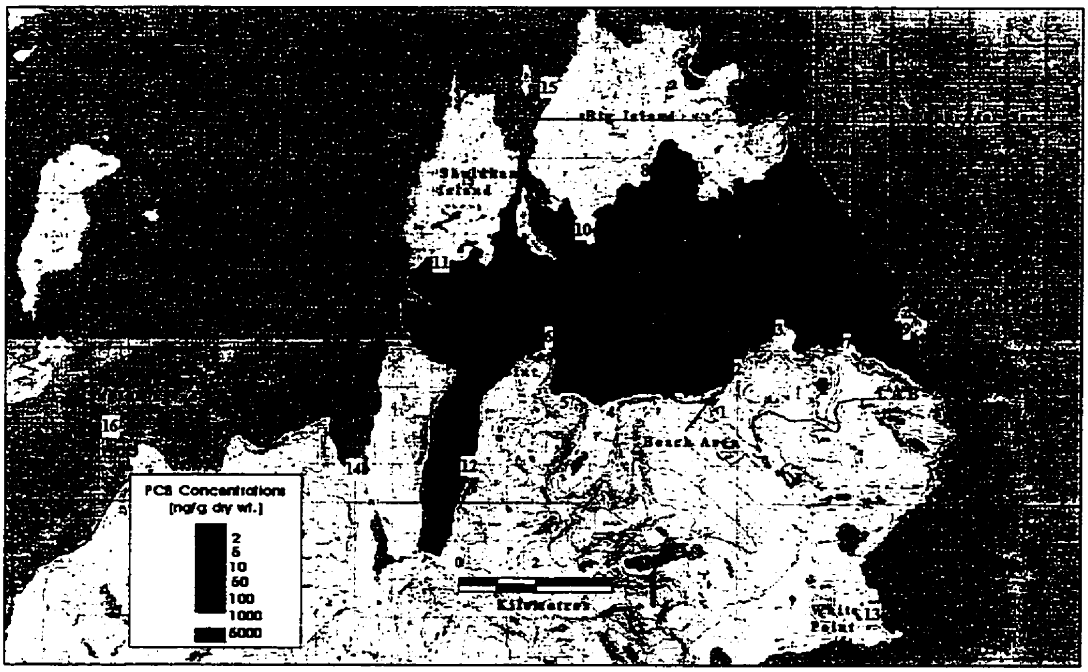

Figure IV-1. Numbered locations of shorthorn sculpin sampling and estimated distribution of PCBs (ng/g dry wt.) in Saglek Bay sediments.

C. Results and Discussion

1. Total PCB Concentrations in Shorthorn Sculpin

PCB concentrations in shorthorn sculpin tissues (whole body minus liver) are briefly outlined in Chapter III and are summarized (mean ± SD) in Table IV-1, along with associated sediment PCB concentrations. A more detailed exploration of sculpin bioaccumulation data was conducted in this portion of the study to examine differences due to tissue lipid content or sculpin age, length and sex. Age class information by site is indicated in Table IV-1 and the overall profile provided in Figure IV-2. These results are also discussed in detail below.

PCB concentrations in sculpin whole livers were measured in a subset of samples to examine the tissue distribution of PCBs. Consistent with partitioning theory, liver PCB concentrations were tightly correlated with whole body concentrations (Pearson $r=0.99$, $p<0.001$, $n=25$) and approximately equivalent on a lipid weight basis. The lipid content of livers and whole body homogenates averaged 7.2% ± 3.70% and 1.52% ± 0.59%, respectively (mean ± SD, n=25, 140), and did not significantly differ according to either sex or age.

Sculpin ages ranged from 3 to 9 years and age classes were not equally represented at the sample sites (ANOVA, $p<0.001$, $n=125$). Eight and 9-year old fish were collected at only two sites (9.5 and 13.5 km west of the beach), while collections were exclusively 3-year fish at two other sites (3 and 4 km west). Overall, the sampled population had a skewed age distribution (Figure IV-2). Among female sculpin, both age and length had significant negative relationships with PCB concentration ($R^2=0.17$, $p=0.009$, $n=38$; log (PCB ng/g lipid) = -0.32(age in years) + 5.40, and $R^2=0.28$, $p<0.001$, $n=43$, log PCB = -0.10(length in cm) + 6.17, respectively). There were no significant trends among males overall, but at two specific sites, male PCB levels increased in relation to age (sites 6 and 9.5 km from LAB-2: $R^2=0.52$, $p=0.066$, $n=7$ and $R^2=0.94$, $p=0.002$, $n=6$, respectively).

Table IV-1. PCB Concentrations in Shorthorn Sculpin and Sediments and Corresponding BSAFs.

No.	Description	Shorthorn Sculpin N	Age (yr)	Lipid (%) Mean (SD)	ΣPCB (ng/g wet wt.)[b] Mean (SD)	Sediment PCB (ng/g dry wt.) 500 m x 500 m	BSAF[a]
1	Beach at LAB-2	10	4-5	1.3 (0.43)	3920 (3510)	751	1.2
2	East of Beach (1 km)	10	3-7	1.8 (0.78)	786 (244)	48.5	3.1
3	Major Point East (3 km)	5	4-6	1.6 (0.65)	292 (300)	10.6	7
4	First Bay West (3 km)	14	3-6	1.5 (0.38)	786 (726)	40.3	3.7
5	Second Bay West (4 km)	5	3	1.8 (0.52)	565 (142)	10.0	11
6	Marker Point (5 km W)	6	4-6	1.3 (0.24)	144 (102)	7.3	5.2
7	Below Old Station, Mouth of Saglek Bay (5 km E)	5	3-7	1.6 (0.35)	422 (200)	5.6	14
8	Anchorage Cove, Big Island (6 km N)	6	4-5	2.0 (0.81)	43.4 (8.67)	3.4	2.2
9	Bluebell Island, Mouth of Saglek Bay (6 km E)	7	4-7	1.1 (0.24)	61.0 (45.2)	1.6	10
10	Eastern Harbour, Big Island (6 km NW)	6	4-7	1.8 (0.75)	38.6 (22.6)	1.8	3.9
11	Shuldham Island (8 km NW)	5	3-5	1.4 (0.22)	25.0 (7.77)	1.3	4
12	St. John's Harbour (9 km W)	4	3-4	1.2 (0.84)	43.9 (6.42)	2.0	6.6
13	White Point, Outside Saglek Bay (7 km S)	10	3-6	1.6 (0.57)	28.8 (10.0)	-	-
14	Torr Bay (10 km W)	10	3-8	1.1 (0.44)	17.6 (19.9)	-	-
15	North Shore of Big Island (11 km N)	10	3-6	2.0 (0.82)	16.4 (14.2)	-	-
16	Background Sites in Saglek Fjord (>13 km)	17	3-9	1.5 (0.60)	10.4 (8.93)	0.4	5.8

[a] BSAF = ratio of lipid-normalized sculpin PCB concentration to 0.3% organic carbon-normalized sediment PCB concentration.

[b]ΣPCB (ng/g wet wt.) measured in whole body minus liver.

[c] Age estimated from growth curve of rest of dataset.

