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Unifying Ecosystem Concepts and Mercury Biomagnification in an Estuarine Environment Using Stable Isotopes ($\delta^{13}C$ and $\delta^{15}N$)

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ABSTRACT

Isotope ratios of carbon ($^{13}C/^{12}C$) and nitrogen ($^{15}N/^{14}N$), on a parts per thousand (‰) basis relative to a standard, were used to trace carbon flows ($\delta^{13}C$) and trophic positions of organisms ($\delta^{15}N$). Values of $\delta^{13}C$ and $\delta^{15}N$ were obtained for sediments, suspended particulate matter (SPM), plants, and animals found in the Miramichi River Estuary (New Brunswick, Canada) and used to show the relationship between food web structure and patterns of mercury biomagnification.

On a $\delta^{13}C$ and $\delta^{15}N$ basis, three different sources of energy were identified: terrestrial carbon, *in situ* estuarine primary production, and marine phytoplankton. Isotopically depleted $\delta^{13}C$ and $\delta^{15}N$ values verified terrestrial carbon was a major source of energy to estuarine sediments and SPM.

A cluster analysis of mean $\delta^{13}C$ and $\delta^{15}N$ values for 47 abiotic and biotic groups in this study helped to structure the community of plants and animals. Eight distinct clusters were formed: 1) estuarine sediment, and estuarine and freshwater SPM; 2) estuarine and marine primary producers; 3) freshwater fish and submerged terrestrial leaf litter, and estuarine oysters; 4) estuarine filter-feeding invertebrates; 5) estuarine deposit-feeding invertebrates; 6) estuarine planktivorous and benthivorous fish, some benthic invertebrates, and two filter-feeding marine fish; 7) estuarine carnivorous and two benthivorous fish; and 8) double crested cormorant eggs (whites and yolks). The results of this analysis show that for this coastal ecosystem, no distinction can be made in $\delta^{13}C$ and $\delta^{15}N$ values between estuarine and marine primary producers and filter-feeding fish,

whereas freshwater fish and submerged terrestrial leaf litter were characterised by their isotopically light $\delta^{13}C$ values.

Based on measurements of $\delta^{13}C$ and $\delta^{15}N$ differences between a predator and its prey, an average $\delta^{13}C$- and $\delta^{15}N$-trophic enrichment factor (TEF) of 1.87 ± 0.16‰ and 2.94 ± 0.14‰, respectively, were calculated for the Miramichi River Estuary food web. Consistent with observations in other aquatic studies, a total of 4.7 $\delta^{15}N$-defined trophic levels were identified for the Miramichi River Estuary food web. This calculation was done assuming the double crested cormorant was the top predator ($\delta^{15}N$ of egg yolk was 15.43‰), estuarine SPM ($\delta^{15}N$ of 4.94‰) represented trophic level # 1, and a $\delta^{15}N$-TEF of 2.94.

Planktivorous fish were depleted in $\delta^{13}C$ when compared to bottom-feeding fish by 1.81‰. Similarly, filter-feeding clams were depleted in $\delta^{13}C$ by 3.68‰ when compared to deposit-feeding invertebrates. This evidence supports the use of $\delta^{13}C$ in separating pelagic- from benthic-oriented organisms, different sources of food, and pathways of mercury uptake in the Miramichi River Estuary.

The relationship between $\log_{10}$[Hg] versus $\delta^{15}N$, using the slopes as an indicator of biomagnification potential, was not significant for the Miramichi River Estuary food web. Conversely, this relationship was significant for nine lake and two marine food webs in other studies. Biomagnification slopes (BMSs) for lake and marine food webs ranged from 0.17 and 0.74. Similar BMSs for eight lake and one marine food web indicates mercury biomagnifies in a similar manner in these ecosystems. A lack of relationship between $\log_{10}$[Hg] versus $\delta^{15}N$, as seen for the Miramichi River Estuary food web, could

be attributed to a number of factors: 1) estuarine organisms may feed on foods with differing mercury and $\delta^{15}N$ values, 2) inorganic mercury may bind with a number of complexing agents in the estuary thereby rendering it unavailable for methylmercury production and bioaccumulation in the estuarine food web, and 3) a large variability in $\log_{10}[Hg]$ and $\delta^{15}N$ values may be inherent in estuarine organisms due to the high degree of organism mobility, and dynamic exchange between i) fresh- and salt-waters, and ii) sediments and water column.

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INTRODUCTION

The thesis is divided into a general introduction, three main chapters, followed by an overall summary. The first chapter describes how $\delta^{13}C$ and $\delta^{15}N$ can be used to determine energy sources and food web structure in the Miramichi River Estuary. Chapter 2 uses $\delta^{13}C$ and $\delta^{15}N$ to differentiate mercury patterns in an estuarine food web. In chapter 3, mercury biomagnification in estuaries is compared to other aquatic food webs (lake and marine systems) using $\delta^{15}N$-defined biomagnification slopes (BMSs).

Food webs and stable isotopes

Energy is transferred from primary producers through a network of diverse groups of organisms to top carnivores (Odum 1989). The complex array of plants and animals is referred to as a food web, typically between 3 to 5 trophic levels (Briand 1985, Cohen *et al.* 1990, Atwell *et al.* 1998). The main constraint on the maximum number of trophic levels in a food web is the loss of energy at each trophic level (80-90%) (Wiegert 1988, Odum 1989, Baird and Ulanowicz 1989, Jørgensen *et al.* 1997). Identifying the number of levels may be obscured by our ability to describe lower trophic level organisms, such as heterotrophic bacteria and parasites (Pimm 1988, Wiegert 1988). It is also difficult to identify food web interactions by traditional methods (i.e., gut contents and behavioural/observation studies) (Crane 1999). Uncertainty is inherent due to food web complexity, seasonal differences in food availability, individual diet preferences, ontogenic diet shifts, omnivory, variations in assimilation efficiencies, and difficulties in

quantifying unidentifiable or partially digested food items, especially in smaller-sized organisms (Crane 1999).

To overcome these limitations, scientists have recently used ratios of $^{13}C/^{12}C$ and $^{15}N/^{14}N$ to help identify food web interactions and trophic positions. Carbon and nitrogen isotope ratios are commonly expressed as "delta notation" (δ) and have the units of parts per thousand or "per mil" (‰) difference from a standard; Vienna Pee Dee Belemnite (VPDB) for carbon and atmospheric N_2 for nitrogen. Carbon isotopes ($\delta^{13}C$) behave like conservative tracers in food webs with little change (between 0.5 and 1.0‰) between one trophic level and the next (Deniro and Epstein 1979, Hesslein *et al.* 1993). This enables $\delta^{13}C$ to be used to trace the source of carbon from lower trophic levels to top consumers. In contrast, a 3 to 5‰ enrichment of $\delta^{15}N$ occurs at each trophic level (Minagawa and Wada 1984, Fry 1988, Atwell *et al.* 1998). This enrichment is believed to be due to the preferential excretion of the lighter ^{14}N (Minagawa and Wada 1984). Vander Zanden *et al.* (1997) verified a close relationship between mean dietary trophic positions (using traditional dietary methods) and $\delta^{15}N$-defined trophic positions of fish. In addition, many researchers have used $\delta^{15}N$ to determine food chain lengths in aquatic ecosystems which ranged from 3.8 to 5.1 (Fry 1988, Hobson and Welch 1992, Atwell *et al.* 1998, Yoshii *et al.* 1999). These predictable relationships have enabled the trophic position of organisms and food web lengths to be quantified, carbon flows to be traced, and the functional feeding groups (trophic guilds) to be determined.

The biomagnification of some toxic chemicals, including polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated

biphenols, total chlorinated bornanes (∑CHBs), total hexachlorocyclohexane (∑HCH), total DDT (∑DDT), and mercury were significantly related to $\delta^{15}N$ (Broman *et al.* 1992, Kidd *et al.* 1995a, Kidd *et al.* 1995b, Jarman *et al.* 1996). This was achieved by using the biomagnification slope (BMS) of a plot of contaminant concentration versus $\delta^{15}N$ (‰). Recently, Kidd *et al.* (1995) published BMSs for mercury that ranged from 0.17 ± 0.02 and 0.48 ± 0.05 for 6 boreal forest lake food webs. Cabana and Rasmussen (1994a) also showed a strong correlation ($r=0.89$, $P<0.01$) between mean mercury levels in lake trout from seven lakes and their mean $\delta^{15}N$ values. In this same study, they found the $\delta^{15}N$ for lake trout varied from 7.5 to 17.5, and the length of the food web could explain this range of $\delta^{15}N$.

Estuaries

Estuaries are amongst the most productive aquatic ecosystems of the world and are constantly kept in early stages of ecological succession with low species diversity (Day *et al.* 1989, Costanza *et al.* 1993, Alongi 1998). This is a result of the rapid water renewal times (both from the sea and fresh water) and the fortuitous combination of nutrients and sunlight. Fish production (g C m^{-2} y^{-1}) is amongst the highest of all natural ecosystems, rivalled only by managed fish ponds (Nixon 1988, Day *et al.* 1989).

Estuaries along Canada's east coast are unique aquatic habitats. Many of these estuaries are river-dominated and highly stratified as a result of the high volumes of fresh water entering over a salt wedge. In the Miramichi River Estuary, an average annual flow rate of 305 m^3 s^{-1} enters as freshwater. Consequently, the pelagic and benthic environments are usually separated by salinity (≥ 12ppt) and temperature (≥ 2 °C)

gradients.

It has been estimated that at least 70% of all Atlantic coastal fish species spend some time in an estuary (Clark 1967). The Miramichi River Estuary, for example, is a critical feeding, over-wintering and nursery grounds for many fish species (Hanson and Courtenay 1995). Very little work has been conducted to identify the sources of carbon that supply energy to organisms, the food web structure, or the bioaccumulation pathways of mercury in these important habitats.

Unique chemical and physical properties of estuaries favour the aggregation and settling of riverine dissolved organic carbon (DOC) and suspended particulate matter (SPM) to sediments at low salinities between 1 and 5 ppt (Day *et al.* 1989). Freshwater particles (silts and clays) and DOC entering estuaries usually have negative electrovalent charges. In the presence of the strong ionic charges of salt water, van der Waals forces cause the negatively charged DOC and SPM to flocculate and settle. Ionic species of mercury have a charged state (i.e., Hg^{2+} and CH_3Hg^{+}) and are found associated with negatively charged DOC (including colloidal matter) and SPM (Stordal *et al.* 1996). Thus estuarine sediments function as both a sink (via settling) and a source (via resuspension) of carbon, SPM, and mercury to aquatic food webs (Baird and Ulanowicz 1989, Stordal *et al.* 1996). In addition, the stratified conditions of some estuaries, such as the Miramichi River Estuary, may lead to anoxic conditions in the benthic environment which promotes mercury methylation (Compeau and Bartha 1985, Berman *et al.* 1990).

Mercury

All forms of mercury are toxic, but methylmercury is a potent neurotoxicant that biomagnifies in food webs (World Health Organisation 1990, Harris and Snodgrass 1993, Rodgers 1994, Hall *et al.* 1997). For humans and animals, there is substantive evidence that shows methylmercury affects the neurological system (i.e., cognitive, motor and sensory functions) as summarised in a report by a committee of the National Research Council (2000). In addition, the committee concluded methylmercury affects the developing and adult cardiovascular system (i.e., blood-pressure, regulation, heart rate variability, and heart disease). Evidence to support methylmercury as a carcinogen was inconclusive (National Research Council 2000).

Atmospheric concentrations of mercury are believed to have increased by 2- to 3-fold since pre-industrialised times (Fitzgerald and Mason 1997). Unlike other metals, elemental mercury has a sufficiently high vapor pressure to volatilize from surfaces into the atmosphere and can travel by long-range transport in its elemental form (AMAP 1998).

It has been reported that 29% of Inuit women from Baffin Island (Nunavut, Canada) and 37% from Nunavik (Northern Québec, Canada) ingest levels of mercury in their traditional foods that exceed the Tolerable Daily Intake (TDI) set by the World Health Organisation of 5 μg/kg bw/week (AMAP 1998). Unfortunately, this corresponds to blood mercury levels of 60 μg L^{-1}, that are over the maternal blood levels of 50 μg L^{-1} set by the World Health Organisation to protect the foetus (AMAP 1998). However, these levels are well below the minimum known to cause neurological impairment in adults

(200 μg L^{-1}) (AMAP 1998).

The Canadian mercury guideline set to protect people consuming fish is 0.5 μg g^{-1} wet wt (Health and Welfare Canada 1990). In 1997, there were two Canadian province-wide consumption advisories for mercury levels in fish (Nova Scotia and New Brunswick), and more than 2,500 individual advisories throughout the other provinces (USEPA 1999). Recently, Burgess (1998a, 1998b) observed impaired reproductive (i.e., chick survival and lower nesting rates) in loons from Kejimkujik National Park (Nova Scotia, Canada) and linked these effects to mercury levels in fish from their diet (< 0.30 μg g^{-1} wet wt).

In Canada, industrial emissions of mercury are regulated under the United Nations Economic Commission for Europe's (UNECE's) Protocol for Heavy Metals (UNECE 1979). More reductions are recommended in the North American Regional Action Plan on Mercury (NARAP 1999). New Canada-wide Standards (CWS) have been set in order to reduce mercury emissions from incinerators and base metal smelters (Canadian Council of Ministers of the Environment 2000). In order to have a direct affect on future policies aimed at reducing anthropogenic releases of mercury, the routes and magnitude of mercury uptake in a wide range of aquatic habitats, including estuaries, need to be further defined.

Cross System Comparison

As discussed previously, predictable BAFs for mercury and methylmercury occur in river and lake food webs. As dietary transfer is the main uptake route of mercury, it can be argued that once mercury enters the food web it will biomagnify in a similar manner,

independent of the type of aquatic ecosystem. To test this hypothesis, we compared the BMSs obtained from a $\log_{10}$[Hg] versus $\delta^{15}N$ for the Miramichi River Estuary food web with those obtained for 8 lake and 2 marine food webs (Kidd *et al.* 1995b, Grimard 1996, Jarmen *et al.* 1996, Atwell *et al.* 1998).

Chapter 1. STABLE ISOTOPES ($\delta^{13}C$ and $\delta^{15}N$) HELP DEFINE ENERGY FLOW AND FOOD WEB STRUCTURE IN A COMPLEX TIDAL ESTUARY, THE MIRAMICHI RIVER ESTUARY (New Brunswick, Canada)

Abstract

Ratios of carbon ($^{13}C/^{12}C$) and nitrogen isotopes ($^{15}N/^{14}N$) of estuarine samples, calculated as parts per thousand (‰) difference from a standard, were used to determine the main sources of carbon ($\delta^{13}C$) and the trophic positioning of organisms ($\delta^{15}N$) in an complex estuarine environment, the Miramichi River Estuary (New Brunswick, Canada). Terrestrial carbon was an important source of carbon to estuarine suspended particulate matter (SPM) and sediments as identified by their isotopically light $\delta^{13}C$ and $\delta^{15}N$ values. On the basis of a cluster analysis on the mean $\delta^{13}C$ and $\delta^{15}N$ values for 47 estuarine, freshwater, and marine samples (abiotic and biotic) were separated into eight trophic categories: 1) estuarine sediment, and estuarine and freshwater SPM; 2) estuarine and marine primary producers; 3) freshwater fish and submerged terrestrial leaf litter, and estuarine oysters; 4) estuarine filter-feeding invertebrates; 5) estuarine deposit-feeding invertebrates; 6) estuarine planktivorous and benthivorous fish, and some benthic invertebrates, and two filter-feeding marine fish; 7) estuarine carnivorous and two

benthivorous fish; and 8) double crested cormorant eggs (whites and yolks). Enriched $\delta^{13}C$ values separated benthivorous from planktivorous fish by 1.81‰, and filter-feeding invertebrates from deposit-feeding invertebrates by 3.68‰. Carnivorous fish were significantly enriched in both $\delta^{15}N$ and $\delta^{13}C$ when compared to bottom- and pelagic-feeding fish. Marine fish could not be differentiated from estuarine fish on the basis of $\delta^{13}C$, however freshwater fish have significantly lower $\delta^{13}C$ values. For the Miramichi River Estuary food web, the average $\delta^{15}N$-Trophic Enrichment Factor ($\delta^{15}N$-TEF), defined as the $\delta^{15}N$ difference between a predator and its prey, was 2.94 ± 0.14‰, and the average $\delta^{13}C$-TEF was 1.87 ± 0.16‰. In this study, a total of 4.7 $\delta^{15}N$-defined trophic levels was calculated, with the assumptions that the double crested cormorant was the top predators ($\delta^{15}N$ of egg yolk was 14.43‰), SPM represents trophic level #1 ($\delta^{15}N$ of 4.94‰), and a $\delta^{15}N$-TEF of 2.94‰.

Introduction

Recently, the use of tracers, such as ^{13}C and ^{15}N, have enabled the carbon flows and food web structure to be identified in aquatic ecosystems (Peterson *et al.* 1986, Fry 1988, Deegan and Garrit 1997). In marine and lake food webs, an enrichment of the heavier nitrogen isotope by 3 to 5‰ was observed between a predator and its prey (Minagawa and Wada 1984). This was attributed to organisms preferentially eliminating the lighter ^{14}N isotope. This trend has enabled the relative trophic positions of individual organisms in food webs to be quantified and placed on a continuous spectrum, in which the lowest $\delta^{15}N$ values (‰) are found for primary producers, and the highest for top predators. Conversely, consumer organisms are only slightly enriched in $\delta^{13}C$ relative to

their diet, usually between 0.5 and 1‰ (Deniro and Epstein 1978). Peterson *et al.* (1986) found a large $\delta^{13}C$ range of 17‰ existed between three main carbon sources in the Sapelo Island Estuary (Georgia, USA). Freshwater, marine and estuary primary producers had $\delta^{13}C$ values of -30‰, -20‰ and -13‰, respectively. With this $\delta^{13}C$ range, these researchers were able to demonstrate phytoplankton and locally produced *Spartina* grass were the main sources of carbon to consumer organisms, with little contribution from terrestrial plants. In salt marsh and mangrove estuaries along the east coast of the United States, locally produced estuarine and marine primary production have been repeatedly identified as important carbon sources to the food using carbon isotopes (Coffin *et al.* 1994, Deegan and Garrit 1997, Sullivan and Moncreiff 1990).

A number of factors were found to contribute to the different $\delta^{13}C$ values of freshwater, marine, and estuary primary producers: different sources of dissolved inorganic carbon (DIC) (freshwater $\delta^{13}C$ between -5‰ and -10‰, saltwater $\delta^{13}C$ of 0‰, and $\delta^{13}C$ of atmospheric CO_2 of -8‰), isotopic discrimination of the carboxylating enzyme (e.g., $\delta^{13}C$ for C_4 plants of -12‰, and C_3 plants of -26‰), DIC concentration, cell density, temperature, rate of diffusion and flow, and boundary layers (Fry and Sherr 1984, Peterson *et al.* 1996). Schematic differences in the $\delta^{13}C$ values for inorganic carbon and primary producers from terrestrial, freshwater, and marine sources are summarized in Figure 1.

The Miramichi River Estuary is highly stratified throughout the year, which is mainly due to the large volumes of fresh water that enter the estuary with an annual flow rate of 305 $m^3 s^{-1}$ (Chiasson 1995). It is also shallow with an average depth of 5 m, and

tidal ranges between 0.2 to 1.2 m. This estuary is a critical feeding, over-wintering and nursery grounds for many Atlantic coastal fish species (Hanson and Courtenay 1995). Yet very little work has been conducted to identify the trophic structure and main sources of carbon to the food web.

The main objectives of this study were: i) to determine the food web structure using carbon and nitrogen isotopes, and ii) to verify whether terrestrial-derived carbon is the main source of energy to the estuarine food web.

Methodology

Study Site

The study site is located in the Miramichi River Estuary (Loggieville, New Brunswick, Canada) at latitude 47°04′57″ and longitude 65°23′80″ (Figure 2). Physical characteristics of the Miramichi River Estuary are well documented (Philpott 1978, Vilks and Kraul 1981, Chiasson 1995). Waters flow into the Miramichi River Estuary from two major rivers, the Northwest Miramichi and the Southwest Miramichi. They have drainage areas of 3,900 km^2 and 7,700 km^2, respectively. Smaller tributaries drain a watershed area of 3,400 km^2. Sand dunes separate the estuary from the Gulf of St. Lawrence at its mouth (22 km wide). At the Loggieville sampling site (1 km wide), a highly stratified salt wedge occurs throughout the year (Vilks and Kraul 1981). During high freshwater inflows (>1,600 $m^3 s^{-1}$) the upper layer of the salt wedge layer (≈2 m depth) has a salinity of 4 parts per thousand (ppt) and the bottom layer of 20 to 22 ppt (≈3 m depth) (Vilks and Kraul 1981). During low inflow (<73 $m^3 s^{-1}$) the upper layer has a salinity of 12 ppt and bottom of 22 to 24 ppt. Although this appears to be a large volume of freshwater, it is

only 5 to 10% of the total quantity of tidal water (Philpott 1978). Temperature differences are usually between 1 and 2 °C colder in the bottom layer. Approximately 100,000 tonnes of suspended particulate matter (SPM) enters the estuary each year from freshwater flows (Philpott 1978). Annual ranges of SPM are from 1.8 to 70.4 mg L^{-1}, with an average of about 11 mg L^{-1} (Chiasson 1995). Total dissolved solids were estimated to be 22 mg L^{-1} (Chiasson 1995).