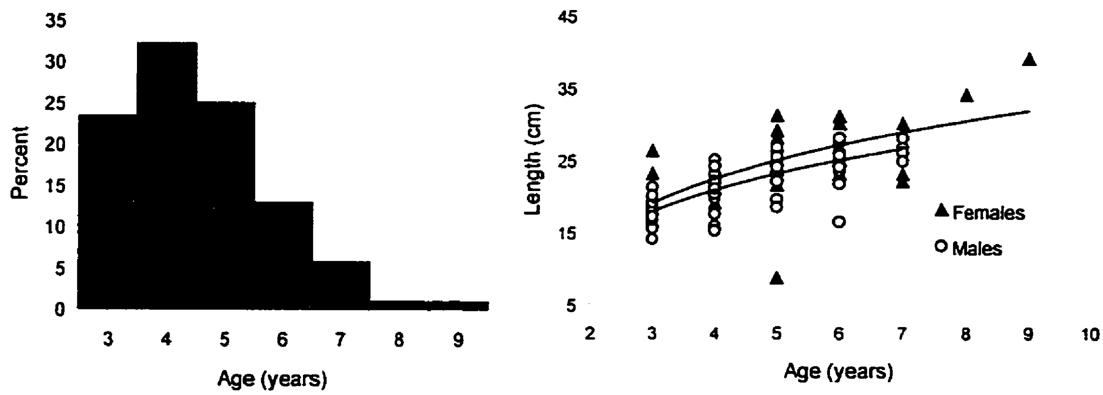

Figure IV-2. Age composition of Saglek Bay shorthorn sculpin (n=125) and growth curves for males and females.

The negative relationship between female sculpin PCB concentrations and age is generally counter to predicted relationships (e.g. Jensen *et al.* 1982; Sijm *et al.* 1992). While fish growth effectively dilutes PCBs in fish biomass, uptake tends to exceed this and other routes of elimination as fish growth rates decline with age (Pastor *et al.* 1996). As suggested by the growth curve in Figure IV-2, the sculpin sampled in this study appear to be past the age of most rapid growth. Because food intake does not decline with age, concentrations after this time are expected to increase or, as a minimum, attain steady state concentrations (Norstrom *et al.* 1976; Thomann and Connolly 1984; Sijm *et al.* 1992). Nevertheless, decreasing contaminant concentrations with fish age have been observed in previous studies (Larsson *et al.* 1992; Pastor *et al.* 1996). The decreases have been attributed to continuing growth dilution effects, improved metabolic capacity with age, and reproduction (Larsson *et al.* 1992; Pastor *et al.* 1996). In this study, reproduction is the most likely explanation because the concentration decreases are observed only in female fish. Sijm *et al.* (1992) incorporated reproductive elimination into a biomagnification model as a repeated 30% loss every reproductive cycle but predicted effectively steady state concentrations over the life of an adult. In female sculpin, sixty percent reach sexual maturity between the ages of 3 and 6 and subsequently spawn every year (Ennis 1970a, b). Fecundity is believed to increase throughout a sculpin's reproductive years, from an average of 15 105 eggs at age 6, to 40 960 eggs at age 11 (Ennis 1970b, younger ages not considered). With these increases in fecundity, reproduction could become an increasingly important means of PCB elimination in aging female fish and produce the overall age trend observed in this study.

2. Sediment-Sculpin Transfer

Sculpin tissue PCB concentrations strongly reflect the level of sediment contamination. The biota-sediment accumulation factors (BSAF) approach was employed to examine the sediment-sculpin PCB relationship, because this technique has been used successfully to assess and predict accumulation in several other studies (e.g. Connor 1984; Breck 1985; van der Oost *et al.* 1988, 1996; Froese *et al.* 1998). It is also a straightforward empirical approach, which does not have the extensive data requirements of most other bioaccumulation models (Lee 1992). BSAFs were calculated as the ratio of sculpin PCB concentrations (lipid-normalized) to sediment PCB concentrations (organic carbon-normalized). BSAF ratios were $\log_{10}$-transformed to improve normality prior to all analyses.

BSAFs were remarkably consistent across 100 sculpin samples with an average value of 3.6 (geometric mean; 95% confidence limits of 2.9 and 4.4, Table IV-1). This average value is also consistent, within a factor of two to four, with BSAF values that have been reported for other benthic species. Benthic infauna BSAFs typically vary between less than 1 and 5 with the majority slightly higher than 1, consistent with equilibrium partitioning theory (Tracey and Hansen 1996). For instance, Lake *et al.* (1990) found an overall BSAF of 1.60 ± 1.34 (mean ± SD, n=30) for various benthic invertebrates (*Yoldia limatula, Nephtys incisa, Mercenaria mercenaria, Glycera* sp., *Astarte* sp., and an unidentified Nemartine) at field sites in the New Bedford-Long Island Sound area. Similar or slightly higher BSAFs have been measured in freshwater invertebrates such as clams (*Elliptio complanata,* 2.7-10.4) and crayfish (*Procambarus* sp., 2.0-23.7) in temperate lakes (Macdonald *et al.* 1993). At the low end of the range are freshwater worms (primarily *Lumbriculus variegatus*), with BSAFs averaging 0.87 in the field (Ankley *et al.* 1992).

Reported BSAFs for sediment-associated fish also tend to be in the range of 1 to 10, although higher values have been obtained for long-lived benthic predators such as eels (*Anguilla anguilla*) (van der Oost *et al.* 1988, 1996). Tracey and Hansen (1996) reviewed data from several monitoring studies and found that median BSAFs for 10 fish species were all in the range of 0.66 to 4.31. Macdonald *et al.* (1993) found BSAFs of 1.6-13.8 among bluntnose minnows (*Pimephales notatus* Rafinesque) in temperate lake systems: when data for two shallow, eutrophic lakes were excluded, the BSAFs were less variable (1.6-4.3). Striped mullet (*Mugil cephalus*) BSAFs were also in this range (3.1 ● 1.9, mean ± SD) at a tidal creek with contaminated sediments (Maruya and Lee 1998) and in fourhorn sculpin (*Oncocottus quadricornis)* in the Gulf of Bothnia (median 4.8, van Bavel *et al.* 1995).

Considering the differences between marine and freshwater environments (e.g. organic carbon, salinity, circulation, temperature) and the likely variability among organisms' ecology and physiology, the similarity among reported BSAFs is quite surprising. For instance, the level of total organic carbon (TOC) in the sediments that have been examined typically varies from 1 to 5% in marine systems to 10-12% in some freshwater lakes (Lake *et al.* 1990; Ankley *et al.* 1992; Macdonald *et al.* 1993; van Bavel *et al.* 1995).

The present study is the first to examine bioaccumulation from contaminated sediments with TOC values consistently less than 0.5%, so it is interesting that BSAF results are also in the range of 1 to10. Because of the BSAF definition, order of magnitude decreases in TOC could bring about equivalent changes in BSAFs, if all other parameters remained unchanged. One explanation for the observed BSAF consistency (in this and other studies) may be enhanced PCB bioavailability from low TOC sediments; this factor would tend to increase biota tissue PCB concentrations, and exert a compensatory effect on BSAFs.

While there is general consistency for BSAF values among studies and sites, several possible sources of variability have also been noted. In particular, a general trend is for a negative relationship between BSAFs and sediment contaminant concentrations (Lee 1992). This relationship has not been confirmed, primarily because of a possible interaction effect of TOC, which tends to co-vary with sediment contaminant concentrations (Knezovich *et al.* 1987; Boese *et al.* 1995). The particle size distribution of sediments and water-body parameters such as depth, nutrient status, and circulation, are also potential confounding factors (Lake *et al.* 1990; Macdonald *et al.* 1993). Nevertheless, Lake *et al.* (1990) observed distinctly higher invertebrate BSAFs at sites with lower contaminant concentrations (15.0-48.3 ng/g dry wt.) than at more contaminated sites (328-9 00 ng/g). This large difference in PCB concentration appeared to be the causal factor in the BSAF difference, but the relationship could not be confirmed because the sediments also differed in TOC by a factor of 1.5 (Lake *et al.* 1990). van der Oost *et al.* (1996) have recently reported similar suggestive, but inconclusive, results.