Sample Preparation, Collection, and Storage

Between May 8 and 16 of 1996, a total of 787 abiotic and biotic samples were collected at the Loggieville study site. Smooth flounder (*Pleuronectes putnami* Gill) and winter flounder (*Pleuronectes americanus* Walbaum), Atlantic tomcod (*Microgadus tomcod* Walbaum), rainbow smelt (*Osmerus mordax* Mitchell), and white suckers (*Catostomus commersoni* Lacépède) were collected daily from Fyke nets (2.4 cm mesh size). Eels (*Anguilla rostrata* Lesueur), and striped bass (*Morone saxatilis* Walbaum) were obtained from Gaspereau nets (3.1 cm mesh size). Sand shrimp (*Crangon septemspinosa* Say) and small fish were obtained with a Beach seine (30 x 1.8 m and 6 mm mesh). Small fish consisted of three-spine sticklebacks (*Gasterosteus wheatlandi* Linnaeus), rainbow smelt, winter flounder, and mummichog (*Fundulus heteroclitus* Linnaeus). Soft-shell clams (*Mya arenaria* Linnaeus) were obtained by shoveling into the soft silty-clay during a low tide. Ribbon leaf sea grass (*Vallisneria americana* Michx), and deposit-feeding clams (*Macoma balthica* Linnaeus) clams were obtained from an Ekman Grab. Brown algae (*Ascophyllum nodosum* Le Jolis), oysters (*Crassostrea virginica* Say) and ribbed mussels (*Geukenisa demissa* Dilwyn) were picked off the

sediment/rocky bottom during low tides. Only three polychaetes (*Nereis* sp.) were retrieved by shoveling at low tide. A plankton net (500 μm mesh size and 1 m diameter) was towed to obtain zooplankton for stable isotope analysis.

On May 24, ten double crested cormorant (*Phalacrocorax auritus* Lesson) eggs were collected in collaboration with N. Burgess (Canadian Wildlife Service, St. John's, Nfld, Canada) from Egg Island, in the Miramichi Inner Bay.

Archived marine phytoplankton and fish samples were obtained from the Department of Fisheries and Oceans (Doris Dangle, Moncton, New Brunswick, Canada). Phytoplankton (233 μm tows) was collected from the Northumberland Strait between August 8 and 10, 1994. Atlantic herring (*Clupea harengus harengus* Linnaeus) and gaspereau (*Alosa pseudoharengus* Wilson), entering the Miramichi to spawn from the Northumberland Strait were sampled between May 19 and 21, 1996.

Freshwater samples were collected at two sites: Southwest Miramichi River (at Renous Indian Reserve 12 Bridge; latitude 46°49' and longitude 65°48'), and Northwest Miramichi River (at Red Bank Indian Reserve; latitude 46°56' and longitude 65°49'). Water samples, black nose dace (*Rhinichthys atratulus* Hermann), and submerged terrestrial leaf litter (species unknown) were collected from both sites.

All water samples were collected in 18 L stainless steel canisters that were pre-rinsed three times with water from the sampling site. All zooplankton were placed into mason jars with estuarine water. Sediment samples were collected with an Ekman Grab and placed into glass jars using a stainless steel spoon.

All samples were transported in coolers with ice packs to the Department of

Fisheries and Ocean's contaminant lab. At the lab, the species, length, weight, and sex of each fish was determined. Three zooplankton species (*Chaoborus flavicans* Meigen, *Eurytemora affinis* Poppe, and *Neomysis americana*) and ichthyoplankton (species unknown) were separated and placed into glass scintillation vials. Egg yolks were separated from whites and placed into glass jars. Fish were individually wrapped in tin foil pre-washed with three rinses of acetone followed by three rinses of hexane. After sample preparation, all samples were frozen and stored at -20 °C.

Stomach Contents

Stomach contents were removed from thawed fish and preserved in 10% formalin. With the aid of a dissecting microscope, food items were identified to the lowest order of classification (species for estuarine primary producers, invertebrates and fish, and family for worms). The number of individuals in each food category was recorded and expressed as a percentage of the total number of food items (Hyslop 1980) for each class as given by the following formula:

$$\textit{Percent composition by number} = \frac{\textit{No. of specific food item}}{\textit{Total No. of all food items}} \times 100$$

In this study, planktivorous fish are defined as species that consume phytoplankton and/or zooplankton. Benthivorous fish consume a combination of sediments, submerged terrestrial leaf litter, and estuarine invertebrates. Carnivorous fish consume a combination of invertebrates and fish.

Fish Ageing

Saccular otoliths were extracted from most fish and embedded in a plastic resin on a glass slide. Each otolith was ground in half with a Hillquist Thin Section grinder (Athol, Mass., USA), and then polished with a Hillquist Polisher (Seattle, Wash, USA). Annuli were counted under a dissecting microscope (Brothers *et al.* 1976, Chilton and Beamish 1982).

Total Carbon and Nitrogen Content

For sediments (n=3), the total carbon and nitrogen content was determined using an elemental C & N analyzer (CE Instrument, EA-110) by GG Hatch Isotope Laboratories (Ottawa, ON, Canada).

Stable Isotope Analysis

Stable carbon and nitrogen isotope ratios are expressed as "delta" notation (δ) using the following formula, and have units of parts per thousand or "per mil" (‰). $\delta^{15}N$ values were calculated using atmospheric N_2 as the nitrogen standard. $\delta^{13}C$ values were calculated using Vienna Pee Dee Belemnite (VPDB) as the carbon standard.

$$\delta^{13}C = \frac{(^{13}C/^{12}C_{sample}) - (^{13}C/^{12}C_{standard})}{(^{13}C/^{12}C_{standard})} \times 1000$$

All samples in direct contact with the estuarine water (i.e., submerged terrestrial leaf litter, SPM, sediment, polychaetes, and invertebrates) and marine water (phytoplankton and zooplankton) were soaked for 2 hrs in 10% HCl, and rinsed three times with deionized water to remove any dissolved inorganic carbon (DIC). Frozen water samples from Loggieville, and the Southwest and Northwest Miramichi Rivers

were thawed, and then filtered for SPM using GF/C filter papers (0.7 μm). Enough water was filtered to obtain a 2 mg sample of SPM for isotope analysis (N=3). Subsamples of skinless dorsal fish muscle, and skeltonless larged-sized invertebrate muscle were used for carbon and nitrogen isotope analysis. Prior to isotope analysis, all samples were freeze-dried.

At the GG Hatch Isotope Laboratories (University of Ottawa, Ottawa, ON, Canada), 250 μg of biological, 2 mg of SPM, and 5 mg of sediment sub-samples were weighed and folded into tin combustion capsules (5 x 3.5 mm). All samples were then analyzed in dual isotope mode for C and N with an automated CE Instrument EA-110 (elemental C & N analyzer) coupled to a Finnigan Mat Delta^{PLUS} IRMS with a Conflow II Interface (Finnigan Mat, San Jose, CA, USA).

During each run of 27 samples, four standard reference materials (NIST and IAEA) were analysed: two carbon (USGS24 graphite and NBS No.21 graphite) and two nitrogen (USGS-25 No. 12 and IAEA-N-2 No. 245). In one run, a mean $\delta^{13}C$ of -16.99 ± 0.05‰ (± SE) and for $\delta^{15}N$ of 13.99 ± 0.45‰ was obtained for ten tomcod samples of the same fish. To further test for accuracy, muscle tissue from one striped bass from this study was used to determine if there was any internal drift between runs. Between runs, the $\delta^{13}C$ and $\delta^{15}N$ of the striped bass tissue were always within 0.18 ‰ and 0.31‰ of each other, respectively

$\delta^{13}C$- and $\delta^{15}N$-TEFs

In this study, the Trophic Enrichment Factor (TEF) is defined as the average $\delta^{13}C$ difference between a predator and its prey, and determined with the following equation:

$$\delta^{13}C\ TEF = \delta^{13}C\ predator - \left(\sum_{i=1}^{n} \delta^{13}C\ prey_i \times fraction\ of\ prey\ consumed_i\right)$$

where the fraction of prey consumed$_i$ for each predator was estimated on the basis of the results of the gut content analysis; and n is the number of main prey items.

δ^{15}N-TEFs were determined the same way, except δ^{15}N was substituted for δ^{13}C. Further descriptions of the field/lab methods are described in Appendix A.

Statistics

An analysis of variance test (ANOVA, α=0.05) was conducted to test the null hypothesis that SPM from the Northwest Miramichi River (SPM-NW), Southwest Miramichi River (SPM-NW), and Miramichi River Estuary (SPM-EW), sediment, marine phytoplankton, and estuarine macro-algae and sea grass have the same mean δ^{13}C and δ^{15}N values. A Tukey's "post-hoc" test (α=0.05) was used to determine which means were significantly different from each other.

To determine if "natural distinct clusters" were formed for 47 groups of freshwater, estuarine, and marine samples (abiotic and biotic), a Joining Tree Cluster Analysis was conducted on their mean δ^{13}C and δ^{15}N values, using Euclidean distances and the weighted pair-group average. All statistics was conducted with Statistica Software, version 5.1 (Statsoft, Inc. Tulsa, OK, USA).

Results

Primary Producers, Sediments, and SPM

Submerged terrestrial leaf litter obtained from the Northwest and Southwest Miramichi Rivers had δ^{13}C values that ranged from -22.16 to -33.46‰, and δ^{15}N values

that ranged from 5.75 to 10.83‰.

Following a significant ANOVA test ($P<0.05$), a Tukey's test ($\alpha=0.05$) was conducted to determine which $\delta^{13}C$ means were significantly different from each other for seven potential freshwater, estuarine and marine carbon sources. A significant difference in $\delta^{13}C$ means was seen for at least one pair of the following: SPM from the Northwest and Southwest Miramichi Rivers, and the Miramichi River Estuary; estuarine sediments, macro-algae and sea grass; and marine phytoplankton (ANOVA, $P<0.05$). A post-hoc test revealed significant differences in $\delta^{13}C$ means for three groups. Estuarine sea grass was enriched in $\delta^{13}C$ when compared to marine phytoplankton and estuarine macro-algae, which in turn were significantly enriched relative to estuarine sediment and freshwater and estuarine SPM (Tukey, $P<0.05$). These results are summarized in Table 1. Results from the cluster analysis on $\delta^{15}N$ and $\delta^{13}C$ also grouped estuarine sediments to freshwater sources of SPM as shown in Figure 3.

These same samples also showed a significant difference in $\delta^{15}N$ means (ANOVA, $P<0.05$). Marine phytoplankton, and estuarine macro-algae and sea grass were significantly enriched in $\delta^{15}N$ relative to freshwater and estuarine SPM, and estuarine sediments (Tukey, $P<0.05$). In this same comparison, $\delta^{15}N$ means of freshwater SPM and the estuarine sediment were not significantly different from each other (Tukey, $P>0.05$). However, the $\delta^{15}N$ mean for freshwater SPM from the Northwest Miramichi River was only similar to freshwater SPM from the Southwest Miramichi River as shown in Table 1.

Zooplankton

Estuarine zooplankton (>500 μm) had $\delta^{15}N$ values that varied from 7.15‰ for *Chaoborus flavicans* to 9.53 ± 0.26‰ for *Eurytemora affinis* (Table 2). A $\delta^{15}N$ difference of 3.91‰ was seen between the mean $\delta^{15}N$ values of estuarine SPM and zooplankton. Ratios of ^{13}C were lowest for zooplankton composites ($\delta^{13}C$ of -23.27 ± 0.54‰) and most enriched for *Neomysis americana* ($\delta^{13}C$ of -22.52 ‰). Ichthyoplankton (n=9) had a $\delta^{13}C$ of -21.73 ± 0.16‰, and was surprisingly enriched in $\delta^{15}N$ (13.75 ± 0.37‰) as shown in Figure 4 and Table 2.

Deposit-Feeding Invertebrates

Three deposit-feeding species: polychaetes (*Nereis* sp.), clams (*Macoma balthica*), and sand shrimp (*Crangon septemspinosa*) did not differ significantly in their mean $\delta^{13}C$ or $\delta^{15}N$ values (ANOVA, $P>0.05$). These $\delta^{13}C$ or $\delta^{15}N$ values are summarized in Table 2. Eight amphipods (*Gammarus* sp.) collected in this study were the lowest trophic level consumer organism as shown in Table 2 and Figure 4. They were significantly depleted in both $\delta^{13}C$ and $\delta^{15}N$ relative to the three deposit-feeders mentioned above (ANOVA, $P<0.05$).

Filter-Feeding Clams

Three filter-feeding clams species, oysters, ribbed mussels and soft-shell clams did not significantly differ in their mean $\delta^{15}N$ or their $\delta^{13}C$ values (ANOVA, $P>0.05$) and are summarized in Table 2. However, filter-feeding clams were significantly depleted in $\delta^{15}N$ (9.43 ± 0.20‰) when compared to deposit-feeding invertebrates ($\delta^{15}N$ of 10.86 ± 0.29‰) by 1.43‰ (*t*-test, $P<0.05$). They were also significantly depleted in $\delta^{13}C$ (-24.20

± 0.32‰) when compared to deposit-feeding invertebrates ($\delta^{13}C$ of -20.52 ± 0.35‰) by 3.68‰ (*t*-test, $P<0.05$).

Estuarine Fish

On the basis of the gut content analysis, fish were divided into the three categories as defined earlier: planktivores (stickleback, age-1 and -2 rainbow smelt), benthivores (winter and smooth flounder, mummichog, and eel), and carnivores (age-3 rainbow smelt, tomcod, and striped bass). All planktivorous fish had stomachs full of zooplankton as shown in Table 3. Benthivorous fish consumed a diet mainly of deposit-feeding invertebrates (such as *Nereis* polychaetes and deposit-feeding clams) sediments, and minor amounts of estuarine sea grass. In this study, rainbow smelt (age-3+), tomcod, and striped bass fed on larger-sized estuarine invertebrates (i.e., mysids and sand shrimp) and fish, and were classified as carnivores. Individual gut contents for fish are summarized in Appendix B.

Planktivorous Fish

Mean $\delta^{15}N$ and $\delta^{13}C$ values of planktivorous fish (sticklebacks, and age-1 and -2 rainbow smelt) did not significantly differ from each other (ANOVA, $P>0.05$) and are summarized in Table 4. An average $\delta^{15}N$ of 12.68 ± 0.24‰ and $\delta^{13}C$ of -21.03 ± 0.27‰ was obtained for these fish (n=27).

Benthivorous Fish

Winter flounder from two size classes were caught in the estuary with total lengths <8.2 cm or >15.8 cm. Hanson and Courtenay (1997) suggested this bimodal distribution may represent age-0 and age-1 winter flounder, respectively. Both age classes

occupied the same $\delta^{15}N$-defined trophic position as identified by non-significant differences in $\delta^{15}N$ values (*t*-test, $P>0.05$). These results are not surprising, as both age classes fed on a similar $\delta^{15}N$-diet. Sediments ($\delta^{15}N$ of $3.32 \pm 0.05‰$) represented about 30% of the gut contents for both age classes. Polychaetes ($\delta^{15}N$ of $10.33 \pm 0.33‰$) made up 33% of the diet for the younger winter flounder, whereas 39% of the diet of the older winter flounder was deposit-feeding clams ($\delta^{15}N$ of $9.66 \pm 0.49‰$). These gut content results can be seen in Table 3.

Gut contents also support the placement of eels into the same trophic functional group as other bottom-feeding fish. Stomach contents of eels consisted of 20% fish eggs, 40% sea grass, and 40% sediments (Table 4). Fish eggs had a higher $\delta^{15}N$ (13.63‰) than eels ($13.01 \pm 0.75‰$), indicating eels generally feed on lower trophic level $\delta^{15}N$-food items, and are likely to be opportunistic feeders.

Mean $\delta^{15}N$ and $\delta^{13}C$ values for bottom-feeding fish (mummichog, eels, age-0 and age-1 winter flounder, and smooth flounder) are summarized in Table 4. There were no significant differences in $\delta^{15}N$ and $\delta^{13}C$ among benthivorous fish (ANOVA, $P>0.05$). These benthic fish (n=51) had a $\delta^{15}N$ of $12.55 \pm 0.17‰$ and $\delta^{13}C$ of $-18.09 \pm 0.29‰$.

Carnivorous Fish

Fish and large-sized invertebrates (such as sand shrimp and mysids) were the only dietary items found in the guts of carnivorous fish (Table 3). Mean $\delta^{13}C$ and $\delta^{15}N$ values for carnivorous fish (age-3+ rainbow smelt, tomcod, and striped bass) were not significantly different among species (ANOVA, $P>0.05$). These mean values are summarized in Table 4. For all carnivorous fish (n=51), a mean $\delta^{13}C$ of $-18.09 \pm 0.22‰$

and $\delta^{15}N$ of 13.82 ± 0.08‰ was obtained.

In this study, older rainbow smelt switched their diet to larger-sized invertebrates, such as sand shrimp, whereas age-1 and -2 rainbow smelt, as seen earlier, selectively feed on zooplankton. This change in diet indicates a life-history diet shift for rainbow smelt. With this shift, older rainbow smelt (n=10) had $\delta^{13}C$ (-17.56 ± 0.39‰) and $\delta^{15}N$ values (13.78 ± 0.15‰) which were significantly enriched when compared to age-1 and -2 rainbow smelt (*t*-test, $P<0.05$). Age-1 and -2 rainbow smelt had $\delta^{13}C$ values of -21.05 ± 0.93‰ and -19.96 ± 0.09‰, respectively, and $\delta^{15}N$ values of 13.02 ± 0.49‰ and 12.30 ± 0.13‰, respectively.

In this study the majority of striped bass stomachs were empty. Only two striped bass had remains in their stomachs. One age-1 striped bass had 20 large-sized mysids (*Neomysis americana*), and an older striped bass (age-5) had fish remains in its stomach. Older striped bass (age-3+) were the most $\delta^{13}C$- and $\delta^{15}N$-enriched fish captured in the estuary, -16.78 ± 0.77 and 14.36 ± 0.51, respectively.

Marine Fish

Two marine fish species, Atlantic herring (*Clupea harengus harengus*) and gaspereau (*Alosa pseudoharengus*), entered the Miramichi in early May to spawn. Their $\delta^{15}N$ and $\delta^{13}C$ values were not significantly different (*t*-test, $P>0.05$) and summarized in Table 4. Gaspereau are known to feed on zooplankton whereas herring consume smaller-sized phytoplankton (Scott and Scott 1988). Although not significant, a $\delta^{13}C$ difference of 0.50‰ was seen between the mean values for gaspereau and herring.

Freshwater Fish

Few white suckers (n=8) were captured in the Miramichi River Estuary. The small size of these white suckers suggest they are likely to be one year old (Scott and Scott 1988). Even though white suckers were caught at the Loggieville sampling site, a stomach full of terrestrial invertebrates (such as adult wasps) and their isotopically light $\delta^{13}C$ values of -29.43 ± 1.30‰ helped to confirm their freshwater origins.

Double Crested Cormorant Eggs

In this study, double crested cormorant were the top predator as identified by their $\delta^{15}N$ values. Egg yolk and whites had $\delta^{15}N$ values of 15.43 ± 0.34‰ and 16.35 ± 0.11‰, respectively. Egg yolks were depleted in $\delta^{13}C$ values relative to egg whites, -22.80 ± 0.15‰ and -19.72 ± 0.71‰, respectively.

Trophic Structure

Eight distinct clusters were formed during the Joining Cluster Tree Analysis on the mean $\delta^{15}N$ and $\delta^{13}C$ values for 47 groups of fresh water, marine, and estuarine samples (abiotic and biotic):

1. Estuarine sediment, and estuarine and freshwater SPM
2. Estuarine and marine primary producers
3. Freshwater fish and submerged terrestrial leaf litter, and estuarine oysters
4. Estuarine filter-feeding invertebrates
5. Estuarine deposit-feeding invertebrates
6. Estuarine planktivorous and benthivorous fish, two marine planktivorous fish, and some estuarine benthic invertebrates
7. Estuarine carnivorous and two benthivorous fish
8. Double crested cormorant eggs (whites and yolks).

Meaningful results did occur from the Joining Tree Cluster Analysis, such as estuarine

sediments and estuarine and freshwater SPM, with similar $\delta^{13}C$ and $\delta^{15}N$ values, forming one group. Freshwater fish and submerged terrestrial leaf litter, and estuarine oysters with isotopically light $\delta^{13}C$ values, formed another group. In addition, all the carnivorous fish formed one group, along with two benthivorous fish. Double crested cormorant egg yolks and whites were separated into their own group. Some parts of the analysis resulted in more robust groupings. This was seen for planktivorous and benthivorous that formed one group even though they had significantly different mean $\delta^{13}C$ values (*t-test*, $P<0.05$).

Trophic Enrichment Factors

$\delta^{13}C$- and $\delta^{15}N$-TEF for planktivorous, benthivorous, and carnivorous fish are summarized in Tables 5 and 6, respectively. For 134 Miramichi River Estuary invertebrates and fish, the average $\delta^{15}N$-TEF was 2.94 ± 0.14‰, and the average $\delta^{13}C$-TEF was 1.87 ± 0.16‰ (Tables 5 and 6). A total of 4.7 $\delta^{15}N$-defined trophic levels was calculated for the Miramichi River Estuary food web. This number was calculated using a $\delta^{15}N$-TEF of 2.94‰, suspended particulate ($\delta^{15}N$ of 4.94‰) as trophic level #1, and yolk of the double crested cormorant ($\delta^{15}N$ of 15.43‰) to represent the top trophic predator.

Discussion

The Miramichi River Estuary has a high degree of physical (i.e., tidal and wind) and chemical heterogeneity (i.e., salinity) which creates diverse conditions for estuarine organisms. Despite these conditions, a definable estuarine food web structure was found in this study. The Joining Tree Cluster Analysis on mean $\delta^{13}C$ and $\delta^{15}N$ values for 47 groups of freshwater, estuarine, and marine samples (abiotic and biotic) resulted in eight

meaningful clusters: 1) estuarine sediment, and estuarine and freshwater SPM, 2) estuarine and marine primary producers, 3) freshwater fish and submerged terrestrial leaf litter, and estuarine oysters 4) estuarine filter-feeding invertebrates, 5) estuarine deposit-feeding invertebrates, 6) estuarine planktivorous and benthivorous fish, two marine fish, and some benthic invertebrates 7) estuarine carnivorous and two benthivorous fish and 8) double crested cormorant eggs (yolk and whites).

On the basis of the stomach contents, benthivorous and planktivorous fish could be separated into two classes of fish. Planktivorous fish consume zooplankton only, whereas benthivorous fish feed mainly on deposit-feeding invertebrates, estuarine sea grass, and sediments. On the basis of the results of the Joining Tree Cluster Analysis on mean $\delta^{15}N$ and $\delta^{13}C$ values, these same fish formed one group, along with the two marine planktivorous fish (gaspereau and herring), and some estuarine benthic invertebrates. As shown earlier, benthivorous fish were also significantly enriched in $\delta^{13}C$ by 1.81‰ relative to planktivorous fish. These results show some limitations of the cluster analysis to resolve the food web into meaningful trophic guilds.

Trophic Structure

A 3 to 5‰ $\delta^{15}N$-trophic enrichment factor ($\delta^{15}N$-TEF) usually denotes a trophic level (Minagawa and Wada 1984, Hobson and Welch 1992). In this study, we obtained an average $\delta^{15}N$-TEF of 2.94 ± 0.14‰ for 134 organisms. Further sampling would be required to determine if this $\delta^{15}N$-TEF is a representative number temporally and spatially. These $\delta^{15}N$-TEF values were also consistent with those observed in lakes and marine habitats (Minagawa and Wada 1984, Wada *et al.* 1987, Hobson and Welch 1992,

Kidd *et al.* 1995b, Yoshii *et al.* 1999). Minagawa and Wada (1984) obtained a δ^{15}N-TEF of 3.14‰ for marine and freshwater food webs. A δ^{15}N-TEF of 3.3‰ was recorded for a pelagic food web in Lake Baikal (Yoshii *et al.* 1999). A similar δ^{15}N-TEF was obtained for a sub-Arctic freshwater lake (Lake Laberge) of 3.3‰ (Kidd *et al.* 1995a). A δ^{15}N-stepwise enrichment of 3.8‰ was seen for a high Arctic marine food web, and 3.3‰ for an Antarctic marine food web (Wada *et al.* 1987, Hobson and Welch 1992).

The δ^{13}C-TEF obtained in this study (1.87 ± 0.14‰) was higher than those predicted for estuaries (0.5‰) in a cross-system comparison by France and Peters (1997). After collating δ^{13}C-TEFs data for different aquatic food webs, France and Peters (1997) concluded the average δ^{13}C-TEF was 0.2‰ for freshwater ecosystems, 0.5‰ for estuarine waters, 0.8‰ for coastal, and 1.1‰ for marine waters. However, from the values reported in the literature, it appears that the δ^{13}C-TEF can vary considerably among aquatic ecosystems as seen for Narrangansett Bay (0.5 to 0.6‰), a California coastal pelagic food web (0.74‰), Gulf of Mexico (0.5 to 1‰), an eastern tropical Pacific food web (1.38‰), Bering Sea (1.5‰), Georges Bank (1.6‰), and St. Margaret's Bay (3‰) (McConnaughey and McRoy 1979, Rau *et al.* 1983, Gearing *et al.* 1984, Stephenson *et al.* 1986, Fry 1988, Fry and Wainright 1991).

To date, cross-system comparisons of the number of δ^{15}N-defined trophic levels among aquatic food webs has proven challenging. Many studies have chosen to define trophic level #1 differently, such as SPM, POM, or phytoplankton. Also, it is difficult to characterise top predators in aquatic ecosystems with different species composition. Bearing these limitations in mind, the total number of δ^{15}N-defined trophic levels in

aquatic ecosystems varied little, from 3.8 to 5.1 (Fry 1988, Hobson and Welch 1992, Atwell *et al.* 1998, Yoshii *et al.* 1999). For the Miramichi River Estuary, a total of 4.7 $\delta^{15}N$-defined trophic levels was calculated. This value was obtained using a $\delta^{15}N$-TEF of 2.94‰, and a $\delta^{15}N$-difference of 9.68‰ between SPM ($\delta^{15}N$ of 4.94‰) which was assumed to represent trophic level #1 and egg yolk ($\delta^{15}N$ of 15.43‰) which was assumed to represent the adult double crested cormorant. As indicated by Jarman *et al.* (1996), $\delta^{15}N$ values of egg albumen reflect the diet consumed by the double crested cormorant during the egg-laying period (short-term). Lipids move into the eggs from the adult cormorant in the period preceding egg-laying (i.e., into the egg yolk) which would indicate a longer-term trophic level average.

The number of $\delta^{15}N$-defined trophic levels calculated for the Miramichi River Estuary (4.7) was similar to the number determined for Georges Bank of 4.2 (Fry 1988). However, for Georges Bank, the number of trophic levels was calculated using a $\delta^{15}N$-TEF of 3.1‰, a $\delta^{15}N$ of 5.1‰ for SPM, and a piscivorous fish as the top trophic level ($\delta^{15}N$ of 15.2‰). Similar calculations showed a total of 3.7 trophic levels for a pelagic food web in Lake Baikal (Yoshii *et al.* 1999). A $\delta^{15}N$-TEF of 3.3‰ was used in Lake Baikal, with phytoplankton ($\delta^{15}N$ of 4.2‰) representing the base of the food web, and sculpin ($\delta^{15}N$ of 13.9‰) as the top predator. Hobson and Welch (1992) measured a total of 5.1 trophic levels using a $\delta^{15}N$-TEF of 3.8‰, with a $\delta^{15}N$ value for particulate organic matter (POM) of 5.4 ± 0.8‰ and 21.1 ± 0.6‰ for polar bears. In one study by Rau *et al.* (1983), a $\delta^{13}C$-TEF of 1.38‰ was used to determine 4.8 trophic levels for an eastern tropical Pacific food web. In this study Silky shark (*Carcharhinus falciformis*) was the

top predator.

It could be hypothesised that systems with higher trophic efficiencies (such as estuaries) could translate into longer-chained food webs (Nixon 1988). In this study however, a similar number of $\delta^{15}N$-defined trophic levels was seen for lake, estuarine [this study] and marine food webs (Fry 1988, Hobson and Welch 1992, Atwell *et al.* 1998, Yoshii *et al.* 1999). Although these data are preliminary, it does show the strengths of using $\delta^{15}N$ in the future to make quantitative comparisons of food chain lengths among aquatic ecosystems.

Carbon Flow

No difference was observed in $\delta^{13}C$ values, total nitrogen and carbon content, and C/N ratios for sediments in this study and for those published by Rashid and Reinson at the same site in 1979 as summarized in Table 7. High C/N ratios of 15 were obtained for the Miramichi River Estuary's sediments. As observed by Matson and Brinson (1990), and Ruckelshaus *et al.* (1993), C/N ratios greater than 12 are usually indicative of terrestrial sources of carbon whereas lower C/N ratios (i.e., 6 to 7) are characteristic of marine sources of carbon. One explanation for these distinct freshwater and marine C/N ratios is that marine PON is highly nitrogenous, whereas, terrestrial macrophyte debris is relatively nitrogen deficient (Thornton and McManus 1994). C/N ratios are influenced by decomposition processes (i.e., microbial and leaching), the type of organic matter, and particle size (Thornton and McManus 1994). Higher C/N ratios were measured in coarser-sized particles (Thornton and McManus 1994). As the Miramichi River Estuary has a rapid renewal time of fresh and salt waters, the impact of decomposition processes

on C/N ratios is likely to be minimal.

In this study, isotopically light $\delta^{13}C$ values of filter-feeding clams (e.g., oysters, ribbed mussels and soft-shell clams) supports terrestrial carbon supplied most of their energy needs. These results are similar to those obtained by Hackney and Haines (1980) where upland terrestrial plants were identified as a major source of energy to filter-feeding bivalves from one coastal estuary (Mississippi Estuary, USA). However, in another tidally influenced estuary, freshwater algae were shown to provide the bulk of the carbon using molecular and isotopic tracers (Chl *a*, C/N ratios, [$\delta^{13}C$]POC, and sterol and phospholipid ester-linked fatty acid biomarkers) to the suspension-feeding bivalve *Potamocorbula amurensis* (Canuel *et al.* 1995).

Terrestrial carbon sources for the estuary came from the two main freshwater tributaries (Northwest and Southwest Miramichi Rivers). Cunjak *et al.* (1990) estimated the tree composition in a section along the Southwest Miramichi River to be 65% coniferous and 35% deciduous. Balsam fir (*Abies balsamea)* and spruce (*Picea glauca*) and the deciduous speckled alder (*Alnus rugosa*) were the most common trees. Doucett (1994) found $\delta^{13}C$ values for submerged decomposing leaves of terrestrial plants from the Southwest Miramichi River fell within a range of -28.59‰ to -31.47‰ and used -29.47‰ to represent the average value for SPM. In this study, $\delta^{13}C$ values varied from -22.17 to -33.46‰ for submerged terrestrial leaf litter collected from within the Northwest and Southwest Miramichi Rivers.

Typical ratios of ^{15}N for plants (-5 to +2‰) usually reflect atmospheric values ($\delta^{15}N$ of 0‰), as nitrogen supply is often rate-limiting (Mariotti 1983, Nadelhoffer and

Fry 1994). In Doucett's study (1994), the $\delta^{15}N$ values of decomposing leaf litter and aquatic algae typically varied between 0.11‰ and 1.68‰. In this study, a $\delta^{15}N$ of 5.75 to 10.84‰ was obtained for freshwater submerged terrestrial leaf litter. One possible explanation offered for the $\delta^{15}N$ and $\delta^{13}C$ enrichment observed in this study is the preferential leaching of the lighter ^{14}N and ^{13}C isotopes during decomposition processes (e.g., autolysis, and microbial mineralization). Doucett (1994) also analyzed for carbon isotopes on deciduous and coniferous leaves that were collected in August, and nitrogen analysis on two leaf samples (*Alcer saccharum* and *Abies balsamea*) collected in May. In this study, the submerged terrestrial leaf litter that was collected in May showed advance stages of decomposition and plant identification was not possible. Further studies need to be conducted in order to determine the temporal and seasonal variability of the $\delta^{13}C$ and $\delta^{15}N$ values of freshwater sources of carbon to the riverine and estuarine food webs.

Conclusions

Distinct $\delta^{13}C$ values of freshwater, marine, and estuarine primary producers helped to identify terrestrial carbon as a major source of energy to estuarine sediments and SPM. The results of the Joining Tree Cluster Analysis on mean $\delta^{13}C$ and $\delta^{15}N$ values assisted in structuring the 47 groups of freshwater, estuarine, and marine samples (abiotic and biotic) into a meaningful clusters: 1) estuarine sediment, and estuarine and freshwater SPM; 2) estuarine and marine primary producers; 3) freshwater fish and submerged terrestrial leaf litter, and estuarine oysters; 4) estuarine filter-feeding invertebrates; 5) estuarine deposit-feeding invertebrates; 6) estuarine planktivorous and benthivorous fish, some benthic invertebrates, and two filter-feeding marine fish; 7) estuarine

carnivorous and two benthivorous fish; and 8) double crested cormorant egg whites and yolks. For the Miramichi River Estuary invertebrates and fish (n=134), a $\delta^{13}C$-TEF of $1.87 \pm 0.16‰$ and a $\delta^{15}N$-TEF of $2.94 \pm 0.14‰$ was estimated. The total number of $\delta^{15}N$-defined trophic levels for the Miramichi River Estuary was 4.7. This is within the range of levels reported for other freshwater and marine food webs (3.8 to 5.1). The results of this study show that even though estuaries are characterized by a high degree of organism mobility and continuous changes in salinity and water movement, the trophic interactions and food web structure, as defined by $\delta^{13}C$ and $\delta^{15}N$, were predictable and similar to those observed in fresh and marine food webs.

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Table 1. Results of a post-hoc test for significant differences between mean $\delta^{13}C$ and $\delta^{15}N$ values of freshwater (FW) SPM from the Northwest (SPM-NW) and Southwest Miramichi Rivers (SPM-SW), estuarine (EW) macro-algae, sea grass, sediments and SPM (SPM-EW), and marine (MW) phytoplankton.

$\delta^{13}C$	FW	FW	EW	EW	MW	EW	EW
Material	SPM-NW	SPM-SW	Sediment	SPM-EW	Phytoplankton[1]	Macro-Algae	Sea grass
Mean	-27.85	-27.45	-27.82	-25.69	-20.09	-17.01	-12.09
± SE	0.57	0.38	0.15	0.006	1.00	0.20	1.43
n	3	3	5	3	12	4	5

$\delta^{15}N$	FW	FW	EW	EW	MW	EW	EW
Material	SPM-NW	SPM-SW	Sediment	SPM-EW	Phytoplankton[1]	Sea grass	Macro-Algae
Mean	1.31	2.63	3.32	4.94	6.49	7.05	7.64
± SE	0.13	0.71	0.05	1.12	0.21	0.07	0.34

1. Archived phytoplankton samples, collected from Northumberland Strait between August 8-10, 1994, were supplied by the Department of Fisheries and Oceans in Moncton (NB, Canada).

Table 2. Trophic position (TP), mean $\delta^{15}N$ and $\delta^{13}C$ values, and number of samples (n) of lower trophic invertebrates collected from the Miramichi River Estuary. Values are given as the mean ± SE.

	TP[1]	$\delta^{15}N$ (‰) ± SE	$\delta^{13}C$ (‰) ± SE	n
Invertebrates:				
Gammarus sp.	1.8	6.70 ± 0.37	-24.15 ± 0.43	8
Chaoborus flavicans	1.9	7.15	-22.43	1
estuarine zooplankton	2.5	8.85 ± 0.96	-23.27 ± 0.54	9
Neomysis americana	2.5	8.95	-22.52	2
Eurytemora affinis	2.7	9.53 ± 0.26	-22.65 ± 0.23	7
Nereis sp.	2.7	9.56 ± 0.11	-20.92 ± 0.81	3
Crangon septemspinosa	3.6	12.03 ± 0.23	-20.51 ± 0.47	14
Bivalves:				
Geukenisa demissa	2.5	9.01 ± 0.35	-23.86 ± 0.71	9
Crassostrea virginica	2.7	9.54 ± 0.26	-25.62 ± 0.44	10
Macoma balthica	2.8	9.66 ± 0.49	-19.96 ± 0.70	11
Mya arenaria	2.8	9.68 ± 0.40	-23.19 ± 0.22	11

1. Calculation is based on following assumptions: estuarine SPM ($\delta^{15}N$ of 4.94‰) represents trophic level #1, and a $\delta^{15}N$-TEF of 2.94‰.

Table 3. The number of individuals in each food category in 10 species of fish captured in the Miramichi River Estuary, May 1996, expressed as a percentage of the total number of food items for each class[1]. Abb: polychaetes and oligochaetes (Worms), deposit-feeding clams (Clams), and unidentifiable organic matter (Uniden. OM), gaspereau (GS), herring (HR), mummichog (MC), striped bass (SB), smooth flounder (SF), rainbow smelt (SM), tomcod (TC), winter flounder (WF), eels, and stickleback (STS). Age of fish in parentheses.

	No. of fish	No. of Empty Stomachs	Phyto-plankton	Zoo-plankton	Freshwater Invertebrates	Worms	Grass Shrimp	Crabs	Clams	Estuarine Eel Grass	Detritus	Sediment	Uniden. OM	Fish Eggs	Fish
HR	11	0	92	8.3											
GS	10	0		100											
STS	11	2		100											
SM (1)	9	1		86	14										
SM (2)	11	5		86	14										
SM (3+)	17	8		11		11							78		
WF (0)	10	2		5.5		33			5.6	5.6	17	28	5.6		
WF (1+)	9	0				3.6		3.6	39	14	7.1	32			
SF	5	0				24		5.9	24	5.9	12	29			
MC	8	0				40		40		20					
Eels	8	4								43	14			43	
TC (1)	10	3							36	27	18		18		
TC (2)	9	2					64		18	9.1	9.1				
TC (3+)	1	0					33			33					33
SB (1)	5	4													100
SB (2)	11	11													
SB (3+)	3	2													100

1. Percent composition by number = $\frac{\text{No. of specific food item}}{\text{Total No. of all food items}} \times 100$

Table 4. Trophic position (TP), $\delta^{15}N$, $\delta^{13}C$, weight, length, and number of samples (n) of fish and double crested cormorant eggs collected from the Miramichi River Estuary. Values are given as the mean ± SE. Age of fish are in parentheses.

		$\delta^{15}N$			$\delta^{13}C$				Weight			Length			
	TP[1]	‰	±	SE	‰	±	SE	n	(g)	±	SE	(cm)	±	SE	n
Catostomus commersoni	3.0	10.46	±	0.25	-29.43	±	1.30	7	30	±	4.3	14.7	±	4.3	8
Pleuronectes americanus (0)	3.8	12.59	±	0.11	-20.71	±	0.37	11	6.7	±	0.76	23.6	±	01.1	12
Pleuronectes americanus (1+)	3.7	12.30	±	0.20	-18.53	±	0.30	9	100	±	16	20.1	±	1.1	9
Fundulus heteroclitus	3.7	12.40	±	0.64	-17.50	±	0.60	8	14	±	1.8	10.3	±	0.40	8
Pleuronectes putnami	3.8	12.63	±	0.35	-19.97	±	0.43	5	120	±	20	19.7	±	1.2	5
Clupea harengus	3.8	12.69	±	0.05	-20.70	±	0.22	7	160	±	9.9	26.9	±	1.4	11
Alosa pseudoharengus	3.8	12.81	±	0.09	-20.20	±	0.07	5	230	±	17	35.2	±	7.3	10
Gasterosteus wheatlandi	3.8	12.82	±	0.57	-22.19	±	0.22	9	0.83	±	0.089	3.5	±	0.15	11
Anguilla rostrata	3.9	13.01	±	0.75	-20.25	±	0.84	6	490	±	60	64.1	±	2.2	8
Osmerus mordax (1)	3.9	13.02	±	0.49	-21.05	±	0.93	8	1.5	±	0.16	6.5	±	0.20	10
Osmerus mordax (2)	3.7	12.30	±	0.13	-19.96	±	0.09	10	4.3	±	0.21	8.8	±	0.16	10
Osmerus mordax (3+)	4.2	13.78	±	0.15	-17.56	±	0.39	13	43	±	3.1	19.2	±	0.38	17
Ichthyoplankton	4.2	13.75	±	0.37	-21.73	±	0.16	3							
Microgadus tomcod (1)	4.2	13.87	±	0.14	-18.95	±	0.31	9	20	±	2.1	14.1	±	0.61	10
Microgadus tomcod (2)	4.3	14.25	±	0.23	-16.92	±	0.39	10	72	±	9.8	21.4	±	1.0	10
Microgadus tomcod (3+)	4.5	14.65			-17.86			1	150			29			1
Morone saxatilis (1)	4.0	13.38	±	0.19	-18.67	±	0.69	5	35	±	2.9	16.0	±	0.30	5
Morone saxatilis (2)	4.1	13.46	±	0.11	-19.09	±	0.49	11	240	±	9.1	28.6	±	0.40	11
Morone saxatilis (3+)	4.7	14.36	±	0.51	-16.78	±	0.77	3	1800	±	500	55.1	±	3.1	3
Phalacrocorax auritus egg yolk	5.0	15.43	±	0.34	-22.80	±	0.15	9	7.5	±	0.31	57.8	±	1.0	9
Phalacrocorax auritus egg white	4.6	16.35	±	0.11	-19.72	±	0.71	9	27	±	1.2	57.8	±	1.0	9

1. Calculation is based on following assumptions: estuarine SPM ($\delta^{15}N$ of 4.94‰) represents trophic level #1, and a $\delta^{15}N$-TEF of 2.94‰.