The present study also suggests that a BSAF-sediment contaminant concentration relationship is possible. Across three orders-of-magnitude difference in sediment PCB concentrations, the data show a weak but significant negative correlation between concentration and BSAF values (both $\log_{10}$ transformed, Pearson $r = -0.46$, $p<0.001$, $n=100$). In Saglek, sediment PCB concentrations and TOC do not positively co-vary as they do elsewhere, so this trend cannot be attributed to enhanced bioavailability in low TOC conditions (Boese *et al.* 1995). A more likely explanation could be the absence of equilibrium between sediment and biota contaminant levels near the high PCB concentration area at Saglek. Because of the processes involved in uptake and accumulation, there is typically a time-delay between sediment PCB contamination and equilibrium-level bioaccumulation (Ankley *et al.* 1992). If, as the sediment PCB distribution suggests, PCB inputs to the beach area occurred recently, the sculpin PCB accumulation may also be early on in its time-course. The time required for benthic fish to attain steady-state BSAFs given constant sediment contaminant levels has been estimated at months to years (Landrum and Robbins 1990; Ankley *et al.* 1992). Unfortunately, the timing of PCB inputs from the terrestrial contamination is unknown, so it is not possible to thoroughly evaluate this hypothesis.

The presence of concentration-related or equilibrium-related differences in BSAF values suggests that the BSAF approach may not be the most suitable screening tool for assessing sediment-biota contaminant transfer (Lee 1992). For the data of this study, an equally simple alternative approach to describe sediment-sculpin PCB transfer is a log-log relationship as illustrated in Figure IV-3. This relationship is described by: log (sculpin PCB in ng/g lipid) = 0.79 (log (sediment PCB in ng/g OC)) + 1.25 (R^2=0.80, p<0.001, n=100). The relationship is better described by a polynomial equation: log y = -0.083 (log x)^2 + 1.38 (log x) + 0.34 (R^2=0.83). These techniques or other nonlinear approaches (e.g. power relationships) may represent more appropriate tools for assessing bioaccumulation when sediment contamination spans a wide range of concentrations, or when conditions may not be at equilibrium.

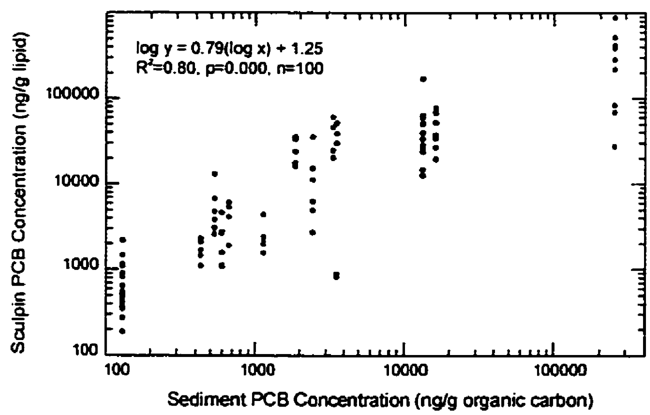

Figure IV-3. Relationship between sediment PCB concentrations and PCB concentrations in shorthorn sculpin tissues from 13 sites in Saglek Bay.

3. Congener-specific Analysis

a. Congener Composition of PCBs in Sediments

Spatial differences in the congener composition of sediment and sculpin PCB residues were examined qualitatively using PCA and visual inspections of congener signatures. The PCA was conducted using the percent contribution of 55 congeners in 130 sculpin samples and 49 sediment samples. This approach eliminates the effect of widely different levels among samples and is commonly used to examine the 'profile' of PCB contamination (Zitko 1994). An arcsine transformation was applied to the data to improve normality. Three principal components were generated that explained 73% of the total variance (39%, 28%, and 6%, respectively).

For sediment samples, the PCA scores create three loose groupings that correspond to distance from the beach remediation site (Figure IV-4). Samples from background sites and exposed, shallow (non-depositional) areas as close as 6 km to the beach, score high on PC(1) and (2). Samples from the subtidal area of the former beach source have low scores on these components. Between these two groups are deepwater samples from the basins of Saglek Bay between the beach and Big Island.

The differences in congener composition among these three groups are illustrated in Figure IV-5. Congeners are more evenly represented in background sediment samples than in samples from close to LAB-2. Background sediments also have a higher proportion of lower chlorinated congeners, consistent with inputs primarily from long-range transport, which tend to be enriched in lower chlorinated congeners (Bright *et al.* 1995a,b; Barrie *et al.* 1997). The congener signatures of sediment samples from the LAB-2 subtidal and basin areas are dominated by congeners which contribute 4% or more to an Aroclor 1260 mixture, which was the original contaminant at LAB-2 (e.g. 149, 153, 138/163/164, 187/182, 174, 180, 170/190; Schulz *et al.* 1989).

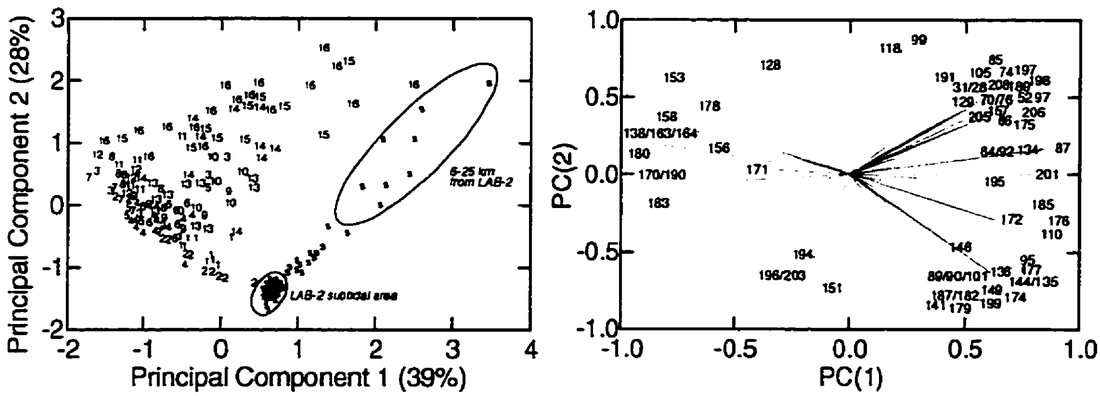

Figure IV-1. Principal components score (left) and loading (right) plots of the congener composition of marine sediments and shorthorn sculpin in the Saglek Bay area. Sediment samples (s) are outlined with respect to their distance from LAB-2. Shorthorn sculpin tissue samples are numbered according to their collection site (Table IV-1).