Table 5. Estimation of $\delta^{13}C$-Trophic Enrichment Factors ($\delta^{13}C$-TEFs) for fish and some lower trophic level invertebrates caught in the estuary. All variances are reported as standard error (±SE). Age of fish in parentheses.

Predator	n	Predator $\delta^{13}C$ (‰)	Prey Item	Fraction of diet x $\delta^{13}C_{prey}$ (‰)	$\delta^{13}C$-TEF
Planktivorous Fish:					
Rainbow smelt (1)	10	-21.05 ± 0.93	EW-zooplankton	1 x -23.27	2.22 ± 0.63
Rainbow smelt (2)	10	-19.96 ± 0.09	EW-zooplankton	1 x -23.27	3.31 ± 0.13
Three-spine stickleback (2+)	9	-22.19 ± 0.22	EW-zooplankton	1 x -23.27	1.08 ± 0.22
				Average for Planktivorous Fish:	**2.24 ± 0.28**
Benthivorous Fish:					
Winter flounder (0)	12	-20.71 ± 0.37	polychaetes	1 x -20.92	0.21 ± 0.37
Winter flounder (1+)	9	-18.53 ± 0.30	*Macoma* clams	1x -19.96	1.47 ± 0.30
Smooth flounder (3)	5	-19.97 ± 0.43	polychaetes	0.5 x -20.92	0.50 ± 0.43
			Macoma clams	0.5 x -19.96	
Mummichog	8	-17.50 ± 0.60	polychaetes	0.7 x -20.92	0.71 ± 0.53
			sea grass	0.3 x -12.09	
				Average for Benthivorous Fish:	**0.71 ± 0.21**
Carnivorous Fish:					
Rainbow smelt (3+)	16	-17.56 ± 0.39	sand shrimp	1 x -20.51	2.95 ± 0.39
Atlantic tomcod (1)	10	-18.95 ± 0.31	*Macoma* clams	0.9 x -19.96	0.48 ± 0.31
			sea grass	0.1 -12.09	
Atlantic tomcod (2)	9	-17.02 ± 0.39	sand shrimp	1 x -20.51	3.58 ± 0.40
Tomcod (3+)	1	-17.86	sand shrimp	0.5 x -20.51	2.00
			fish[1]	0.5 x -19.21	
Striped bass (1)	5	-18.87 ± 0.96	*Neomysis*	1 x -22.52	3.85 ± 0.64
Striped bass (2)	11	-19.09 ± 0.49	sand shrimp	0.5 x -20.51	0.77 ± 0.52
			fish[1]	0.5 x -19.21	
Striped bass (3+)	3	-16.78 ± 0.77	fish[1]	1 x -19.21	2.43 ± 0.77
				Average for Carnivorous Fish:	**2.20 ± 0.26**
Lower trophic levels:					
Gammarus sp.	8	-24.15 ± 0.43	Sediment	1 x -27.82	3.67 ± 0.43
EW-Zooplankton	8	-23.27 ± 0.54	EW-SPM	1 x -25.69	3.97 ± 0.40
				Average for lower trophic level organisms	3.82 ± 0.29
				Average $\delta^{13}C$-TEF for 134 invertebrates and fish = 1.87 ± 0.16	

1. Average $\delta^{13}C$ value for all fish in this study.

Table 6. Estimation of δ^{13}N-Trophic Enrichment Factors (δ^{13}N-TEF) for fish and some lower trophic level invertebrates from the estuary. All variances are reported as standard error (±SE). Age of fish in parentheses.

Predator	n	Predator δ^{15}N (‰)	Prey Item	Fraction of diet x $\delta^{15}N_{prey}$ (‰)	δ^{15}N-TEF
Planktivorous Fish:					
Rainbow smelt (1)	10	13.02 ± 0.49	EW-zooplankton	1 x 8.85	4.17 ± 0.49
Rainbow smelt (2)	10	12.30 ± 0.13	EW-zooplankton	1 x 8.85	3.45 ± 0.09
Three-spine stickleback (2+)	9	12.82 ± 0.57	EW-zooplankton	1 x 8.85	3.97 ± 0.57
				Average for Planktivorous Fish:	3.83 ± 0.24
Benthivorous Fish:					
Winter flounder (0)	12	12.59 ± 0.11	polychaetes	1 x 9.56	3.03 ± 0.11
Winter flounder (1+)	9	12.30 ± 0.20	*Macoma* clams	1x 9.66	2.64 ± 0.20
Smooth flounder (3)	5	12.63 ± 0.35	polychaetes	0.5 x 9.56	3.02 ± 0.35
			Macoma clams	0.5 x 9.66	
Mummichog	8	12.40 ± 0.64	polychaetes	0.7 x 9.56	3.61 ± 0.56
			sea grass	0.3 x 6.60	
				Average for Benthivorous Fish:	3.06 ± 0.16
Carnivorous Fish:					
Rainbow smelt (3+)	16	13.78 ± 0.15	sand shrimp	1 x 9.54	1.75 ± 0.15
Atlantic tomcod (1)	10	13.87 ± 0.14	*Macoma* clams	0.9 x 9.54	4.39 ± 0.14
			sea grass	0.1 x 6.60	
Atlantic tomcod (2)	9	14.29 ± 0.23	sand shrimp	1 x 9.54	2.22 ± 0.23
Tomcod (3+)	1	14.65	sand shrimp	0.5 x 9.54	2.08
			fish[1]	0.5 x 13.11	
Striped bass (1)	5	13.38 ± 0.19	*Neomysis*	1 x 8.95	4.43 ± 0.53
Striped bass (2)	11	13.46 ± 0.11	sand shrimp	0.5 x 9.54	0.89 ± 0.11
			fish[1]	0.5 x 13.11	
Striped bass (3+)	3	14.36 ± 0.51	fish[1]	1 x 13.11	1.25 ± 0.51
				Average for Carnivorous Fish:	2.36 ± 0.21
Lower trophic levels:					
Gammarus sp.	8	6.70 ± 0.37	Sediment	1x 3.3	3.38 ± 0.37
EW-Zooplankton	8	8.85 ± 0.96	EW-SPM	1 x 4.94	6.43 ± 0.17
				Average for lower trophic level organisms	4.94 ± 0.44
				Average δ^{15}N-TEFs for 134 invertebrates and fish = 2.94 ± 0.14	

1. Average δ^{15}N value of fish in this study.

Table 7. A comparison of $\delta^{13}C$, total nitrogen and carbon, and C/N ratios of sediment collected at the sampling site in 1979 and 1996.

Sediment	$\delta^{13}C$ ‰	Total Nitrogen	Total Carbon	C: N Ratios	Reference
1996	-27.82 ± 0.05	0.32 ± 0.26%	4.8%	15	(this study)
1979	-27.5	0.35 to 0.67%	4.4 ± 0.7%	8.1 to 16	Rashid and Reinson (1979)

Figure Headings

Figure 1. Schematic diagram of $\delta^{13}C$ values of inorganic carbon and primary producers from terrestrial, freshwater, and marine sources.

Figure 2. Location of Loggieville study site, Miramichi River Estuary (New Brunswick, Canada).

Figure 3. A Joining Cluster Tree diagram derived from the mean $\delta^{13}C$ and $\delta^{15}N$ of 47 groups of freshwater, estuarine, and marine samples (abiotic and biotic) using Euclidean distances and weighted pair-group averages.

Figure 4. A plot of mean $\delta^{15}N$ and $\delta^{13}C$ values of freshwater, estuarine and marine samples. Bars represent standard errors. The box represent the $\delta^{15}N$ and $\delta^{13}C$ range for freshwater submerged terrestrial leaf litter from the Miramichi River system and was obtained from a study by Doucett (1994). Abb used: Southwest Miramichi River (SW), Northwest Miramichi River (NW), and Suspended Particulate Matter (SPM).

FIGURE I

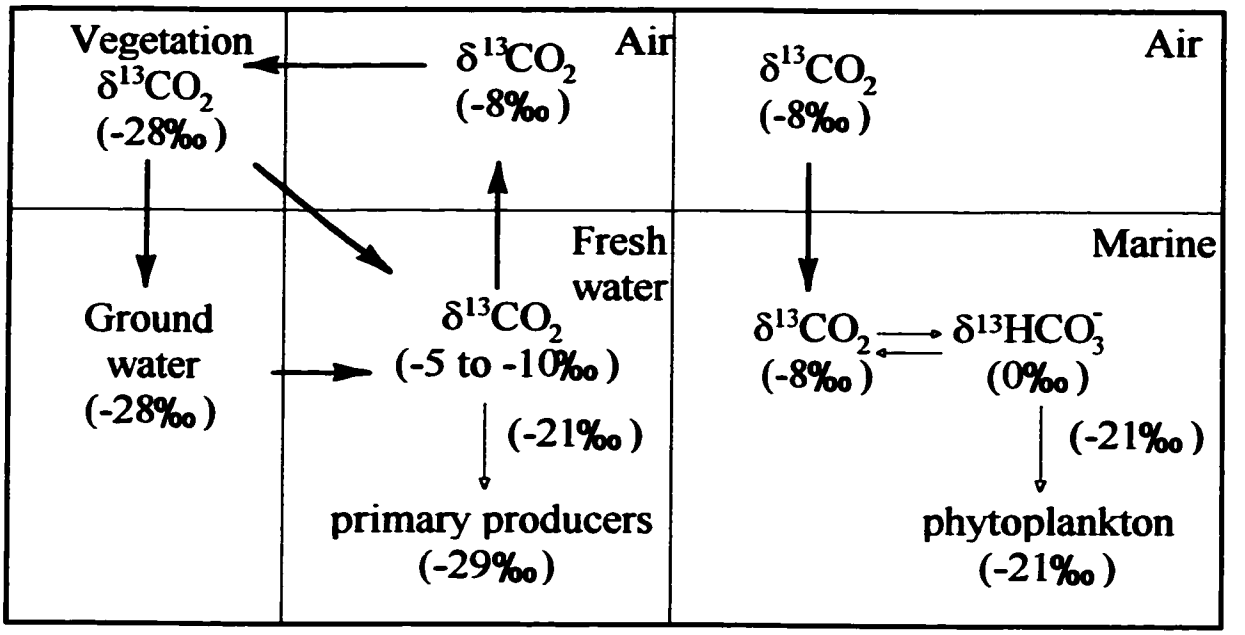

Vegetation
$\delta^{13}CO_2$
(-28‰)
$\delta^{13}CO_2$
(-8‰)
Air
$\delta^{13}CO_2$
(-8‰)
Air
Ground
water
(-28‰)
Fresh
water
$\delta^{13}CO_2$
(-5 to -10‰)
(-21‰)
primary producers
(-29‰)
Marine
$\delta^{13}CO_2$ ⟷ $\delta^{13}HCO_3^-$
(-8‰) (0‰)
(-21‰)
phytoplankton
(-21‰)

FIGURE 2

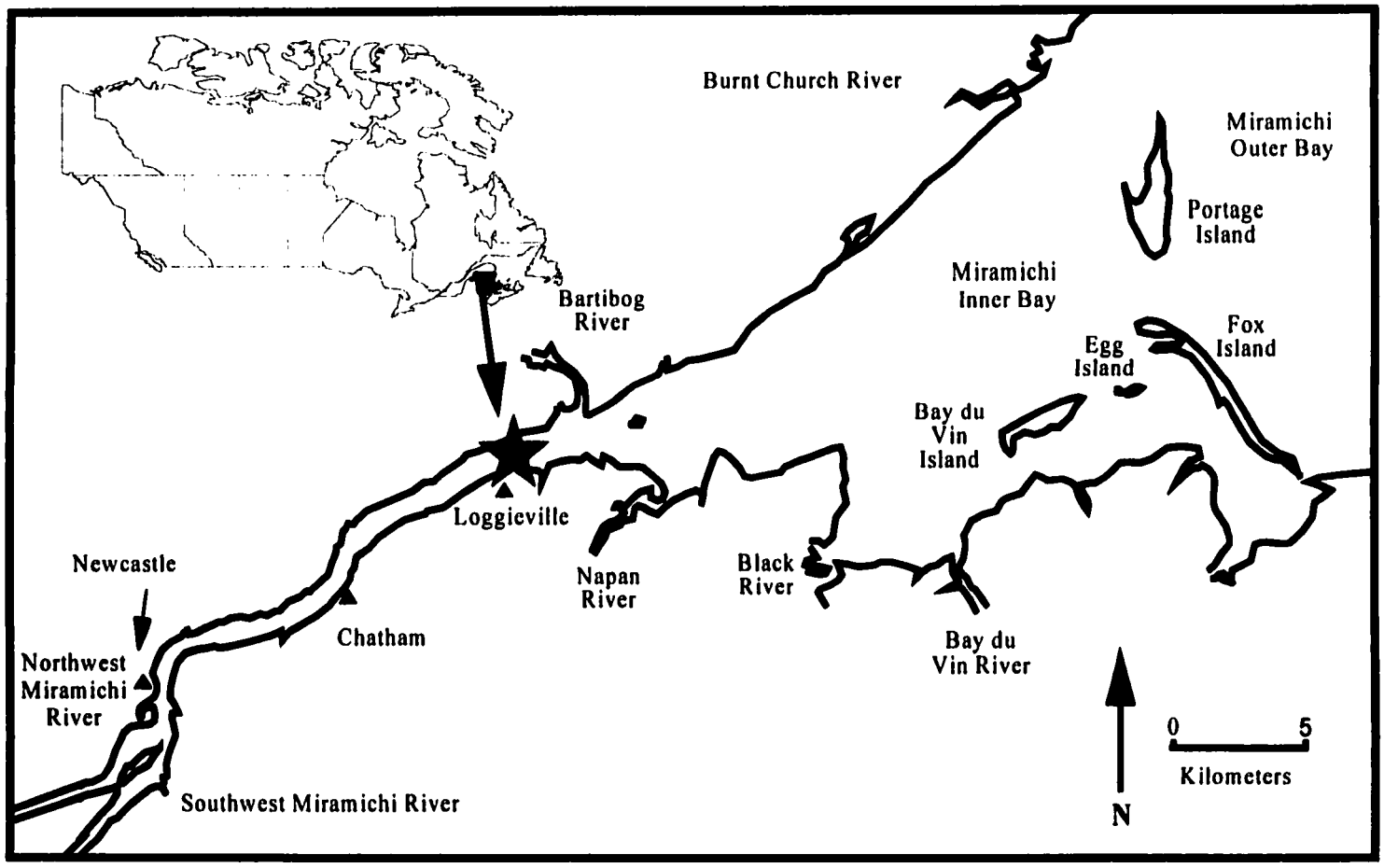

Burnt Church River
Miramichi
Outer Bay
Portage
Island
Miramichi
Inner Bay
Bartibog
River
Fox
Island
Egg
Island
Bay du
Vin
Island
Loggieville
Newcastle
Napan
River
Black
River
Chatham
Bay du
Vin River
Northwest
Miramichi
River
Southwest Miramichi River
0
5
Kilometers
N

FIGURE 3

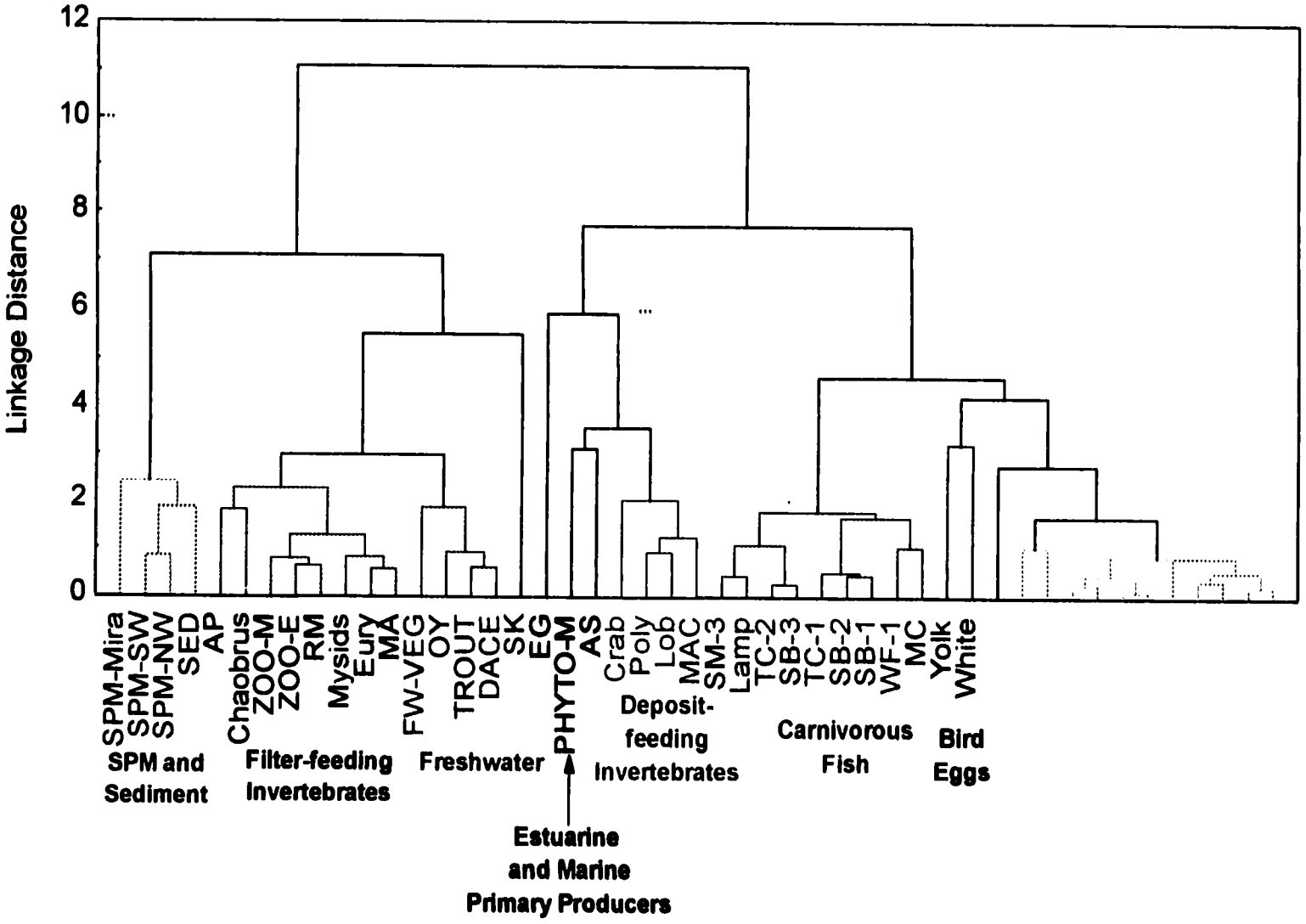
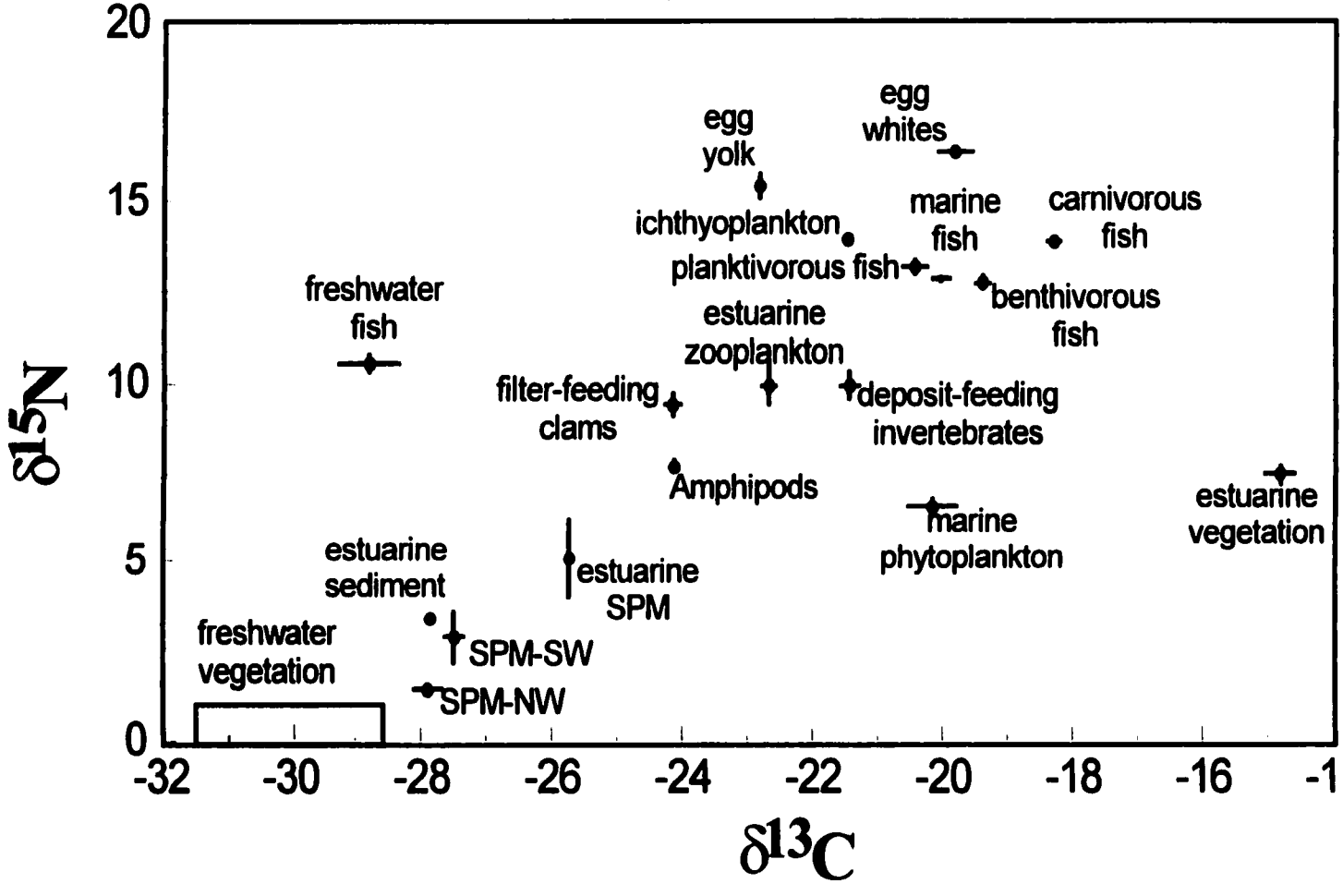

Linkage Distance
12
10
8
6
4
2
0
SPM-Mira
SPM-SW
SPM-NW
SED
AP
Chaobrus
ZOO-M
ZOO-E
RM
Mysids
Eury
MA
FW-VEG
OY
TROUT
DACE
SK
EG
PHYTO-M
AS
Crab
Poly
Lob
MAC
SM-3
Lamp
TC-2
SB-3
TC-1
SB-2
SB-1
WF-1
MC
Yolk
White
SPM and Sediment
Filter-feeding Invertebrates
Freshwater
Deposit-feeding Invertebrates
Carnivorous Fish
Bird Eggs
Estuarine and Marine Primary Producers

FIGURE 4


20
15
10
5
0
δ15N
-32
-30
-28
-26
-24
-22
-20
-18
-16
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egg yolk
egg whites
ichthyoplankton
marine fish
carnivorous fish
planktivorous fish
benthivorous fish
freshwater fish
estuarine zooplankton
filter-feeding clams
deposit-feeding invertebrates
Amphipods
estuarine vegetation
marine phytoplankton
estuarine sediment
estuarine SPM
freshwater vegetation
SPM-SW
SPM-NW

CHAPTER 2: PATTERNS OF MERCURY AND ISOTOPES OF CARBON ($\delta^{13}C$) AND NITROGEN ($\delta^{15}N$) IN AN ESTUARINE FOOD WEB

Abstract

Benthivorous fish were enriched in $\delta^{13}C$ by 1.81‰ when compared to planktivorous fish, and deposit-feeding invertebrates were enriched in $\delta^{13}C$ by 4.32‰ when compared to filter-feeding clams. These results indicate $\delta^{13}C$ values are useful in separating benthic- and pelagic-oriented organisms in a stratified estuary, and could be useful indicators of different food sources and pathways of mercury uptake. The Miramichi River Estuary food web's $\delta^{15}N$ values did not correlate well with total mercury concentrations, as seen in other aquatic studies. This lack of relationship is probably attributed to organisms feeding on foods with different $\log_{10}$[Hg] and $\delta^{15}N$ values, as seen for lower trophic level fish and invertebrates. Benthic fish, of the same $\delta^{15}N$-defined trophic level, had significantly higher mercury concentrations (270 ± 30 ng g^{-1} dry wt) than pelagic fish (240 ± 64 ng g^{-1} dry wt). Significantly higher mercury concentrations were also measured for filter-feeding clams (560 ± 170 ng g^{-1} dry wt) of a significantly lower $\delta^{15}N$-defined trophic level than deposit-feeding invertebrates (250 ± 81 ng g^{-1} dry wt). As expected, top trophic level carnivorous fish had significantly higher mercury concentrations (550 ± 110 ng g^{-1} dry wt) and $\delta^{15}N$ values when compared to pelagic and benthic fish. This observation shows that biomagnification of mercury in top predator fish in the Miramichi River Estuary.

Introduction

As in many parts of the world, mercury contamination of fish continues to be a serious problem in North America. In 1998, the United States had 37 state-wide fish consumption advisories (USEPA 1999). In the same year, Canada had two province-wide advisories (Nova Scotia and New Brunswick) and more than 2,400 individual fish consumption advisories (i.e., fish of a particular size, species, and location) in the rest of Canada where mercury concentrations in fish tissue exceeded 0.5 $\mu g\ g^{-1}$ on a wet wt basis (USEPA 1999).

There is evidence that reactive mercury (Hg II) entering the water column (i.e., from river inputs, surrounding wetlands or atmospheric deposition) is easily methylated and readily bioavailable to the food web (Watras 1995). Pelagic pathways of mercury transfer were identified to be important in certain aquatic ecosystems, such as boreal and humic lakes, reservoirs, and freshwater estuaries (Lindqvist 1991, Krom *et al.* 1994, Meili *et al.* 1994, Francis *et al.* 1998). However, other aquatic studies have shown benthic pathways to be important routes of mercury transfer to food webs. This was seen in food webs from the inner shelf of Terra Nova Bay (Antarctica), the South Adriatic Sea (South Italy), and in a coastal area of Italy (Barghigiani and Ristori 1995, Bargagli *et al.* 1998, Storelli *et al.* 1998). Further work is needed to determine the route and relative magnitude of mercury transfer into food webs.

Ratios of carbon ($^{13}C/^{12}C$) and nitrogen isotopes ($^{15}N/^{14}N$) are commonly used in aquatic food web studies to determine food web structure, such as carbon flows ($\delta^{13}C$) and trophic positions ($\delta^{15}N$) (McConnaughey and McRoy 1979, Peterson *et al.* 1986, Fry

1991, France 1997, Deegan and Garritt 1997). An average dietary enrichment for the heavier nitrogen ($\delta^{15}N$) isotope is usually between 3 and 5‰ (Minagawa and Wada 1984, Fry and Wainright 1991, France 1995, France and Peters 1997). This trend has enabled the relative trophic positions of individual organisms in food webs to be quantified and placed on a trophic continuum, from the lowest $\delta^{15}N$ values for primary producers, to the highest for top predators. Little change in ^{13}C and ^{12}C ratios between a heterotroph and its diet (i.e., $\delta^{13}C$ between 0.5 and 1‰) permits energy flows to be traced through the food web (Peterson *et al.* 1986). Deegan and Garritt (1997) found $\delta^{13}C$ was a useful tool to differentiate between benthic and pelagic biota in a well mixed salt marsh, the Plum Island River Estuary, where benthic biota were significantly enriched in $\delta^{13}C$. France (1995) also observed this $\delta^{13}C$ enrichment in biota from four Canadian Shield lakes and other fresh water studies world-wide.

For the Miramichi River Estuary, mercury concentrations are related to the $\delta^{13}C$ and $\delta^{15}N$ values of the food web. The Miramichi River Estuary was chosen for this study, as it is highly stratified throughout most of the year, offering a division of salinity ($\geq$ 12 ppt) and temperature ($\geq$ 2°C) between benthic and pelagic environments, and potentially food and mercury pathways to estuarine biota.

This estuary sustains an important commercial fisheries. About 30% of the total fisheries landings from the southern Gulf of St. Lawrence comes from the this estuary (Chaput 1995).

Methodology

Study Site

In May of 1996, biotic and abiotic samples were collected near Loggieville (latitude 47°04'57" and longitude 65°23'80") in the Miramichi River Estuary, New Brunswick, Canada (Figure 1). All samples were collected in the section of the Miramichi referred to as the "contaminant sink", an area where freshwater suspended particulate matter (SPM) flocculates and settles (MacKnight 1990). Potential sources of metals, including mercury, come from the forestry-associated, manufacturing, food, and metal products industries, discharges from sewage and storm drainage, and freshwater runoff (Buckley 1995, Chiasson 1995). Throughout most of the year, this area is highly stratified, and a potential exists for anoxia and mercury methylation in the estuarine sediments. Physical descriptions of the estuary were collated by Locke and Courtenay (1996) from earlier studies and are briefly described below. This estuary is shallow, with an average depth of 5 m, and tidal range between 0.2 and 1.2 m. Freshwater, from a drainage basin of 14,000 km^2, enters the estuary from two main rivers, the Northwest and Southwest Miramichi Rivers. During high inflows (>291 $m^3 s^{-1}$), the upper layer of the salt wedge has a salinity of 4 parts per thousand (ppt). The bottom layer's salinity is between 20 to 22 ppt. During low inflow (about 73 $m^3 s^{-1}$) the upper layer has a salinity of 12 ppt and the bottom of 22 to 24 ppt. On average the upper layer near Loggieville is about 2 m in depth. Temperature differences between the surface and bottom are typically between 2 and 3 °C. Large freshwater flow rates account for the year round stratification (temperature and salinity) at this site.

Field Methodology

All estuarine samples were collected during May 1996. Smooth flounder (*Pleuronectes putnami* Gill), winter flounder (*Pleuronectes americanus* Walbaum), Atlantic tomcod (*Microgadus tomcod* Walbaum), and rainbow smelt (Osmerus mordax Mitchell) were collected daily from Fyke nets (2.4 cm mesh size). Eels (*Anguilla rostrata* Lesueur), and striped bass (*Morone saxatilis* Walbaum) were obtained from Gaspereau nets (3.1 cm mesh size). Crangon shrimp (*Crangon septemspinosa* Say) and small fish (e.g., rainbow smelt, three-spine sticklebacks (*Gasterosteus wheatlandi* Linnaeus), mummichog (*Fundulus heteroclitus* Linnaeus) and winter flounder), and were obtained with a beach seine (30 x 1.8 m and 6 mm mesh). Soft-shell clams (*Mya arenaria* Linnaeus), and polychaetes (*Nereis* sp.) were obtained by shoveling into the soft silty-clay during a low tide. Deposit-feeding clams (*Macoma balthica* Linnaeus) were obtained from an Ekman grab. Oysters (*Crassostrea virginica* Say) and ribbed mussels (*Geukenisa demissa* Dilwyn) were picked off the sediment/rocky bottom during low tides. Sediment samples were collected with an Ekman Grab. Sediment samples were placed into glass jars with stainless steel spoons. Invertebrates were placed into plastic bags or glass jars.

All tools (i.e., scissors and tweezers) and storage containers (i.e. glass jars and tin foil) used in handling the samples were pre-washed with three rinses of acetone followed by three rinses of hexane, except for ziplock bags.

All samples were transported in coolers to the Department of Fisheries and Ocean's contaminant lab in Moncton (New Brunswick, Canada). At the lab, the species, length, weight, and sex of each fish were recorded. For mercury analysis, each fish

sample was individually wrapped in acetone/hexane pre-rinsed tinfoil. All samples were stored at -20°C.

Mercury Analysis

A total of 111 fish, 61 invertebrates, and 3 sediment samples were analysed for total mercury using Cold Vapor Atomic Absorption Spectroscopy (CVAAS) with the M-6000 Mercury Analyzer (CETAC Technologies Inc., Omaha, Nebraska, USA). Hg standards were made from a "Baker Instra-Analyzed" stock solution (VWR Scientific Products, West Chester, PA, USA). To establish accuracy, a standard reference material, DORM-2 certified dogfish muscle (National Research Council, Ottawa, ON, Canada) was used.

For each fish, the skin was peeled back with acid-washed plastic tweezers and a stainless steel scalpel to obtain a muscle sample for mercury analysis. Of these, 133 fish and 3 sediment samples were run in triplicate. All samples were analyzed for mercury as described in Wagemann *et al.* (1997). Approximately 0.3 g of sample was digested with concentrated sulfuric:nitric acid in Feulen Wu tubes (4:1 v/v) at 90 °C for 2 hrs. Potassium permanganate was added to completely oxidise any remaining material. After 2 hrs, enough hydrogen peroxide was added to bind unused potassium permanganate. A final volume of 25 ml was achieved by adding de-ionised water. Mercury was reduce with a 10% SnCl (stannous chloride) in a 7% HCL solution.

Repeated assays of the same sample resulted in a precision (expressed as the coefficient of variation) which were always below 3.6%. The limit of detection (LOD) was determined by the following formula obtained from Schmitt and Brumbaugh (1990):

$$LOD = 3\ (S^2_b + S^2_s)^{0.5}$$

where $S^2_b + S^2_s$ are the variances of concentrations measured for procedural blanks and low-level samples (i.e., lower trophic level organisms), respectively. The LOD for mercury was 0.55 ± 0.17 ng g^{-1} (dry wt). Average recovery rates of $100 \pm 1.4\%$ were obtained for the standard Reference Material DORM-2 (n=85).

Dry Weight

Sub-samples of each sample analyzed for mercury were freeze-dried to determine dry weights.

BAFs

Dietary Bioaccumulation Factors (BAFs) on a dry wt basis were determined with the following equation:

$$Dietary\ BAF = \frac{[Hg]_{organism}}{[Hg]_{food}}$$

Sediment BAFs were determined in a similar way, except $[Hg]_{sediment}$ was the denominator. Dietary BAFs were only calculated when mercury levels were known for a species of fish and its prey.

Stable Isotope Methods

All stable isotope analysis was conducted at the GG Hatch Isotope Laboratories (University of Ottawa, Ottawa, Ontario, Canada). Each sample was freeze-dried, ground, and weighed into tin capsules. Optimal sample weights of 250 µg (dry wt) for fish muscle and 5 mg (dry wt) for sediment were used. Analysis for carbon and nitrogen isotopes was

carried out with an automated CE Instrument EA-110 (elemental C & N analyzer) coupled to a Finnigan Mat Delta^{PLUS} IRMS with a Conflow II Interface (Finnigan Mat, San Jose, California, USA). The samples were flash-combusted at 1800 °C under a continuous stream of O_2. Isotopes of C & N were measured from the same combustion by separating N_2 and CO_2 gases with a chromatographic column. Helium gas carried the separated gases to the mass spectrometer.

Stable carbon and nitrogen isotope ratios were expressed as "delta" notation (δ) and have units of parts per thousand or "per mil" (‰) difference from a standard using the following equation:

$$\delta^{13}C = \frac{(^{13}C/^{12}C_{sample}) - (^{13}C/^{12}C_{standard})}{(^{13}C/^{12}C_{standard})} \times 1000$$

To determine the $\delta^{13}C$ the standard was Vienna Pee Dee Belemnite (VPDB), and for $\delta^{15}N$ the standard was atmospheric N_2.

In one run, a mean $\delta^{13}C$ of -16.99 ± 0.05‰ (± SE) and mean $\delta^{15}N$ of 13.99 ± 0.45‰ were obtained for ten tomcod samples of the same fish. During each analysis of 27 samples, four standard reference materials (NIST and IAEA) were run: two carbon (USGS24 graphite and NBS No.21 graphite) and two nitrogen (USGS-25 No. 12 and IAEA-N-2 No. 245). For further accuracy, muscle tissue from one striped bass from this study was used to determine if there was any internal drift between runs. Between runs, the $\delta^{13}C$ and $\delta^{15}N$ of the striped bass tissue were always within 0.18 ‰ and 0.31‰ of each other, respectively.

Stomach Contents

Stomach contents were removed from frozen fish and preserved in 10% formalin. With the aid of a dissecting microscope, food items were identified to the lowest order of classification. The number of individuals in each food category was recorded and expressed as a percentage of the total number of food items (Hyslop 1980) for each class as given by the following formula:

$$Percent\ composition\ by\ number = \frac{No.\ of\ specific\ food\ item}{Total\ No.\ of\ all\ food\ items} \times 100$$

Statistics

To conform the data to homoscedasticity and normal distribution, all statistical analysis was conducted using base-10 logarithmic transformations of total Hg concentrations on a $\mu g\ g^{-1}$ dry wt basis (log[Hg]). An ANOVA test (α=0.05) was used to determine if the mean $\delta^{15}N$ and $\delta^{13}C$ values and mercury concentrations were the same between benthic, pelagic, and carnivorous fish. A post-hoc comparison (Tukey, α=0.05) was conducted to determine which groups were significantly different from each other. A *t*-test (α=0.05) was used to determine if the mean $\delta^{15}N$ and $\delta^{13}C$ values and mercury concentrations were the same between filter-feeding clams (oysters, ribbed mussels, and soft shell clams) and deposit-feeding invertebrates (deposit-feeding clams, sand shrimp, and polychaetes). All statistics were performed using STATISTICA Version 5.1 (StatSoft, Inc., Tulsa, OK, USA).

Results

On the basis of gut contents, fish were separated into three main functional

feeding groups: planktivores (stickleback, and age-1 and -2 rainbow smelt), benthivores (mummichog, winter and smooth flounder, and eel), and carnivores (age-3+ rainbow smelt, tomcod, and striped bass). Planktivorous fish (three-spine stickleback, and age-1 and -2 rainbow smelt) selectively fed on zooplankton, whereas bottom-feeding fish (winter and smooth flounder, mummichog, and eels) fed mainly on sediments and deposit-feeding invertebrates (i.e., sand shrimp, polychaetes, and clams). Results from the gut content analysis showed carnivorous fish ate only large-sized invertebrates (i.e., mysids and sand shrimp) and/or other fish. These groups are summarized in Figure 2. Stomach contents are summarized in Table 1.

No significant difference was seen in the mean $\delta^{15}N$ values for benthic and pelagic fish (Tukey, $P>0.05$). Even though benthic and pelagic fish occupied the same $\delta^{15}N$-trophic level, benthic fish had significantly higher $\log_{10}$[Hg] than pelagic fish as summarized in Table 2 (Tukey, $P<0.05$). Benthic fish were also significantly (*t-test*, $p<0.05$) heavier (49 ± 9.5 g) than pelagic fish (2.16 ± 9.5 g). On a dry wt basis, mercury concentrations were 270 ± 30 and 240 ± 64 ng g^{-1}, respectively. The evidence for different routes of carbon and mercury uptake is supported by the significantly enriched $\delta^{13}C$ value in benthic fish by 1.81‰ when compared to pelagic fish, as well as the difference in gut contents. These results are summarized in Table 2.

Carnivorous fish (e.g., tomcod, striped bass, and age-3+ rainbow smelt) were significantly enriched in $\delta^{15}N$, $\delta^{13}C$, and $\log_{10}$ [Hg] when compared to bottom-and pelagic-feeding fish (Tukey, $P<0.05$). These values are summarized in Table 2. Mean $\delta^{15}N$ values for carnivorous fish were enriched by ≥1.14‰ when compared to lower

trophic benthic and pelagic-fish. Similarly the mean $\delta^{13}C$ for carnivorous fish was enriched by ≥1.12‰ when compared to benthic and pelagic fish. Significantly higher $\log_{10}$[Hg] were obtained for carnivorous fish when compared to both benthic and pelagic fish (Tukey, $P<0.05$). Higher mercury levels in top predator fish relative to lower trophic level fish demonstrates that biomagnification occurs at this level of the food web.

Filter-feeding clams were significantly depleted in $\delta^{15}N$ and $\delta^{13}C$ and significantly enriched in $\log_{10}$[Hg] when compared to deposit-feeding invertebrates as summarized in Table 3 and shown in Figure 3 (*t*-test, $P<0.05$). Filter-feeding clams were significantly depleted in $\delta^{15}N$ by 1.43‰ when compared to deposit-feeding invertebrates, and depleted in $\delta^{13}C$ by ≥3.68‰ (Table 3). Filter-feeding clams of a significantly lower $\delta^{15}N$-defined trophic level had significantly higher concentrations of mercury (560 ± 170 ng g^{-1} dry wt) than deposit-feeding invertebrates (250 ± 81 ng g^{-1} dry wt) (*t*-test, $P<0.05$).

Dietary BAFs ($[Hg]_{fish}/[Hg]_{food}$ on a dry wt basis) and sediment BAFs ($[Hg]_{fish}/[Hg]_{sediment}$ on a dry wt basis) from the Miramichi River Estuary are summarized in Tables 4. Dietary BAFs were calculated for 4 fish groups: age-1 winter flounder (1.1 ± 0.15), age-3+ rainbow smelt (1.8 ± 1.2), age-2 tomcod (3.4 ± 1.1), and age 3+ tomcod (5.7). For 3 sediment samples, the average mercury concentration on a dry weight basis was 140 ± 7.0 ng g^{-1}. Sediment BAFs were lowest for age-1 rainbow smelt (0.96 ± 0.15) and highest for age-3+ striped bass (18 ± 11) as shown in Table 5. Sediment BAFs for filter-feeding clams and deposit-feeding invertebrates were 4.0 ± 1.2 and 1.8 ± 0.57, respectively (Table 5).