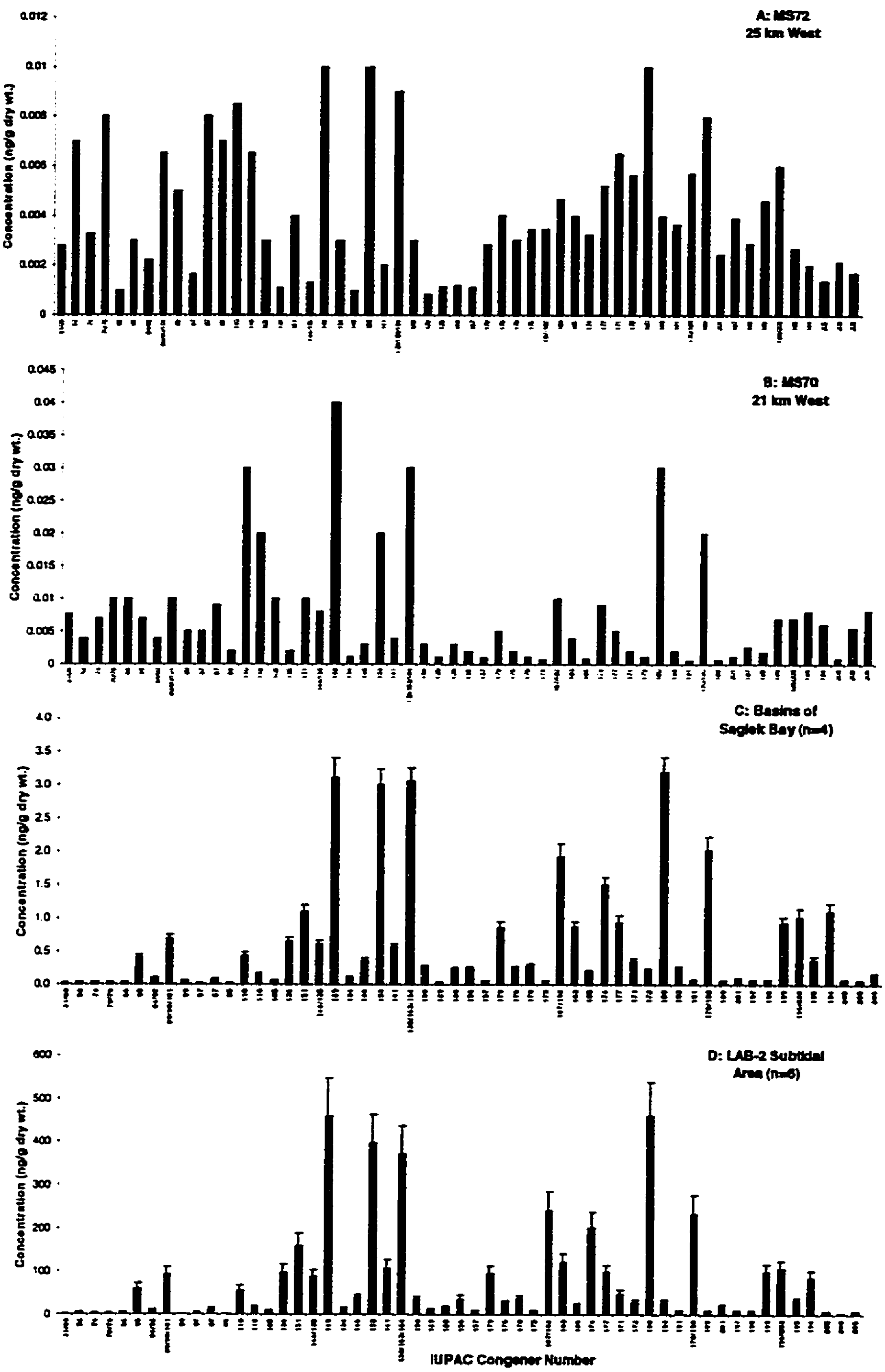

Figure IV-2. PCB congener composition of marine sediment samples from (A & B) background sites in Saglek Fjord, (C) the basins of Saglek Bay, and (D) the subtidal area near LAB-2. (C) and (D) represent mean ± SE.

The PCA congener loadings implicitly reflect these two factors: contribution to Aroclor 1260 and degree of chlorination. Congener loadings on the second principal component, as a function of the abundance of these congeners in Aroclor 1260, are indicated in Figure IV-6. If four outlying congeners (153, 138/163/164, 170/190, 180) are excluded, there is a significant negative regression relationship between PC(2) loadings and the proportion that congeners contribute to Aroclor 1260. This relationship explains the fact that samples from close to LAB-2, which have similar congener signatures to Aroclor 1260, are projected low in the PCA scores plot. The excluded congeners are ones which separate sediments and sculpin on the scores plot, so this role likely explains their lack of fit to the PC(2)-Aroclor 1260 relationship. The regression relationship is described by: PC(2) loading = -7.4 ($\sin^{-1}(\sqrt{(\text{proportion of Aroclor 1260}))}$ + 0.77 (R^2=0.68, $p<0.001$). Degree of chlorination was a less significant factor in the PCA but explained approximately 29% of the variance in PC(3) congener loadings (PC(3) loading = -0.096(# chlorine atoms) +0.61, $p<0.0001$).

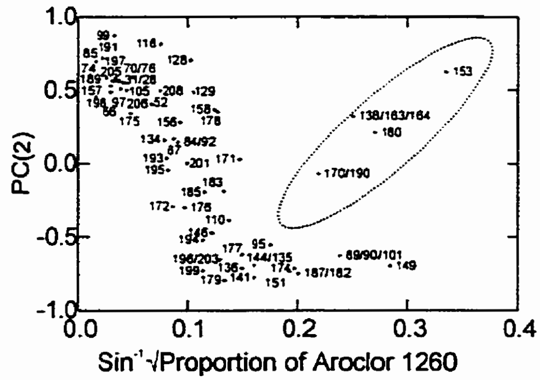

Figure IV-6. Relationship between PCB congener loadings on PC(2) and the (arcsine transformed) percent contribution of these congeners to Aroclor 1260, the commercial mixture used at LAB-2. Excluding the four outlined congeners, the relationship is described by: y = -7.4x +0.77 (R^2=0.68, $p<0.001$).

4. Congener Composition of PCBs in Sculpin

Sculpin tissue PCA scores distribute the samples in a parallel manner to sediments (Figure IV-4). Samples are represented on the plot according to their sampling site (#1-13, Table IV-1). Sculpin from background sites (>13 km from LAB-2) generally score high on PC(1) and (2), along with most sculpin from sites 7-12 km from LAB-2 (#11-15). Sculpin from sites 3-6 km away (#3-10) are loosely clustered lower on these components. Samples from the beach itself and the next closest site (#1 and 2) group independently and have the lowest scores on PC(2). The similarity between this distribution and the distribution of sediment samples reflects the fact that the spatial changes are qualitatively similar. Like sediment, sculpin from background sites have higher proportions of lower chlorinated congeners and reduced proportions of dominant Aroclor 1260 congeners (especially 187/182, 180, and 170/190), compared to samples near LAB-2. Quantitatively, the changes in sculpin PCB residues are much less substantial than the changes in sediment, because congeners 153, 138/163/164, 170/190, and 180 contribute a large majority to all sculpin PCB residues (~60%). These congeners are typically among the most dominant congeners in biological tissues (e.g. van der Oost *et al.* 1988, 1996; Bright *et al.* 1995a,b). To illustrate the relative dominance of these congeners in sculpin PCB residues, average sculpin congener signatures for sites #4 (3 km west of LAB-2) and #16 (>13 km from LAB-2) are presented in Figure IV-7. Bars represent the proportion each congener contributes to the total sculpin PCB concentration (mean ± 95% CI of arcsine transformed data).