Discussion

Carbon Isotopes

In this study, a significant enrichment of $\delta^{13}C$ by 1.81‰ clearly separated benthic- from pelagic-feeding fish, indicating different sources of food and pathways of mercury uptake. Benthic food webs are usually enriched in $\delta^{13}C$ when compared to pelagic ones in lakes, estuaries, and coastal and marine waters (McConnaughey and McRoy 1979, Fry and Wainright 1991, France 1995, Deegan and Garritt 1997, France and Peters 1997). McConnaughey and McRoy (1979) observed this $\delta^{13}C$-enrichment in benthic organisms when compared to pelagic organisms of the Bering Sea. As their data was lipid corrected, they believed this enrichment was due to preferential respiration of the light $^{12}CO_2$. France (1995) attributes lower water turbulence around benthic primary producers to the enrichment of $\delta^{13}C$ observed in benthic primary consumers. Under low flow conditions (i.e., low turbulence), CO_2 has a high diffusion resistance in water, potentially causing $\delta^{13}C$ enrichment of inorganic carbon around the cell of benthic primary producers (Osmond *et al.* 1981). As seen in a marine study by Fry and Wainright (1991), enrichment of $\delta^{13}C$ in filter-feeding scallops was correlated with depth and the corresponding $\delta^{13}C$ values of phytoplankton.

Very little difference in $\delta^{13}C$ between benthic and pelagic fish may suggest a tight benthic-pelagic coupling of matter (France 1997). A $\delta^{13}C$ difference of 2.9‰ was noted between benthic and pelagic fish in a well-mixed estuary, the Plum Island River Estuary (Deegan and Garritt 1997). However, for the Miramichi River Estuary, which is stratified throughout the year, a smaller $\delta^{13}C$ enrichment of 1.81‰ was observed between benthic

and pelagic fish. These preliminary results do not support using $\delta^{13}C$ differences in benthic and pelagic organisms to denote the degree of benthic-pelagic coupling or the degree of stratification in estuaries.

Mercury

Mercury biomagnification was observed in carnivorous fish relative to benthivorous and planktivorous fish of a lower $\delta^{15}N$-defined trophic level. However, there was no significant difference between mercury concentrations and $\delta^{15}N$ values for the Miramichi River Estuary food web (n=134). This lack of relationship may be due to estuarine organisms feeding on foods with differing $\log_{10}$[Hg] and $\delta^{15}N$ values, as observed for benthic and pelagic invertebrates and fish. Significantly higher mercury levels were seen in benthic when compared to pelagic fish occupying the same $\delta^{15}N$-defined trophic level. One possible explanation for this observation is that mercury is more bioavailable via the benthic pathway. However, filter-feeding clams of a significantly lower $\delta^{15}N$-defined trophic level than deposit-feeding invertebrates had significantly higher mercury concentrations. These results indicate the limitations of using $\delta^{13}C$ and $\delta^{15}N$ values to explain the pathways of mercury bioaccumulation without information of the feeding behaviors of estuarine organisms.

Elevated levels of total mercury in filter-feeding clams relative to deposit-feeding invertebrates was also observed in other estuarine studies (Kiørboe *et al.* 1983, Langston *et al.* 1995). One explanation put forward is that filter-feeding clams filter out the mercury-rich particles (Langston *et al.* 1995). Another explanation is that they feed on the finer particulate matter resuspended from the estuarine bottoms which may contain higher

mercury levels. Freshwater POC and DOC transported into the estuary could also be another source of mercury as proposed by Cossa and Martin (1991) for the Rhône delta.

In this estuarine study, tomcod fed higher up the food web, and had significantly higher mercury concentrations than winter flounder. Conversely, higher mercury concentrations were reported for flounder (*Platichthys flesus* L.) than cod (*Gadus morhua* L.) in the Glomma Estuary (Norway) (Staveland *et al.* 1993). In their study, flounder were between 4 and 6 yrs (~300 g) and cod were between 1 and 3 yrs (900 g), and probably of different trophic levels. The results from the Miramichi River Estuary show the usefulness of using $\delta^{15}N$ values to determine the different trophic positioning of different species of fish prior to comparing their mercury levels.

BAFs

A comparison of literature values for BAFs has proven difficult, as the data are often reported in different units. Average dietary BAFs reported per trophic level ranged from 1.95 for more than 29 Canadian Shield lakes in Ontario to 3.3 for boreal forest lakes (Meili 1991, Cabana *et al.* 1994). These dietary BAFs ($[Hg]_{fish}/[Hg]_{food}$) are similar to those obtained from this study which ranged from 1.0 to 5.7 (Table 4).

In this study, sediment BAFs for invertebrates varied from 0.61 to 8.4 (Table 5). Sediment BAFs ($[Hg]_{fish}/[Hg]_{sediment}$) ranged from 0.96 in lower trophic level fish (age-1 rainbow smelt) up to 18 for higher trophic level fish (age-3+ striped bass). These results are also similar to those obtained for coastal biota from the Pacific Coast (British Columbia, Canada) where sediment BAFs ranged from 0.90 to 8.6 for fish (Harding and Goyette 1989). One possible explanation for the higher BAFs obtained for the Miramichi

River Estuary is that fish of a higher trophic status may have been used.

Management

In the Mersey Estuary, concentrations of mercury and methylmercury have decreased significantly in invertebrates from 1981 to 1995 (Langston *et al.* 1995). It was proposed that implementation of control measures during this time played a role in this reduction. Similar reductions were obtained for mercury levels in sediments from the Miramichi River Estuary. At this same sampling site, mercury levels in sediments (60 ± 2.7 ng g^{-1} wet wt) were five times lower than measured in 1980 (296 ng g^{-1} wet wt) (Willey and Fitzgerald 1980). These results may reflect a reduction in anthropogenic inputs over the past 20 years and/or changes in sampling methods. As seen from studies with flooded reservoirs, the length of time for mercury levels to return to background levels for fish could take more than 15 years for omnivorous fish and more than 20 years for piscivorous fish (Anderson *et al.* 1995).

On a dry wt basis, the mercury levels in the sediment were 140 ± 7.0 ng g^{-1}. These levels slightly exceed the recommended interim marine sediment quality guideline for mercury in marine sediments of 130 ng g^{-1} (dry wt) (Environment Canada 1997).

All estuarine fish fell within the safe consumption guideline set to protect human health from mercury contaminated fish (0.5 μg g^{-1} wet wt). However, in a recent study conducted by Scheuhammer *et al.* (1998), reproductive and behavioural effects were seen in common loons (*Gavia immer*) consuming fish with mercury concentrations between 0.3 and 0.4 μg g^{-1} (wet wt). Barr (1986) also saw reproductive and behavioural effects in common loons (*Gavia immer*) consuming food with mercury concentrations within this

range. No loon chicks were produced when the levels exceeded 0.4 $\mu g\ g^{-1}$ (wet wt). Higher trophic level fish from the Miramichi River Estuary have mercury concentrations that exceed this level. It could be important to determine whether the current mercury levels in fish can cause reproductive and behavioural impairment to fish-eating birds that use the Miramichi River Estuary as feeding and breeding grounds.

Conclusions

As expected, higher levels of mercury and $\delta^{15}N$-defined trophic positions were observed for carnivorous fish when compared to benthivorous and planktivorous fish. This indicates biomagnification of mercury occurs in predator fish in the Miramichi River Estuary. Also Sediment and Dietary BAFs were similar to those observed in other coastal and lake studies. However, for 134 Miramichi River Estuary organisms, a non-significant relationship existed between mercury concentrations and $\delta^{15}N$ values. This lack of relationship was attributed to estuarine organisms feeding on prey with different $\log_{10}$[Hg] and $\delta^{15}N$ values. This was observed for lower trophic level fish and invertebrates. Mercury levels in benthic fish were significantly higher than pelagic fish of the same $\delta^{15}N$-defined trophic level. Conversely higher bioaccumulation of mercury was seen for filter-feeding clams (of a lower $\delta^{15}N$-defined trophic level) than deposit-feeding invertebrates. These results indicate the importance of using dietary information to help explain the relationship between mercury concentrations and $\delta^{15}N$ values. In this study, $\delta^{13}C$ values were useful in separating benthic- from pelagic-orientated invertebrates (>3.68‰) and fish (>1.81‰).

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Table 1. The number of individuals in each food category in 10 species of fish captured in the Miramichi River Estuary, May 1996, expressed as a percentage of the total number of food items for each class[1]. Abb: polychaetes and oligochaetes (Worms), deposit-feeding clams (Clams), and unidentifiable organic matter (Uniden. OM), gaspereau (GS), herring (HR), mummichog (MC), striped bass (SB), smooth flounder (SF), rainbow smelt (SM), tomcod (TC), winter flounder (WF), eels, and stickleback (STS). Age of fish in parentheses.

	No. of fish	No. of Empty Stomachs	Phyto-plankton	Zoo-plankton	Terrestrial Invertebrates	Worms	Grass Shrimp	Crabs	Clams	Estuarine Sea Grass	Detritus	Sediment	Uniden. OM	Fish Eggs	Fish
HR	11	0	92	8.3											
GS	10	0		100											
STS	11	2		100											
SM-1	9	1		86	14										
SM-2	11	5		86	14										
SM-3+	17	8		11		11							78		
WF-0	10	2		5.5		33			5.6	5.6	17	28	5.6		
WF-1+	9	0				3.6		3.6	39	14	7.1	32			
SF	5	0				24		5.9	24	5.9	12	29			
MC	8	0				40		40		20					
Eels	8	4								43	14			43	
TC-1	10	3							36	27	18		18		
TC-2	9	2					64		18	9.1	9.1				
TC-3+	1	0					33			33					33
SB-1	5	4													100
SB-2	11	11													
SB-3+	3	2													100

1. Percent composition by number = $\frac{\text{No. of specific food item}}{\text{Total No. of all food items}} \times 100$

Table 2. Comparison of mean $\delta^{15}N$ and $\delta^{13}C$ values, and $\log_{10}$[Hg] ($\mu g\ g^{-1}$ dry wt) between planktivorous, benthivorous, and carnivorous fish (ANOVA, α=0.05). Means followed by the same superscript letter are not significantly different (Tukey test, P<0.05).

	$\delta^{15}N$			$\delta^{13}C$			$\log_{10}$[Hg]		
Tukey test	F	P		F	P		F	P	
Fish Group	3.66	<0.05*		33.73	<0.01 **		5.87	<0.01 **	
	n	Mean	SE	n	Mean	SE	n	Mean	SE
planktivorous	27	12.68[a]	0.24	27	-21.03[a]	0.27	30	-0.86[a]	0.07
Benthivorous	33	12.47[a]	0.17	33	-19.22[b]	0.29	31	-0.64[b]	0.10
Carnivorous	51	13.82[b]	0.08	51	-18.10[c]	0.22	55	-0.50[c]	0.16

* P<0.05, ** P<0.01

Table 3. Comparison of mean $\delta^{15}N$ and $\delta^{13}C$ values, and $\log_{10}$[Hg] ($\mu g\ g^{-1}$ dry wt) between filter-feeding clams and deposit-feeding invertebrates (*t-test*, P<0.05). Means followed by the same superscript letter are not significantly different.

	$\delta^{15}N$			$\delta^{13}C$			$\log_{10}$[Hg]		
t-test	T	P		T	P		T	P	
Invertebrate Group	-4.047	<0.01**		-7.699	<0.01 **		2.102	<0.05*	
	n	Mean	SE	n	Mean	SE	n	Mean	SE
Filter-feeders	30	9.43[a]	0.20	30	-24.20[a]	0.32	27	-0.60[a]	0.10
Deposit-feeder	31	10.86[b]	0.29	31	-20.52[b]	0.35	22	-0.91[b]	0.11

* P<0.05, ** P<0.01

Table 4. Concentrations of total mercury, $\delta^{15}N$ and $\delta^{13}C$ values, and Dietary and Sediment Bioaccumulation Factors (BAFs) on a dry wt basis for fish caught in the estuary. All variances reported are standard errors (±SE).

Common name	Age	n	$\delta^{15}N$	$\delta^{13}C$	$[Hg]_{total}$ ng g^{-1} dry wt	Dietary BAFs[1]	Sediment BAFs[2]
Planktivores:							
Rainbow smelt	1	10	13.02 ± 0.49	-21.05 ± 0.63	140 ± 21		0.96 ± 0.15
Rainbow smelt	2	10	12.30 ± 0.09	-19.96 v 0.13	230 ± 67		1.6 ± 0.47
Three spine stickleback	2+	9	12.82 ± 0.57	-22.19 ± 0.22	320 ± 170		2.2 ± 1.2
Average for Planktivorous Fish:			12.68 ± 0.24	-21.03 ± 0.27	240 ± 64		1.7 ± 0.46
Benthivorous Fish:							
Winter flounder	0	12	12.59 ± 0.11	-20.71 ± 0.37	150 ± 22		1.1 ± 0.15
Winter flounder	1+	9	12.30 ± 0.20	-18.53 ± 0.30	330 ± 77	1.0 ± 0.6[3]	2.3 ± 0.54
Smooth flounder	3+	5	12.63 ± 0.35	-19.97 ± 0.43	220 ± 29		1.5 ± 0.22
Mummichog		8	12.40 ± 0.56	-17.50 ± 0.53	280 ± 48		2.0 ± 0.34
Eels	8-10	8	13.01 ± 0.75	-20.25 ± 0.84	380 ± 100		2.7 ± 0.71
Average for Benthivorous Fish:			12.55 ± 0.17	-19.38 ± 0.29	270 ± 30		1.9 ± 0.22
Carnivores:							
Rainbow smelt	3+	16	13.78 ± 0.15	-17.56 ± 0.39	150 ± 25	1.8 ± 1.2[3]	1.1 ± 0.18
Atlantic tomcod	1	10	13.87 ± 0.14	-18.95 ± 0.31	160 ± 17		1.1 ± 0.12
Atlantic tomcod	2	9	14.25 ± 0.23	-16.92 ± 0.39	290 ± 31	3.4 ± 1.1[3]	2.0 ± 0.22
Atlantic tomcod	3+	1	14.65	-17.86	1800	5.7[3]	12
Striped bass	1	5	13.37 ± 0.19	-18.67 ± 0.69	530 ± 120		3.8 ± 0.82
Striped bass	2	11	13.46 ± 0.11	-19.09 ± 0.49	1100 ± 140		7.6 ± 0.96
Striped bass	3+	3	14.36 ± 0.51	-16.78 ± 0.77	2600 ± 1600		18 ± 11
Average for Carnivorous Fish:			13.82 ± 0.08	-18.53 ± 0.22	550 ± 110		4.0 ± 0.82

1. Dietary BAF = $[Hg]_{fish}/[Hg]_{food}$
2. Sediment BAF = $[Hg]_{fish}/[Hg]_{sediment}$, where $[Hg]_{sediment}$ = 140 ng g^{-1} dry wt.
3. Diet of WF (1+) was deposit-feeding clams, and the diet for TC (2), TC (3+), and SM (3+) was and grass shrimp

Table 5. Concentrations of total mercury, $\delta^{15}N$ and $\delta^{13}C$ values, and Sediment Bioaccumulation Factors (BAFs) on a dry wt basis for invertebrates from the estuary. All variances reported are standard errors (±SE).

Common name	n	$\delta^{15}N$	$\delta^{13}C$	$[Hg]_{total}$ ng g^{-1} dry wt	Sediment BAFs[1]
Bottom-feeding invertebrates:					
Crangon sand shrimp	14	12.03 ± 0.25	-20.51 ± 0.47	90 ± 18	0.65 ± 0.13
Polychaetes	6	10.33 ± 0.37	-20.92 ± 0.56	--	--
Deposit-feeding clams	11	9.66 ± 0.49	-19.96 ± 0.70	540 ± 190	3.9 ± 1.3
Average for Bottom-feeders:		10.81 ± 0.29	-20.52 ± 0.35	250 ± 81	1.8 ± 0.57
Filter-feeding clams:					
oysters	10	9.56 ± 0.26	-23.86 ± 0.44	330 ± 100	2.3 ± 0.73
ribbed mussels	9	9.01 ± 0.35	-25.62 ± 0.71	1300 ± 500	9.0 ± 3.5
soft-shell clams	11	9.68 ± 0.40	-23.19 ± 0.21	220 ± 39	1.6 ± 0.27
Average for Filter-feeders:		9.43 ± 0.20	-24.20 ±0.32	560 ± 170	4.0 ± 1.2

1. Sediment BAF on a dry wt basis = $[Hg]_{invertebrate}/[Hg]_{sediment}$, where $[Hg]_{sediment}$ = 140 ng g^{-1}.

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Figure 1. Location of Loggieville study site, Miramichi River Estuary (New Brunswick, Canada).

Figure 2. A plot of $\delta^{15}N$ and $\delta^{13}C$ values, and mercury concentrations ($\mu g\ g^{-1}$ dry wt) in filter- and deposit-feeding invertebrates from the Miramichi River Estuary. Bars represent standard errors (±SE). Mercury concentrations on a $\mu g\ g^{-1}$ dry wt basis in parenthesis.

Figure 3. A plot of $\delta^{15}N$ and $\delta^{13}C$ values, and mercury concentrations ($\mu g\ g^{-1}$ dry wt) in benthivorous, planktivorous, and carnivorous fish from the Miramichi River Estuary. Bars represent standard errors (±SE). Abbr.: mummichog (MC), striped bass (SB), smooth flounder (SF), juvenile rainbow smelt (SMS), rainbow smelt (SM), tomcod (TC), juvenile winter flounder (WFS), winter flounder (FL), eel (Eel), and stickleback (STS), age-1 (-1), age-2 (-2), and age-3 and older (3+). Mercury concentrations on a $\mu g\ g^{-1}$ dry wt basis in parenthesis.

FIGURE 1

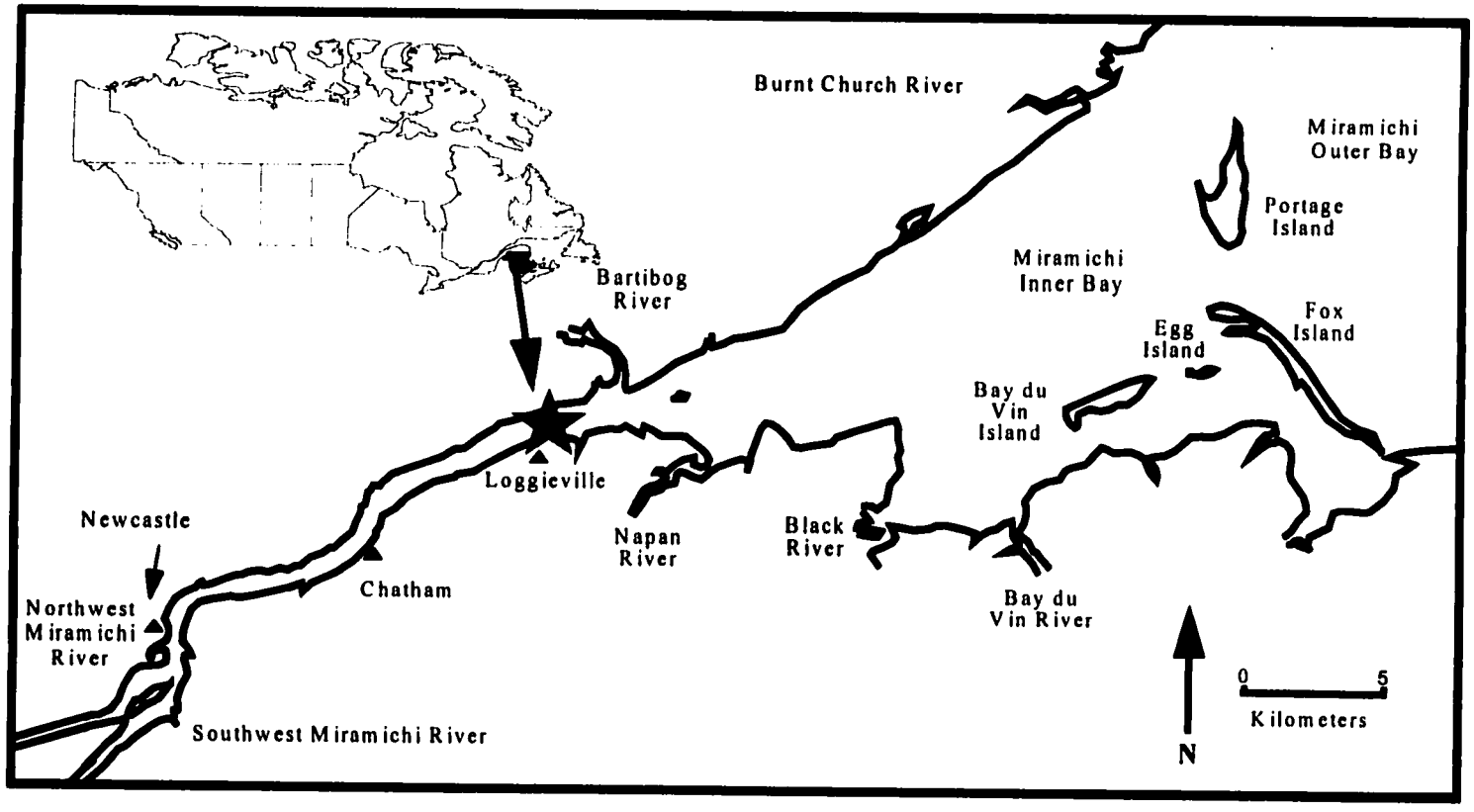

Burnt Church River
Miramichi Outer Bay
Portage Island
Miramichi Inner Bay
Bartibog River
Egg Island
Fox Island
Bay du Vin Island
Loggieville
Newcastle
Napan River
Black River
Chatham
Northwest Miramichi River
Bay du Vin River
Southwest Miramichi River
0
5
Kilometers
N

FIGURE 2

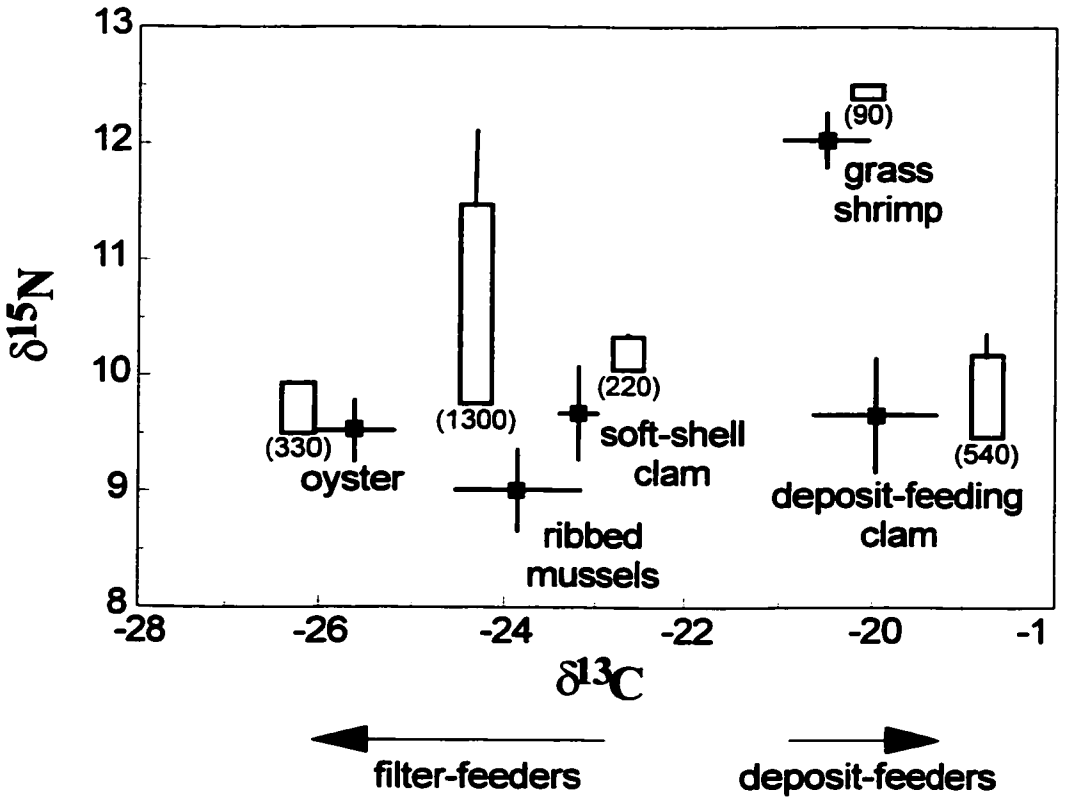
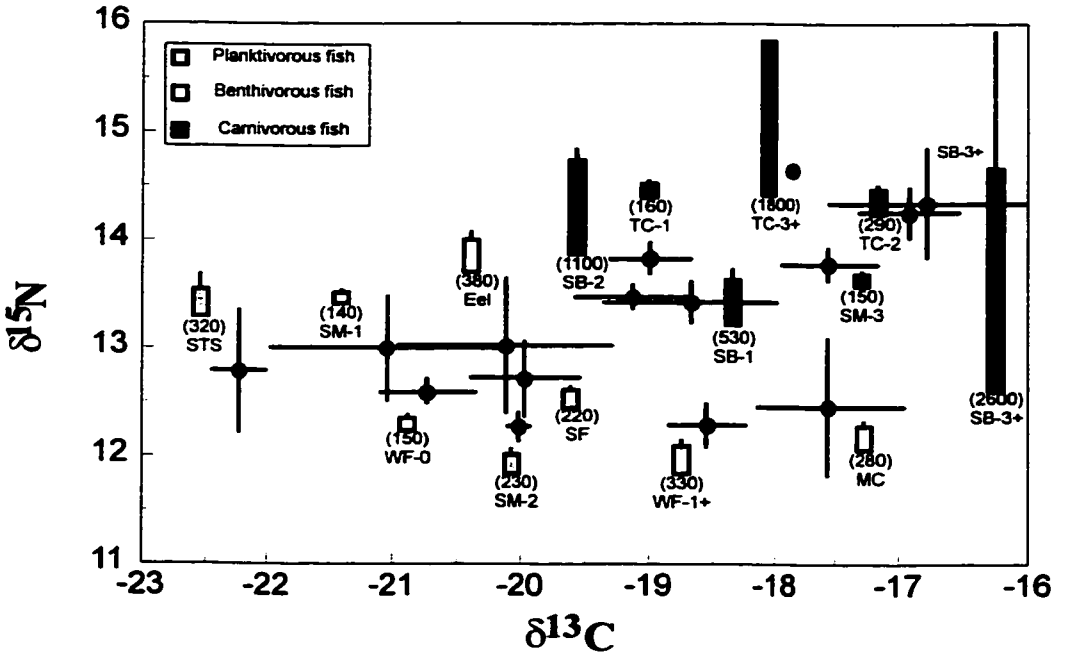

13
12
11
10
9
8
δ15N
-28
-26
-24
-22
-20
-1
δ13C
(90)
grass shrimp
(220)
soft-shell clam
(1300)
(330)
oyster
ribbed mussels
deposit-feeding clam
(540)
filter-feeders
deposit-feeders

FIGURE 3


Planktivorous fish
Benthivorous fish
Carnivorous fish
(320) STS
(140) SM-1
(380) Eel
(150) WF-0
(230) SM-2
(220) SF
(1100) SB-2
(160) TC-1
(330) WF-1+
(530) SB-1
(1800) TC-3+
(290) TC-2
(150) SM-3
(280) MC
SB-3+
(2600) SB-3+
16
15
14
13
12
11
-23
-22
-21
-20
-19
-18
-17
-16
δ15N
δ13C

CHAPTER 3: COMPARISON OF MERCURY BIOACCUMULATION IN LAKE, MARINE, AND ESTUARINE FOOD WEBS USING BIOMAGNIFICATION SLOPES

Abstract

The biomagnification slope (BMS), obtained from a plot of $\log_{10}$[Hg] versus δ^{15}N, was used to compare patterns of mercury biomagnification in three aquatic environments: the Miramichi River Estuary, nine lakes (Ontario and Québec) and two marine food webs (Farallon Islands and Lancaster Sound). A significant relationship was seen between $\log_{10}$[Hg] versus δ^{15}N for the nine lake food webs and the two marine food webs. There were no difference in BMSs for eight lake food webs which permitted the data to be pooled to obtain a BMS of 0.20 ± 0.0080. This value was the same as the one published for Lancaster Sound marine food web of 0.20, and similar to the one obtained for Farallon Islands of 0.32. This indicates mercury biomagnifies in a similar way in these ecosystems. A significant relationship was seen between $\log_{10}$[Hg] versus δ^{15}N for Green Lake (Ontario). However, its BMS (0.48 ± 0.05) was significantly higher than those observed for the other lake ecosystems. A significant relationship between $\log_{10}$[Hg] versus δ^{15}N was not seen for the estuarine food web. A number of factors may contribute to this lack of relationship between $\log_{10}$[Hg] versus δ^{15}N values: 1) estuarine organisms may feed on foods with varying $\log_{10}$[Hg] and δ^{15}N values, 2) mercury may bind to a wide range of complexing agents in estuaries (such as, Cl^-, Br^-, I^-, OH^-, sulfides and organic ligands) rendering it unavailable for methylation and bioaccumulation, and 3) estuaries are complex environments in a constant state of physical change (i.e., variations

in salinity and water movement).

Introduction

Only a small percentage of the total mercury in water and sediments is methylmercury. However, it is the most toxic form of mercury which biomagnifies[1] in the food web to levels that may cause harmful neurological, and possibly immunological effects (AMAP 1998, National Research Council 2000). As dietary transfer is the main uptake route of mercury in higher trophic level organisms, there is some concern that North Americans who consume fish, especially women of childbearing age, may be exposed to dangerous levels of mercury (Hall *et al.* 1997, Harris and Snodgrass 1993). A number of health effects have been found to be associated with mercury exposure during fetal development, including cerebral palsy, mental retardation, and lack of cell growth and brain development (National Research Council 2000). It was recently reported that 1 to 3% of women in United States eat fish with sufficient quantities of mercury to be at risk (National Research Council 2000). In Canada, a recent review of two studies showed that 29% of Inuit women from Baffin Island and 37% from Nunavik consumed food with mercury levels that exceeded the acceptable Tolerable Intake Dose of 5 μg/kg bw/week (AMAP 1998). In 1999, there were two province-wide consumption advisories, and more than 2,800 individual advisories for fish that have mercury levels that exceed 0.5 μg/g on a wet wt basis (Health and Welfare Canada 1990, USEPA 1999).

In aquatic food webs, nitrogen isotope ratios (^{14}N and ^{15}N) are used to quantify

1 Biomagnification is defined as the net increase of a contaminant in an organism relative to its food source.

trophic positions and food chain lengths (Minagawa and Wada 1984). Nitrogen isotope ratios are commonly expressed as "del notation" (δ) and have the units of parts per thousand or "per mil" (‰) difference from the standard (atmospheric N_2) using the following equation:

$$\delta^{15}N = \frac{(^{15}N/^{14}N_{sample}) - (^{15}N/^{14}N_{standard})}{(^{15}N/^{14}N_{standard})} \times 1000$$

Consistently, a trophic enrichment factor of 3 to 5‰ of the heavier nitrogen isotope ($\delta^{15}N$) is seen in biota compared to their food (Minagawa and Wada 1984). This enrichment is due to preferential elimination of the lighter ^{14}N isotope (Minagawa and Wada 1984). A major advantage in using $\delta^{15}N$ as an indicator of an organism's trophic position is that it represents the assimiliable nitrogen from an organism's diet. Van der Zanden *et al.* (1997) verified a close relationship between mean dietary trophic positions (using traditional dietary methods) and $\delta^{15}N$-defined trophic positions of fish. In their study, walleye and northern pike (with a diet of 85% fish) had higher $\delta^{15}N$ values than smallmouth and largemouth bass (with a diet of 37 to 50% fish), followed by pumpkinseed, yellow perch and rock bass (with a diet of <17% fish). Cabana and Rasmussen (1994) also published a study that showed a showed a strong correlation between mean mercury levels in lake trout from seven Ontario and Québec lakes and their mean $\delta^{15}N$ values.

The slope of a plot of $\log_{10}$[Hg] versus $\delta^{15}N$, known as the Biomagnification Slope (BMS), has been used to represent the degree of biomagnification. A larger BMS indicates a greater degree of biomagnification. This approach has been useful in

comparing the degree to which different organochlorines biomagnify, such as toxaphene, PCBs, α-HCH, *p,p'*-DDE, ΣDDT, *trans*-nonachlor, mirex, and PCDDs (Broman et al. 1992, Kidd *et al.* 1995a, Kiriluk *et al.* 1995, Jarmen *et al.* 1996, Kidd *et al.* 1998). In this study, BMSs were used to determine whether there are cross-system differences in the biomagnification of mercury. A comparison of BMSs is made with mercury and $\delta^{15}N$ data from the Miramichi River Estuary (this study) and nine lake food webs (Kidd *et al.* 1995b, Grimmard 1996), along with those reported for two marine food webs (Jarman *et al.* 1996, Atwell *et al.* 1998).

Methodology

Estuarine Data. Detailed descriptions of the estuarine study site[2], field and lab methodologies (mercury[3] and isotope methods[4]) are provided in Chapter 2 of this thesis, and Appendix 4.

Lake Data. $Log_{10}[Hg]_{wet\ wt}$ and $\delta^{15}N$ data published for fish from six Northwestern Ontario Lakes (Trout, Sydney, Musclow, Linge, Orange, Green) were obtained from Kidd (May 2000, person. comm.). Kidd's data was transformed to dry wt by assuming that 85% of the fish weight was water. This transformation did not change the slopes published by Kidd *et al.* (1995b), however it did raise the Y-intercepts. In this study, up to seven species of fish were analyzed for each lake.

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2 Samples were collected from the Miramichi River Estuary (Loggieville, New Brunswick, Canada) at latitude 47°04'57" and longitude 65°23'80"

3 A total of 3 sediments, 61 deposit- and filter-feeding invertebrates, and 111 planktivorous, benthivorous, and carnivorous fish were collected from the Miramichi River Estuary in May 1996 and analyzed for total mercury using Cold Vapor Atomic Absorption Spectroscopy (CVAAS) with a M-6000 Mercury Analyzer (CETAC Technologies Inc., Omaha, Nebraska, USA).

$Log_{10}[Hg]_{dry\ wt}$ and $\delta^{15}N$ values were published for one reservoir (Réservoir La Grande) and two lake food webs from Québec (Lac Ducan and Lac Detcheverry) and obtained from Grimard (1996). Grimard's sampling was more extensive with data for sediments, zooplankton, five families of invertebrates, and six species of fish.

Marine Data. BMSs for two marine food webs were published (Jarman *et al.* 1996, Atwell *et al.* 1998). In these studies, a BMS of 0.20 was recorded for Lancaster Sound (NWT). A BMS of 0.74 was published for the Farallon Islands food web (Gulf of Farallones). However, this calculation was done using natural logarithm ($ln[Hg]_{dry\ wt}$). This value converts into a BMS of 0.32 on a $log_{10}[Hg]_{dry\ wt}$ basis.

Statistics. An ANOVA (α=0.05) was used to determine if there was a significant regression between $log_{10}[Hg]$ versus $\delta^{15}N$ for the nine lakes one estuarine food web. An ANCOVA (α=0.05) was then conducted to determine if the BMSs were the same. All statistical analysis was conducted on mercury levels, on a $\mu g\ g^{-1}$ dry wt basis, using with Statistica Software, version 5.1 (Statsoft, Inc. Tulsa, OK, USA).

Results

No significant relationship between $log_{10}[Hg]$ versus $\delta^{15}N$ (ANOVA, P>0.05) was found for the estuarine food web. Conversely, a significant relationship between $log_{10}[Hg]$ versus $\delta^{15}N$ values was found for the nine lake food webs and those published for the two marine food webs. The BMSs for the nine lake ranged from 0.17 to 0.48 and are summarized in Table 1. For the marine ecosystems, the reported BMSs for the

4 All samples were analyzed for $\delta^{15}N$ using a Finnigan Mat Delta^{PLUS} IRMS with a Conflow II Interface (Finnigan Mat, San Jose, CA, USA).

Lancaster Sound (NWT) food web was 0.20 and for the Gulf of Farallones food web was 0.32 (Jarman *et al.* 1996, Atwell *et al.* 1998). Only Green Lake (0.48 ± 0.05) had a significantly different BMS (ANCOVA, $P<0.05$) from the other eight lakes (Trout, Sydney, Musclow, Linge, Orange, Lac Ducan, Lac Detcheverry, and Réservoir La Grande). Non-significant differences in BMSs among the eight lakes permitted the data to be pooled (ANCOVA, $P>0.05$) with a BMS of 0.20 ± 0.0080.

Discussion

Non-significant differences in BMSs for the eight lake food webs indicates mercury biomagnifies in a fairly consistent manner in these ecosystems. These lakes had a pooled BMS of 0.20 ± 0.0080. A BMS of 0.2 was also obtained for one marine food web, Lancaster Sound (NWT) which supports mercury biomagnifies in a similar manner to the eight lake ecosystems.

Green Lake had a significantly higher BMS (0.48 ± 0.05) when compared to the other eight lakes (Table 1). This may be attributed to Green Lake's limited sample size ($n=12$) with only two species of fish, or that mercury may biomagnify differently in this lake. The other eight lakes had larger sample sizes ($n\geq24$) and at least five fish species were sampled at each lake.

A BMS of 0.32 for mercury was calculated for the Gulf of Farallones food web (Jarman *et al.* 1996). This food web also appears to be highly contaminated with organochlorines. This study reports a BMS for PCBs of 0.88 and for ΣDDT of 0.79. In comparison, the BMS for PCBs was close to a order of magnitude higher than obtained for the food web from Lake Ontario (0.09 ± 0.01) (Kiriluk *et al.* 1995). Considerably

lower BMSs were recorded for ΣDDT for food webs from Lake Ontario and Lake Laberge of 0.09 ± 0.01 and 0.32 ± 0.03, respectively (Kidd et al. 1998, Kiriluk *et al.* 1995). As reported by Jarman *et al.* 1996, the Farallon Islands study site was highly contaminated from ocean dumping of radioactive and chemical wastes from 1946 to 1962.

There are a number of factors that may contribute to the lack of relationship between $\log_{10}$[Hg] versus $\delta^{15}N$ for the Miramichi River Estuary food web. First, as seen from Chapter 2, estuarine organisms may feed on foods with differing mercury and $\delta^{15}N$ values. Secondly, inorganic mercury may bind with a number of complexing agents in the estuary environment (such as, Cl^-, Br^-, I^-, OH^-, sulfides and organic ligands) thereby rendering it unavailable for methylmercury production and bioaccumulation in the estuarine food web. Finally, a large variability in $\log_{10}$[Hg] and $\delta^{15}N$ values may be inherent in estuarine organisms due to their high degree of mobility, and dynamic exchange between fresh- and salt-waters, sediments and water column (Day 1989, Costanza *et. al.* 1993). Even though there is limited data on mercury and $\delta^{15}N$ values for aquatic food webs, the results of this study indicate cross-system comparisons of BMS are useful in comparing similarities and differences in mercury bioaccumulation.

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Table 1. Summary of regression statistics: sample size (n), slope ± standard error (SE), Y-intercept, and r^2 from a regression of $\log_{10}$[Hg] versus $\delta^{15}N$ values for nine lake and two marine food webs (ANOVA, P<0.05).

	n	Food web organisms included in regression	Slope ± SE	Y-intercept ± SE	r^2	References
Trout Lake, Ontario	30	lake cisco, lake trout, lake whitefish, walleye, white sucker, northern pike	0.21 ± 0.037	-1.8 ± 0.29	0.58	Kidd *et al.* 1995b
Sydney Lake, Ontario	39	burbot, lake cisco, lake trout, lake whitefish, walleye, yellow perch, white sucker	0.17 ± 0.028	-1.5 ± 0.23	0.51	Kidd *et al.* 1995b
Musclow Lake, Ontario	26	lake cisco, lake whitefish, yellow perch white sucker, northern pike	0.19 ± 0.044	-1.8 ± 0.40	0.47	Kidd *et al.* 1995b
Linge Lake, Ontario	31	lake cisco, lake trout, lake whitefish, walleye, northern pike and white sucker	0.22 ± 0.040	-2.0 ± 0.37	0.53	Kidd *et al.* 1995b
Orange Lake, Ontario	24	lake cisco, northern pike, white sucker, walleye, yellow perch	0.29 ± 0.031	-2.1 ± 0.27	0.81	Kidd *et al.* 1995b
Green Lake, Ontario	12	white sucker, northern pike	0.48 ± 0.05	-5.1 ± 0.50	0.91	Kidd *et al.* 1995b
Lac Ducan and Lac Detcheverry, Québec	72	sediments, zooplankton, invertebrates, white suckers, lake whitefish, burbot, walleye, northern pike	0.22 ± 0.017	-1.7 ± 0.11	0.69	Grimmard 1996
Réservoir La Grande 2, Québec	84	sediments, zooplankton, invertebrates, white suckers, lake whitefish, burbot, walleye, northern pike	0.19 ± 0.013	-1.5 ± 0.11	0.74	Grimmard 1996
Farallon Islands, Gulf of Farallones	48	zooplankton, fish (n=2 species), birds (n=4 species) and sea lion	0.32	unknown	unknown	Jarman *et al.* 1996
Lancaster Sound, NWT	unknown	POM, invertebrates (n=12 species), fish (n=2 species), marine birds (n=8 species) and mammals (n=5 species)	0.2	-3.3	unknown	Atwell *et al.* 1998
Miramichi River Estuary, New Brunswick	134	sediments, sand shrimp, oysters, ribbed mussels, deposit-feeding clams, soft-shell clams, rainbow smelt, tomcod, stickleback,	0.043 ± 0.021	-1.26 ± 0.26	0.032	Pastershank 2001 (this study)

winter flounder, striped bass

OVERALL CONCLUSIONS

On a $\delta^{13}C$ and $\delta^{15}N$ basis, three different sources of energy were identified: terrestrial carbon, *in situ* estuarine primary production, and marine phytoplankton. Isotopically depleted $\delta^{13}C$ and $\delta^{15}N$ values verified terrestrial carbon was a major source of energy to estuarine sediments and SPM. This is not surprising, as the average annual freshwater inflow to the estuary is 250 $m^3 s^{-1}$ with an average SPM concentration of 11 mg L^{-1}.