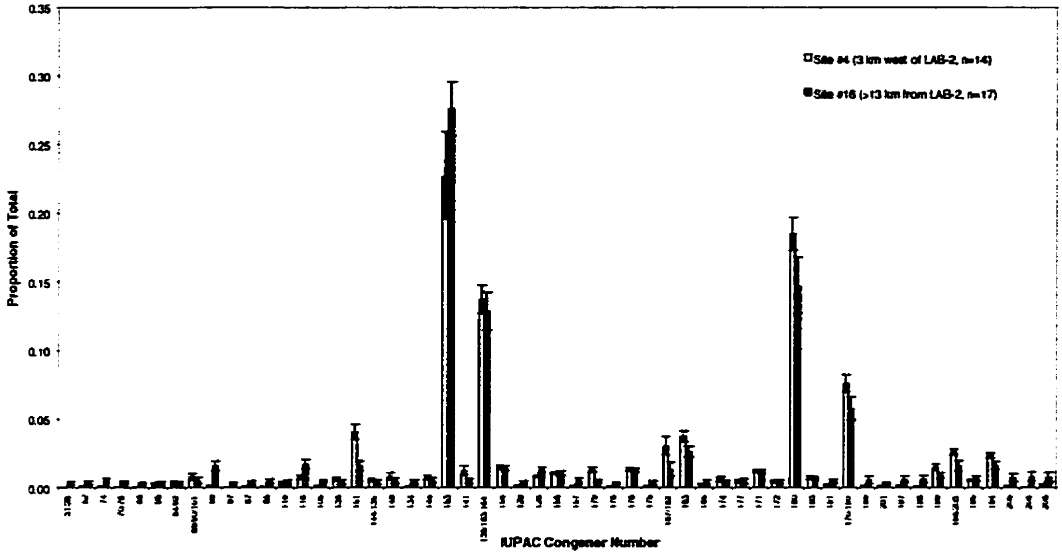

Figure IV-1. PCB congener composition (proportions, mean ± 95% CI) of shorthorn sculpin samples at distances of 3 km and >13 km from LAB-2.

a. Congener-specific BSAFs

To assess whether sculpin-sediment bioaccumulation factors also vary spatially around LAB-2, congener-specific BSAFs for sculpin were examined by PCA (Figure IV-8). Two sites were excluded due to insufficient congener data, leaving 11 sites and 88 samples in total. BSAFs were calculated for the 29 congeners that contributed at least 0.5% to sculpin tissue total PCB concentrations and $\log_{10}$ transformed prior to analysis. The mean sediment congener composition at each sculpin site was scaled according to the total sediment PCB concentration for each site (Table IV-1).

Two principal components were generated which explained 88% of the total variance (77% and 11%, respectively). In contrast to the scores for sediment and sculpin samples, sculpin BSAFs are not separated on the plot according to their distance from LAB-2. The majority of BSAFs are projected into one loose cluster (Figure IV-8). Exceptions to this pattern are the majority of the BSAF values for sites #1 and #2 and two BSAF values for site #3 (the beach and next nearest sites). These sculpin BSAFs are shifted down and to the left by their lower than average BSAF values for most PCB congeners, and unusually high BSAF values for lower chlorinated congeners, especially 89/90/101 and 110 (ANOVA, p=0.046 and 0.013, respectively). Because total PCB BSAFs are unusually low for these sites, it is not unexpected to find low congener-specific BSAFs as well. High BSAFs for congeners 89/90/101 and 110 are surprising for this reason alone, but also because these lower chlorinated congeners have sufficient aqueous solubilities to enable water to act in their transport and transfer (Hawker and Connell 1988). Higher elimination rates are also usually expected for lower chlorinated congeners (Niimi 1996b). These factors should act to minimize their persistence in the environment and biological tissues. BSAFs for these congeners average less than one among the majority of sculpin in Saglek Bay (n=68), and only slightly exceed one at sites #1 and #2 (geometric means = 1.6 and 1.1, respectively, n=20 in total). A possible explanation for these congeners having higher BSAFs near the beach is that there has been a recent input of these congeners to this area, and environmental and biological factors have not yet had an opportunity to minimize their prevalence. The time delay between sediment contamination and equilibrium-level bioaccumulation may affect different PCB congeners to varying degrees. Alternatively, uptake from water would tend to enhance the proportion of these lower chlorinated congeners (Spacie and Hamelink 1982), so the results may suggest that this pathway is of relatively greater importance at the beach site.

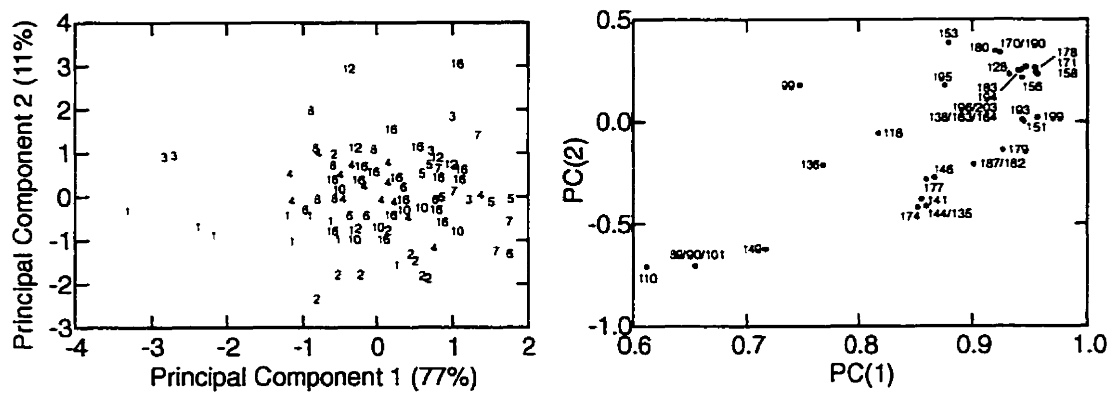

Figure IV-1. Principal components score (left) and loading (right) plots of congener-specific biota-sediment accumulation factors (BSAFs) for shorthorn sculpin. Sculpin are numbered according to their collection site (Table IV-1), although congener-specific BSAFs are consistent across all sites except 1 and 2.

Mean BSAFs for 29 congeners are presented in Figure IV-9 according to IUPAC congener number and octanol-water partition coefficient (log K_{ow}) (geometric means ± 95% CI, excluding sites #1 and #2). Log K_{ow} values are taken from the work of Hawker and Connell (1988). In general, the sculpin BSAF- K_{ow} relationship can be loosely approximated by a bell-shaped or parabolic curve. BSAFs tend to be lowest among congeners with either low (log K_{ow}<6.5) or high (log K_{ow}>7.5) octanol-water partition coefficients. BSAFs are highest among hexa- and heptachlorobiphenyl congeners with log K_{ow} values in the range 6.8 to 7.4.

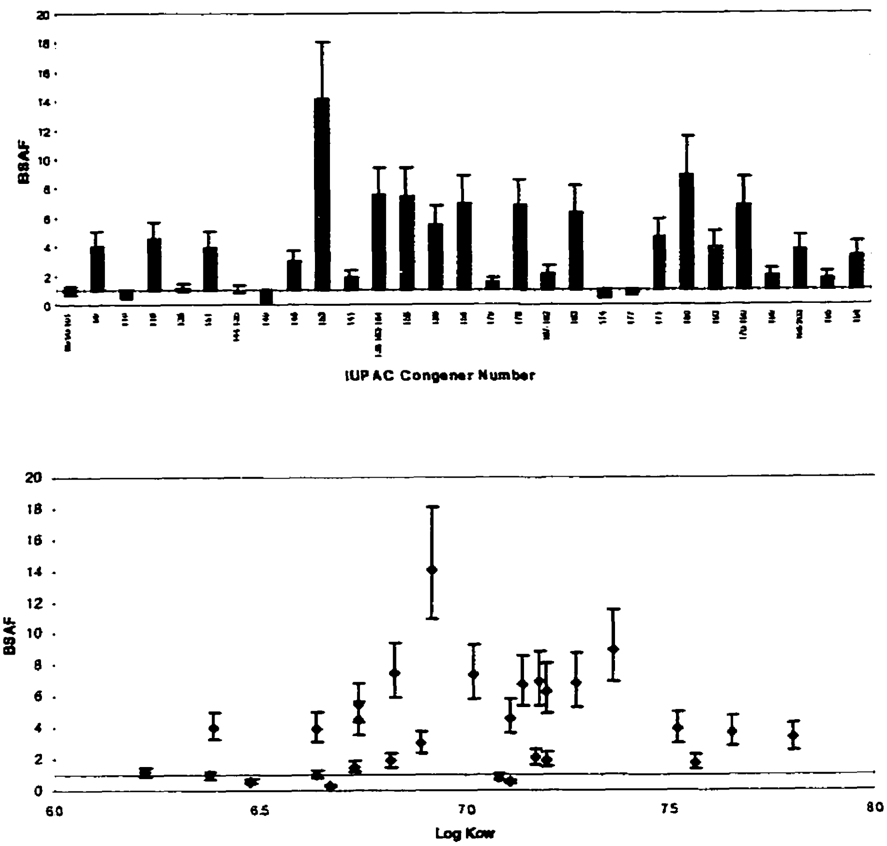

Figure IV-2. Biota-sediment accumulation factors (BSAFs) for 29 PCB congeners (geometric mean ± 95% CI, n = 68). The order of congeners is rearranged in the lower plot according to their octonol-water partition coefficients (log K_{ow} values).

Several different K_{ow}-bioaccumulation relationships for PCB congeners have been reported elsewhere (e.g. van der Oost *et al.* 1988; Ankley *et al.* 1992). There are substantial species differences among benthic invertebrates, with filter-feeders often accumulating lower chlorinated congeners to the greatest degree, and other species showing more complex accumulation patterns (Lake *et al.* 1990; Ferraro *et al.* 1991; Pruell *et al.* 1993). Sandworms (*Nereis virens*), grass shrimp (*Palaemonetes pugio*) (Pruell *et al.* 1993) and crayfish (*Orconectes propinquus*) (Morrison *et al.* 1996) accumulate hexa- and heptachlorobiphenyls to the greatest degree, similar to the sculpin of this study. For invertebrates with this kind of parabolic relationship, congener 153 also tends to be the congener accumulated to the greatest degree (Lake *et al.* 1990; Pruell *et al.* 1993).

Among fish, the role of K_{ow} has often been examined in relation to bioconcentration factors (i.e. chemical uptake from water). Linear bioconcentration- K_{ow} relationships exist for many chemicals with log K_{ow} values 2-5 (Spacie and Hamelink 1982; Shaw and Connell 1986). Spacie and Hamelink (1982) developed an alternative nonlinear bioconcentration model with K_{ow} to account for inconsistencies in the relationship for extremely hydrophobic compounds (log K_{ow}>6). This nonlinear model was supported by studies of PCBs in New Bedford Harbour flounder, where bioconcentration factors increased with log K_{ow} to a maximum value (among hexachlorobiphenyls) and then decreased (Connolly 1992). Other authors have argued that the parabolic or bell-shaped relationship is result of food chain PCB transfer becoming significant (Thomann 1989; Macdonald *et al.* 1993; Metcalfe and Metcalfe 1997). Thomann's (1989) bioaccumulation model predicts that food chain transfer becomes more significant than bioconcentration at log K_{ow} values of 5-6.5 (lower than the log K_{ow} values for most significant Aroclor 1260 congeners; Hawker and Connell 1988; Schulz *et al.* 1989). At this point, bioaccumulation is theoretically a function of uptake, assimilation, and elimination processes; although elimination is largely limited to growth. Uptake and assimilation efficiencies begin to decrease at log K_{ow} values of about 7, such that maximum bioaccumulation factors will be in the log K_{ow} range 6-7 (Niimi and Oliver 1983; Thomann 1989).

Sculpin bioaccumulation patterns (Figure IV-9) also indicate substantial congener-specific variability within homolog and K_{ow} groupings. In total, 12 congeners were bioaccumulated by more than a factor of four; this set includes congeners with 5, 6, and 7 chlorine atoms. Congener 153 was accumulated to the greatest degree (BSAF=14), followed by congener 180 (BSAF=8.9). High BSAF values for these congeners have also been observed in a variety of other studies (Lake *et al.* 1990; Pruell *et al.* 1993; van der Oost *et al.* 1996).

Seven congeners in this study have BSAFs less than or approximately equal to 1 (Figure IV-9). These congeners include two pentachlorobiphenyls (89/90/101 and 110), three hexachlorobiphenyls (136, 144/135, and 149), and two heptachlorobiphenyls (174 and 177). Given that they represent various homolog groups, the low BSAFs are most likely due to structure-related effects on uptake or elimination. Congener structure can influence both of these processes, but large differences among congeners are usually attributed to differences in metabolism and excretion (Lake *et al.* 1995; Niimi 1996b). Fourhorn sculpin (*Myoxocephalus quadricornis*), a relative of the shorthorn sculpin examined in this study, also have a demonstrated ability to metabolize at least some PCB congeners (Bright *et al.* 1995b).

Several chemical structures that influence PCB metabolism have been identified in recent literature (e.g. Boon *et al.* 1989, 1994; Bright *et al.* 1995b; Niimi 1996b; Metcalfe and Metcalfe 1997). In general, PCB metabolism in fish appears to be enhanced by the presence of *meta* and *para* positions that are not substituted with chlorine atoms, while different substitution patterns at the *ortho* position have no systematic effects (Boon *et al.* 1989; Niimi 1996b; Willman *et al.* 1997). These chlorine substitution patterns are illustrated in Figure IV-10. Unsubstituted *meta* or *para* positions alone each have some influence on metabolism, with the *para* position being the preferred site of hydroxylation (Safe 1984; Niimi 1996b). Adjacent unsubstituted *meta-para* positions have a much more consistent positive influence than either position alone. Niimi (1996b) found that this configuration (adjacent unsubstituted *meta-para* sites) was relatively common among congeners with low biomagnification factors for smelt (6 of 6 congeners), alewife (3 of 6), freshwater sculpin (12 of 18), and lake trout (2 of 5). Congeners with substituted *meta-para* positions but an adjacent unsubstituted *meta* position can also be metabolized at the *para* position after a 1,2-shift of the chlorine atom to the adjacent (unsubstituted) *meta* position (Niimi 1996b). Both these configurations, however, represent many PCB congeners and, overall, no configuration consistently explains all observed accumulation differences (Niimi 1996b).

Examining the data of this study leads to similar conclusions about the inconsistency of simple structure-bioaccumulation relationships. Six of the seven congeners with low BSAFs (less than or approximately equal to 1) have adjacent unsubstituted carbons at *meta-para* positions: 89/90/101, 110, 136, 144/135, 149, and 174 (Figure IV-10). Only three other congeners share this configuration, congeners 151, 179, and 199, and their BSAFs are also among the lower values observed (3.9, 1.5, and 1.9, respectively). However, the seventh congener with a very low BSAF does not share this structure (congener 177): it has an unsubstituted *meta* position beside substituted *meta-para* sites, and adjacent unsubstituted *ortho-meta* carbons (Figure IV-10). These substitution patterns are also present in nine congeners with BSAFs ranging 1.8-7.5, so they are certainly not the full explanation for the low BSAF of congener 177. Another factor that may be involved is the overall availability of possible hydroxylation sites. In congener 177, the *para* carbon on the second ring structure is unsubstituted such that possible hydroxylation sites exist on both phenyls. None of the nine congeners with similar substitution on their first phenyls and higher BSAFs have an unsubstituted *para* carbon on their second phenyls. Since particular substitution patterns do not appear to be unique to readily metabolized PCBs (Niimi 1996b), the overall hydroxylation potential of congeners may be an alternative approach for interpreting observed accumulation patterns.

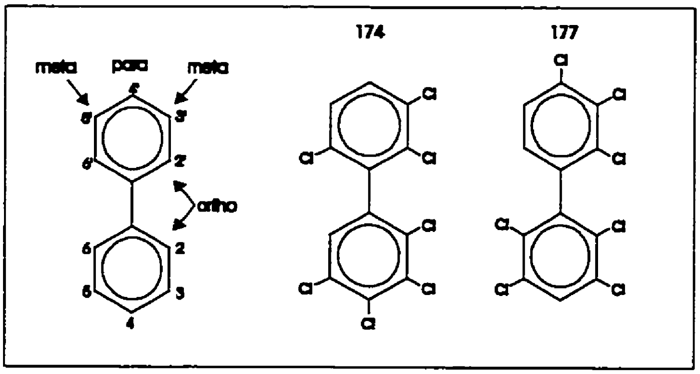

Figure IV-3. Congener substitution patterns. Both indicated congeners were depleted in sculpin PCB residues, suggesting that they were metabolized.

D. Conclusions

In this subarctic coastal marine ecosystem, the accumulation of PCBs in shorthorn sculpin is tightly linked to sediment contaminant levels. Despite extremely low organic carbon levels, biota-sediment accumulation factors are consistent with the range of 1 to 10 that has been observed in many temperate-zone marine and freshwater studies. Trends in fish PCB burdens with age differ between males and females, likely due to elimination via mother-to-young transfer.

On a congener-specific basis, the composition of the PCB source to the ecosystem affects the PCB residues of both sediment and sculpin; for instance, at greater distances from the site of a local PCB input, the influence of long-range transport inputs is evident. Thus, both these environmental matrices would be useful indicators for monitoring local and long-range inputs to the North. A close relative of shorthorn sculpin (fourhorn sculpin, *Myoxocephalus quadricornis*) more common to estuarine environments, has been proposed as an indicator species for Arctic monitoring (Khlebovich 1997); the results of this study support this proposal.

While different PCB sources produce different congener patterns in sediment and sculpin, the transfer of PCB congeners between these matrices is remarkably uniform. In general, congeners with log K_{ow} values between 6.8 and 7.4 (hexa- and heptachlorobiphenyls) were transferred most effectively from sediment to sculpin. Congeners 153 and 180 were selectively bioaccumulated by factors of 14 and 9, respectively. Substantial differences in bioaccumulation factors between congeners with an equivalent number of chlorine atoms (and similar K_{ow} values) suggest that congener structure is also an important factor in the bioaccumulation process. Enhanced metabolism and excretion of congeners with adjacent unsubstituted *meta-para* carbon atoms explains some, but not all, of the observed pattern. The overall number and quality of possible hydroxylation sites per congener (including both phenyls) may be able to explain congener differences that are not obvious from the presence/absence of specific substitution patterns.

V. GENERAL DISCUSSION

Localized sediment PCB contamination from a former military installation in Saglek Bay, Labrador, provided an excellent opportunity to examine PCB bioaccumulation in a subarctic coastal marine ecosystem. Potential receptors for the contamination included marine invertebrates, fish, mammals, and seabirds. The objectives of this thesis were twofold: 1) to determine which components of the system were susceptible to the bioaccumulation of PCBs from the contaminated sediments, and 2) to examine, on a detailed and congener-specific basis, sediment-biota PCB transfer, using the bottom-feeding fish shorthorn sculpin. Very little is known about contaminant levels in benthic and lower trophic level organisms in northern systems, and possible pathways of contaminant transfer from a source, like sediments, through benthos, to higher trophic level biota. The process of sediment-biota PCB transfer may, itself, differ in northern ecosystems because of the unique environmental and biological conditions. This information is of critical significance because the presence of PCBs in northern marine food webs represents a critical pathway of contaminant transfer to Inuit.

The results of this study clearly demonstrate that PCB contaminated marine sediments in subarctic coastal ecosystems can serve as a substantial contaminant transfer pathway to aquatic biota at several levels of the food web. As expected, sediment-associated PCBs were readily available to benthic invertebrates, particularly infaunal species that contact sediment directly. Bioaccumulation was also substantial in bottom-feeding fish (shorthorn sculpin, *Myoxocephalus scorpius*), consistent with food web PCB transfer from benthic invertebrate prey and possibly direct contact with sediment. Filter-feeding mussels, which are affixed to boulders and not in contact with sediment, accumulated very little contamination, consistent with results reported for filter-feeding species in other studies. Uptake from the water column is unlikely to be significant for PCBs, especially the Aroclor 1260 mixture used at Saglek, due to their low aqueous solubility.

The data suggest strong food web and contaminant linkages between benthic invertebrates and fish and a top predator seabird: the black guillemot (*Cepphus grylle*). Although the transfer of PCBs from sediments to aquatic birds has been observed in several temperate freshwater systems (Ankley *et al.* 1993; Bishop *et al.* 1995; Froese *et al.* 1998), the results of this study are the first to demonstrate this transfer in a coastal subarctic system. The PCB transfer through the benthic food web linkages appeared to be highly efficient, and resulted in surprisingly high concentrations in black guillemot eggs and adults. Whether this efficiency reflects properties of the organisms, the trophic interactions, the environmental conditions, or some combination cannot be determined from the available data. However, it appears that this species is a highly localized predator, feeding close to its nesting site, and is vulnerable to substantial biomagnification from contaminated sediments near the nesting site.

Only one of the predator species examined had consistently low PCB burdens in Saglek Bay and elsewhere: arctic char (*Salvelinus alpinus*). Although this species has a relatively high lipid content, a factor expected to promote bioaccumulation, their primarily pelagic diet likely limits their PCB exposure. It is also unlikely that arctic char inhabit Saglek Bay for extended periods of time. As anadromous fish, arctic char undergo seasonal migrations between the marine system and freshwater spawning areas; all potential spawning rivers are well removed from the contaminated area of Saglek Bay.

For other higher trophic level biota, differences in feeding habits introduce substantial variation in contaminant burdens, so impact from the local source was difficult to identify. Some great black-backed gulls (*Larus marinus*) in Saglek Bay have equivalent PCB residues to polar bears (*Ursus maritimus*), which are the top predators in northern marine food webs and experience high PCB biomagnification. The most likely explanation for equally high levels in some great black-backed gulls is that some individuals are feeding at a trophic level that is effectively equivalent to polar bears. Predation on other seabirds or scavenging on marine mammal carcasses could both have this effect. However, it is also possible that some of the high PCB burdens do relate to the local contamination, perhaps via predation on Saglek Bay sculpin or black guillemots.

Ringed seal (*Phoca hispida*) PCB levels were also highly variable and an extremely high PCB load was detected in one Saglek Bay specimen. To attempt to interpret the limited data of this study in the absence of any other northern Labrador seal data, PCB concentrations were examined in comparison to the concentrations of organochlorine (OC) pesticides for which LAB-2 is not a significant source. The principal source of these contaminants to all of northern Canada is long-range atmospheric and marine transport, so local differences in the relative abundance of these contaminants are an indication of the likely presence of a local source. The results of this analysis suggest, but cannot conclusively prove, that PCBs represent a greater proportion of the total OC burden in Saglek seals than in seals elsewhere, which implies that the Saglek sediment contamination has been a source of PCBs to these organisms. This finding is very significant, given the importance of ringed seal as a traditional food resource for Inuit. To date, study has focused on the linear Arctic cod-ringed seal trophic connection and pathway of contaminant transfer. However, the results of this study suggest that ringed seal have benthic food web linkages and may accumulate contaminants via these pathways, as well.

Close analysis of sculpin PCB accumulation patterns provided some additional insights into the mechanisms by which PCBs are introduced, transferred, and accumulated in northern food webs. The phenomenon of bioaccumulation has been well studied in several temperate-zone aquatic systems, but the processes are still poorly understood, and few investigations have considered ecosystems outside the temperate-zone. Overall, the results of the study indicate that both physical (e.g. sediment organic carbon content) and biological (e.g. metabolism) factors influence bioaccumulation. Low sediment organic carbon conditions, which are common in northern coastal ecosystems, appear to enhance the bioavailability of sediment-associated PCBs. This finding is consistent with current theory about PCB bioavailability, but the theory has not previously been tested in equivalent conditions. The consequence of high bioavailability would be efficient PCB transfer from sediments to lower trophic level biota. Since this transfer is the major first step in introducing PCBs to the benthic-based food web, its efficiency would tend to promote PCB accumulation throughout the rest of the food web. This factor may help explain the substantial PCB accumulation that was observed in black guillemots, higher predators of this food web.

Congener-specific analysis of the sediment-sculpin PCB transfer indicated that the composition of bioaccumulated PCBs is highly modified from the composition of PCBs in sediments. This finding implies that toxicity, which varies substantially among different PCB congeners, could not be predicted from sediment PCB measurements alone. Presently, guidelines for PCB contaminated sediments that are aimed at protecting aquatic life are based on the total PCB concentration in sediments, and do not consider either the specific congener composition of the contaminant or the changes that may result from bioaccumulation. The results of this study clearly indicate that both these factors warrant consideration.

The efficiency of sediment-sculpin PCB transfer and the congener-specific accumulation patterns were remarkably uniform across a wide range of sediment (and sculpin) PCB concentrations. Octanol-water partition coefficients (K_{ow} values), which have been used to explain bioaccumulation patterns elsewhere, explained the general patterns observed in this study, but differential metabolism of congeners with different structures also had a substantial effect. Specifically, congeners with adjacent unsubstituted *meta-para* carbon atoms appeared to be more readily metabolized than other congeners with similar K_{ow} values. The presence of adjacent unsubstituted *meta-para* carbon atoms is also known to facilitate PCB metabolism in other species of fish (Niimi 1996b). However, while metabolism affected the pattern of PCB accumulation, there was no evidence that metabolism and excretion of the more polar metabolites represents a significant route for eliminating PCBs and reducing the total PCB burden of exposed organisms.

In summary, this thesis provides some of the first information concerning PCB transfer pathways from subarctic coastal sediments to marine biota with various food web positions. Organisms representing at least three trophic levels are susceptible to PCB accumulation from sediments, including species significant in the diets of Inuit. Linkages to the benthic food web and the corresponding pathways of contaminant transfer have not been identified for many northern species, despite the fact that they ultimately lead to humans. Undoubtedly, the significance of sediments as long-term contaminant sources to northern food webs, and potentially human consumers, warrants further investigation.

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APPENDIX A: QUALITY CONTROL FOR AXYS ANALYTICAL SERVICES LTD.

An internal quality assurance/quality control (QA/QC) program has been implemented throughout the Saglek project to allow the monitoring of data quality on an ongoing basis. Aspects of the QA/QC program and a summary of the results for PCB and organochlorine pesticide analyses are discussed below and described in detail in ESG (1999). All samples were submitted to Axys Analytical Services Ltd. (Axys) with labels that masked any information regarding their site of collection. Analyses were carried out in batches of nine or fewer samples; each batch contained a certified reference material or internal spiked matrix, one procedural blank, and one analytical duplicate.

PCB ANALYSIS

The accuracy of PCB analysis was monitored principally through the use of internal spiked reference materials. The determined values for Aroclor 1242-, 1254- and 1260-spiked soil were within 7% of the expected values (n=23). For congener-specific analyses, the following 8 of the 84 quantified PCB congeners were monitored: 18, 31/28, 52, 95, 118, 138/163/164, 180, 196/203. Recoveries of these congeners from spiked reference materials averaged 97 ± 11% (mean ± standard deviation, n=17) for a soil matrix and averaged 101 ± 12% (n=23) for a tissue matrix. Determined values deviated by more than 30% from the expected values on only two instances. N.I.S.T. Certified Reference Material 1588 (cod liver oil) was also analyzed in seven batches and results were within the margin of error for the standards.

Procedural blanks were below or very close to the limits of detection in all analytical batches. In cases where PCBs were quantified in the blanks (n=5 batches of sediment, 8 batches of tissues), concentrations ranged from 0.001 to 0.39 ng/g.

Precision/repeatability was monitored internally by Axys through the use of analytical duplicates. Relative standard deviations averaged 16, 8.9, and 13% for Aroclors 1242, 1254, and 1260, respectively (n=18). For congener-specific analyses, relative standard deviations averaged 12% for soil/sediment duplicates (n=12) and averaged 11% for tissue duplicates (n=44) across all congeners. PCB congeners that were measured with less than normal precision (average relative standard deviations >30%), which amounted to five congeners in total (16/32, 26, 42, 41/71/64, 137), were excluded from the analyses conducted in this thesis.

External monitoring of precision/repeatability was also conducted by ESG in the course of this research program using blindly submitted field duplicate sediment samples (n=6 pairs). With the exception of one pair, the relative standard deviations for these samples ranged from 3.6% to 30%, consistent with acceptable limits identified in other large QA/QC programs (Zhu 1997). An unacceptably high relative standard deviation (113%) was observed for one pair of sediment samples. Examination of field notes suggests that these samples were likely collected from insufficiently homogenized material, and are therefore not true duplicate samples.

CHLORINATED PESTICIDE ANALYSIS

N.I.S.T. Certified Reference Material 1588 (cod liver oil) and internal spiked reference materials were each analyzed twice in the course of the chlorinated pesticide analyses for this study. Determined values for the certified materials were near or within the error range of the material, at most differing by 36%. For the two internal spiked soil/sediment materials, recoveries for the 23 individual pesticides averaged 101 ± 15% and 86 ± 13% (mean ± standard deviation). No chlorinated pesticides were quantified in procedural blanks (n=5). In analytical duplicates (n=3), the relative standard deviation of quantifiable compounds averaged 10%-13%. Duplicates differed by 30% or more on two instances (31% and 36% for oxychlordane and cis-chlordane, respectively).

SUMMARY

The results of the QA/QC monitoring conducted in the course of the Saglek study provides a high degree of confidence in the quality of the analytical data that has been produced by Axys. PCB analyses, in particular, were thoroughly monitored by the QA/QC program and appeared consistently accurate and precise. Pesticide analyses formed only a minor portion of the study, but also appeared to be conducted reliably, based on the limited number of observations of the monitoring program.

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