Even though the Miramichi River Estuary is dominated by physical and chemical forces, a distinct food web structure was identified on the basis of $\delta^{13}C$ and $\delta^{15}N$ values. A cluster analysis of mean $\delta^{13}C$ and $\delta^{15}N$ values for 47 abiotic and biotic groups in this study structured the community of plants and animals into eight natural clusters: 1) estuarine sediment, and estuarine and freshwater SPM; 2) estuarine and marine primary producers; 3) freshwater fish and submerged terrestrial leaf litter, and estuarine oysters; 4) estuarine filter-feeding invertebrates; 5) estuarine deposit-feeding invertebrates; 6) estuarine planktivorous and benthivorous fish, some benthic invertebrates, and two filter-feeding marine fish; 7) estuarine carnivorous and two benthivorous fish; and 8) double crested cormorant egg (whites and yolks).

The results of this analysis show that for this coastal ecosystem, no distinction can be made in $\delta^{13}C$ and $\delta^{15}N$ values between estuarine and marine primary producers and filter-feeding fish, whereas freshwater fish and submerged terrestrial leaf litter were characterised by their isotopically light $\delta^{13}C$ values.

A $\delta^{13}C$-TEF of 1.87 ± 0.16‰ and a $\delta^{15}N$-TEF of 2.94 ± 0.14‰ were calculated for the Miramichi River Estuary food web. For the Miramichi River Estuary food web, the number of $\delta^{15}N$-defined trophic levels was 4.7, assuming estuarine SPM represents trophic level #1 and the double crested cormorant (egg yolk) was the top predator. This is within the range of levels reported for other freshwater and marine food webs (3.8 to 5.1). The results of this study show that even though estuaries are characterized by a high degree of organism mobility and continuous changes in salinity and water movement, the trophic interactions and food web structure, as defined by $\delta^{13}C$ and $\delta^{15}N$, were predictable and similar to those observed in fresh and marine food webs.

Planktivorous fish were depleted in $\delta^{13}C$ when compared to bottom-feeding fish by 1.81‰. Similarly, filter-feeding clams were depleted in $\delta^{13}C$ by 3.68‰ when compared to deposit-feeding invertebrates. This evidence supports the use of $\delta^{13}C$ in separating pelagic- from benthic-oriented organisms, different sources of food, and pathways of mercury uptake in the Miramichi River Estuary and other aquatic ecosystems.

Generally mercury concentrations correlate well to $\delta^{15}N$ in aquatic food webs, as reported for nine lake and two marine food webs. A lack of relationship between $\log_{10}$[Hg] versus $\delta^{15}N$, as seen for the Miramichi River Estuary food web, could be attributed to a number of factors. First, estuarine organism may feed on foods with differing mercury and $\delta^{15}N$ values, as seen for lower trophic level invertebrates and fish. Benthic fish had significantly higher levels of mercury than pelagic fish of the same $\delta^{15}N$-defined trophic level. Filter-feeding clams, although of a lower $\delta^{15}N$-defined trophic position, had significantly higher mercury levels than deposit-feeding invertebrates.

Secondly, inorganic mercury may bind with a number of complexing agents in the estuary (such as, Cl^-, Br^-, I^-, OH^-, sulfides and organic ligands) thereby rendering it unavailable for methylmercury production and bioaccumulation in the estuarine food web. Finally a large variability in $\log_{10}[Hg]$ and $\delta^{15}N$ values may be inherent in estuarine organisms due to the high degree of organism mobility, and dynamic exchange between fresh- and salt-waters, and sediments and water column.

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APPENDICES

Appendix A: Detailed Description of Lab and Field Methods

Description of Study Site

Physical descriptions of the Miramichi River Estuary are well documented (Philpott 1978, Vilks and Kraul 1981, Chiasson 1995, St-Hilaire *et al.* 1995). It has a drainage area of 14,000 km^2. The average depth of the river estuary is 5 m, with a tidal range is between 0.2 and 1.2 m. Between Loggieville and Chatham, a highly stratified salt wedge occurs throughout the year (even during weak midsummer freshwater flows) and is dominant over currents caused by winds and tides. The upper layer is approximately 2 m in depth and the salinity difference between the upper and bottoms layers is usually 12 ppt (St-Hilaire *et al.* 1995). During high inflows ($\approx$291 m^3 s^{-1}) the upper layer of the salt wedge has a salinity of 4 parts per thousand (ppt) and the bottom layer of 20 to 22 ppt. During low inflow ($\approx$73 m^3 s^{-1}) the upper layer has a salinity of 12 ppt and bottom of 22 to 24 ppt. Temperature differences between the surface and bottom are typically between 1 and 2 °C. This part of the estuary may partially mix if freshwater flow is low, high winds exist, and there is no ice cover (St-Hilaire *et al.* 1995). Annual ranges of SPM were between 1.8 to 70.4 mg L^{-1} (St-Hilaire *et al.* 1995). Total dissolved solids of 22 mg L^{-1} were observed in the Miramichi River Estuary (Chiasson 1995). Based on a flushing time of the estuary of 4 and 5 tide cycles, it was estimated that only 23% of the contaminants entering the estuary will flush out to the ocean, and the rest will settle to the estuary bottom (Vilks and Krauel 1981).

Pre-field Sampling Preparation

All tools (i.e., scissors and tweezers) and storage containers (i.e., glass jars and tin foil) used in handling the samples were pre-washed with three rinses of reagent grade acetone followed by three rinses of reagent grade hexane.

Sample Collection

Two licences were obtained to collect samples. One was with Department of Fisheries and Oceans to collect aquatic samples (M-96-12) and the other was with Canadian Wildlife Service (Sackville, NS) to collect double crested cormorant (*Phalacrocorax auritus*) eggs and chicks.

All fish were obtained in collaboration with the Toxic Chemical Program's sampling crew (J. Williams and C. Vardy), Department of Fisheries full-time and summer staff (J. Arsenault, Gerald Chaput, Erin Taylor) or local fisherman (Paul Kelly). During low tide, Fyke and Gaspereau nets (2.4 and 3.1 cm mesh, respectively) were set and checked daily in a flat-bottom plywood boat (scow). Smooth flounder (*Pleuronectes putnami* Gill) and winter flounder (*Pleuronectes americanus* Walbaum), Atlantic tomcod (*Microgadus tomcod* Walbaum), and rainbow smelt (*Osmerus mordax* Mitchell) were collected from the Fyke nets. Eels (*Anguilla rostrata* Lesueur), and striped bass (*Morone saxatilis* Walbaum) were obtained from the Gaspereau nets. Sand shrimp (*Crangon septemspinosa* Say) and small fish (three-spine stickleback (*Gasterosteus wheatlandi* Linnaeus), rainbow smelt, winter flounder, and mummichog (*Fundulus heteroclitus* Linnaeus) were obtained with a beach seine (30 m x 1.8 with 6 mm mesh). Bar clams (*Mya arenaria* Linnaeus) were obtained by shovelling into the soft silty-clay during a low

tide. Sea grass (*Vallisneria americana* Michx) was hand-picked along the shore line and from an Ekman Grab. Oysters (*Crassostrea virginica* Say) and ribbed mussels (*Geukenisa demissa* Dilwyn) were picked off the sediment/rocky bottom during low tides.

Prior to collecting water samples, 18 L stainless steel canisters were rinsed three times with estuarine water. Water samples were collected by submerging the water canisters one arms length below the surface of the water.

Ten sediment samples were collected using an Ekman Grab near the Loggieville wharf. Sediment samples was placed into glass jars using stainless steel spoons.

Water, minnows, and submerged terrestrial leaf litter samples were collected at one estuary and two freshwater sites: at the Loggieville wharf (Miramichi River Estuary), Renous Indian Reserve 12 Bridge (Southwest Miramichi River), and the Red Bank Indian Reserve Bridge (Northwest Miramichi River), respectively. Minnows were captured using a hand-held minnow net. Submerged terrestrial leaf litter (species unknown) was collected from the bottom of the rivers and estuary and placed directly into plastic ziplock bags.

On May 24, ten double crested cormorant eggs (*Phalacrocorax auritus*) were collected in collaboration with N. Burgess (CWS, Sackville, NS) from Egg Island, Outer Miramichi. A ride to Egg Island was arranged with locals Henry Collins, Ralph Taylor, and Paulette Dickson. Eggs were transported back to the lab in a fishing tackle box with Styrofoam padding.

Atlantic herring from the Northumberland Strait were obtained from field worker Doris Daigle (Dept. of Fisheries and Oceans, Moncton, New Brunswick, Canada).

Sample Transportation and Storage

All invertebrate and fish samples were transported in coolers to the Department of Fisheries and Ocean's (DFO) contaminant lab. At the lab, the species, length, weight, and sex of each fish was recorded. For preservation and for eventual contaminant analysis, large sized fish were individually wrapped in tinfoil and stored at -20 °C. All filter-feeding clams were placed in plastic bags prior to storage in the -20 °C freezer. Invertebrates, such as deposit-feeding clams, polychaetes were placed directly into glass jars, and stored in the freezer upon arrival at the DFO lab. Water, submerged terrestrial leaf litter, and sediment samples were placed directly into -20 °C.

Egg Preparation

At the lab, the weight, maximum length, and two equator widths of each egg was recorded. Egg shells were carefully dissected in half using a scalpel. Egg whites and yolks were separated, weighed, and frozen in glass jars for contaminant analysis. Egg shell thickness was measured after air drying for two months.

Fish Ageing

Fish were aged with methods presented by Chilton and Beamish (1982) and Brothers *et al.* (1976). The largest pair of otoliths (sagittae) were removed from the head of the fish. A single sagitta was embedded in a Buehler Epoxy Resin and Hardener (5:1/v:v) on a glass slide. After 24 hrs, the otoliths were ground to the nucleus with a Hillquist Thin Sector (Athol, Mass., USA) grinder and finely polished with a Hillquist

Polisher (Seattle, Wash., USA) sand paper. To enhance the contrast between opaque and translucent zones, cooking oil was allowed to soak in the sectioned plane. Annuli were counted under magnification with a Bausch & Lomb stereo-microscope.

Stomach Contents

Stomach contents were removed from the cardiac stomach of frozen fish and preserved in 10% formalin. With the aid of a dissecting microscope, food items were identified. The number of individuals in each food category was recorded and expressed as a percentage of the total number of food items (Hyslop 1980) as given by the following formula:

$$\text{Percent composition by number} = \frac{\text{No. of specific food item}}{\text{Total No. of all food items}} \times 100$$

This study was not designed to determine the weight of gut contents for the ten species of fish from this estuary, as they have different feeding times and behaviors.

Isotope Methodology

At the GG Hatch Isotope Laboratories (Ottawa University, Ottawa, Ontario, Canada), all samples were weighed into tin capsules, folded, and placed into the elemental analyzer (EA) sample carousel. The samples were flash-combusted at 1800 °C under a continuous stream of O_2. C & N isotopes were measured from the same combustion after separation of N_2 and CO_2 gases with a chromatographic column. Helium gas carried the separated gases to the mass spectrometer for stable isotope analysis. All isotope analysis was carried out with an automated CE Instrument EA-110 (elemental C & N analyzer) coupled to a Finnigan Mat Delta^{PLUS} IRMS by a Conflow II Interface.

Stable carbon and nitrogen isotope ratios are expressed as "delta" notation (δ) using the following formula, and have units of parts per thousand or "per mil" (‰). $\delta^{15}N$ values were calculated using atmospheric N_2 as the standard. $\delta^{13}C$ values were calculated using Pee Dee Belemnite (VPDB).

$$\delta^{13}C = \frac{(^{13}C/^{12}C_{sample}) - (^{13}C/^{12}C_{standard})}{(^{13}C/^{12}C_{standard})} \times 1000$$

Sub-samples of skinless dorsal muscle were taken from fish and freeze-dried. Similarly skeltonless tissue was freeze-dried for large-sized invertebrates. Optimal fish and invertebrate weights of 250 μg (dry wt) were analyzed for carbon and nitrogen isotopes

To remove all inorganic carbon, all samples in direct contact with estuarine waters were placed into a 10% HCl solution for two hours and rinsed three times with de-ionized water. Samples were then freeze-dried.

Ten samples of an internal reference sample (tomcod) had resulted in a mean $\delta^{13}C$ value of -16.99 ± 0.05‰ (± SE) and $\delta^{15}N$ of 13.99 ± 0.45‰. For every 27 samples, two additional carbon (USGS-24 graphite and NBS No.21 graphite) and nitrogen (USES-25 No. 12 and IAEA-N-2 No. 245) standard reference materials (LIST and IAEA) were run, and one internal striped bass standard. The additional carbon and nitrogen standards were used to help correct for any drift in values between runs.

Total Mercury Analysis

Total mercury was measured by Cold-Vapor Atomic Absorption Spectrophotometer (CVASS) with a Varian M-6000A model (CETAC Technologies,

Omaha, Nebraska, USA).

All fish muscle were analyzed in triplicate. Between 0.3 and 0.4 g of dorsal fish muscle was placed in Feulin-Wu tubes with 5 ml of reagent grade sulfuric:nitric acid (4:1 v/v). Each sample was digested on a block heater (90 °C) for 2 hrs and cooled in a water bath. To oxidized any remaining organic material, three installments (5 ml each) of potassium permanganate (60 g L^{-1}) were added and vortexed into the solution. Samples were allowed to stand for a minimum of two hrs. Finally to decompose any excess permanganate complex, hydrogen peroxide (30% Fisher reagent grade) was added drop-wise until the solution turned slightly pink. De-ionized water was added to make a final volume of 25 ml.

Digested samples were mixed with a strong reducing agent, 10 % stannous chloride (Mallinckrodt AR grade) in 7% HCL and directed over glass column in a gas-liquid separator. Reduced Hg^0 vapor is carried by a carrier gas (Ar reagent grade) and measured for transmitted radiant power (P) at 254 nm.

Mercury Calibration Standards

One of two five-point calibration standards (0.01 to 1.43 μg L^{-1} or 0.1 to 9.14 μg L^{-1}) was prepared daily from a "Baker Instra-Analyzed" (VWR Scientific Products, West Chester, PA, USA) 1,000 μg ml^{-1} Hg stock solution. All standards and blanks were prepared in the same way and time as the estuarine samples

Mercury Standard Reference Material

A full set of standards were analyzed at the beginning of the run, and a second set at the end of the run. To establish accuracy, a standard reference material, DORM-2

certified dogfish muscle (NRC, Ottawa, ON, Canada) was analyzed in triplicate for each sample run. Sample analysis was repeated if the matrix spike was not between 90 and 110% recovery. Mercury recoveries from DORM-2 standards (n=85) were 100 ± 1.4% (±SE). To confirm the instrument response, each day an additional internal reference fish was analyzed and the recovery was 101 ± 12.5%. Six reagent blanks were included in each analysis of 11 samples.

Limit of Detection

The limit of detection (LOD) was determined by the following formula from Schmitt and Brumbaugh (1990):

$$LOD = 3\ (S^2_b + S^2_s)^{0.5}$$

where $S^2_b + S^2_s$ are the variances of concentrations measured for procedural blanks and low-level sample, respectively. The LOD for mercury in fish muscle was 0.83 ± 0.17 ng g^{-1} (dry wt) in mid-sensitivity mode (operating equipment in medium throughput range of 0.05 - 12.0 ppb) and 0.55 ± 0.17 ng g^{-1} (dry wt) for high sensitivity mode (operating equipment in very low concentration range of 0.002 - 0.5 ppb).

Precision

The precision, expressed as the relative standard deviation (RSD) of the analytical method was always below 3.6%.

Appendix B: Gut Contents

Table B-1. Stomach contents of fish from the Miramichi River Estuary based on the presence of prey items. Abb: phytoplankton (PhytoP), zooplankton (ZooP), *Eurytemora affinis* (Eury), *Chaoborus flavicanus* (Chaob), polychaetes and oligochaetes (Worm), Deposit-feeding clams (Worm), estuarine sea grass (Veg), sediment (Sed), and unidentifiable organic matter (Uniden OM).

	Empty	PhytoP	ZooP	Eury	Mysids	Chaob	FW Invert	Worm	Snail	Grass Shrimp	Crabs	Mac	Veg	Detritus	Sed	Uniden OM	Fish Eggs	Fish
GS-1			1															
GS-2			1															
GS-3			1															
GS-4			1															
GS-5			1															
GS-6			1															
GS-7			1															
GS-8			1															
GS-9			1															
GS-10			1															
HR-12		1																
HR-13		1																
HR-14		1																
HR-15		1																
HR-17		1																
HR-18		1																
HR-19		1	1															
HR-20		1																
HR-7		1																

Table B-1 continue: Gut contents of fish.

	Empty	PhytoP	ZooP	Eury	Mysids	Chaob	FW Invert	Worm	Snail	Grass Shrimp	Crabs	Mac	Veg	Detritus	Sed	Uniden OM	Fish Eggs	Fish
HR-8		1																
HR-9		1																
MC-21																		
MC-22																		
MC-23								1			2		1					
MC-24																		
MC-25								1										
MC-26																		
MC-27																		
MC-28																		
SK-1			1				1		1							1'		
SK-2																1'		
SK-3																		
SK-4							1											
SK-5														1		1'		
SK-6														1				
SK-7			1											1		1'		
SK-8			1															
SB-1	1																	
SB-12	1																	
SB-19	1																	
SB-20					1													
SB-2	1																	
SB-5	1																	
SB-9	1																	
SB-15	1																	
SB-14	1																	

Table B-1 continue: Gut contents of fish.

	Empty	PhytoP	ZooP	Eury	Mysids	Chaob	FW Invert	Worm	Snail	Grass Shrimp	Crabs	Mac	Veg	Detritus	Sed	Uniden OM	Fish Eggs	Fish
SB-11	1																	
SB-16	1																	
SB-3	1																	
SB-17	1																	
SB-8	1																	
SB-4	1																	
SB-10	1																	
SB-18	1																	
SB-6																		1
SB-7	1																	
Lamp																		
SF-1								1				1			1			
SF-2								1				1			1			
SF-3								1							1			
SF-4								1			1	1		1	1			
SF-5												1	1	1	1			
sm-12																1		
sm-13																1		
sm-17	1																	
sm-18								1										
sm-19	1																	
sm-2	1																	
sm-20																1		
sm-21																1		
sm-22	1																	
sm-4																1		
sm-6	1																	

Table B-1 continue: Gut contents of fish.

	Empty	PhytoP	ZooP	Eury	Mysids	Chaob	FW Invert	Worm	Snail	Grass Shrimp	Crabs	Mac	Veg	Detritus	Sed	Uniden OM	Fish Eggs	Fish
sm-8					1													
sm-9																1		
SM-24																1		
SM-25	1																	
SM-26	1																	
SM-27	1																	
SMS-10			1	1			1											
SMS-11	1																	
SMS-12				1														
SMS-13				1														
SMS-14				1														
SMS-15	1																	
SMS-16	1																	
SMS-17			1	1														
SMS-18	1																	
SMS-19	1																	
SMS-20				1														
SMS-1																1		
SMS-2																1		
SMS-3				1			1											
SMS-4						1												
SMS-5				1														
SMS-6				1		1												
SMS-7						1												
SMS-8	1																	
SMS-9				1														
TC-21										1			1					

Table B-1 continue: Gut contents of fish.

	Empty	PhytoP	ZooP	Eury	Mysids	Chaob	FW Invert	Worm	Snail	Grass Shrimp	Crabs	Mac	Veg	Detritus	Sed	Uniden OM	Fish Eggs	Fish
TC-22										1								
TC-24										1								
TC-36	1																	
TC-44										1		1						
TC-45										1								
TC-47										1								
TC-48	1																	
TC-49										1		1		1				
TC-42	1																	
TC-56												1						
TC-60												1						
TC-61													1			1		
TC-62	1																	
TC-63												1						
TC-64													1	1		1		
TC-65	1																	
TC-66												1						
TC-69													1	1				
TC-43										1			1					1
TR-1																		
WF-22												1			1			
WF-26											1	1						
WF-27												1			1			
WF-28												1			1			
WF-31												1			1			
WF-32								1				1	1	1				
WF-36												1	1		1			

Table B-1 continue: Gut contents of fish.

	Empty	PhytoP	ZooP	Eury	Mysids	Chaob	FW Invert	Worm	Snail	Grass Shrimp	Crabs	Mac	Veg	Detritus	Sed	Uniden OM	Fish Eggs	Fish
WF-37												1			1			
WF-38												1	1		1			
WF-40												1	1	1	1			
WF-41												1			1			
WFS-1	1																	
WFS-2								1							1			
WFS-3								1						1				
WFS-4								1						1				
WFS-5	1																	
WFS-6								1										
WFS-7															1	1		
WFS-8												1		1	1			
WFS-9					1			1					1		1			
WFS-10								1							1			
EEL-1													1				1	
EEL-2	1																	
EEL-3													1				1	
EEL-4													1				1	
EEL-5	1																	
EEL-6	1																	
EEL-7	1																	
EEL-8														1				
STS-1			1	1														
STS-10				1														
STS-2			1	1														
STS-3				1														
STS-4				1														

Table B-1 continue: Gut contents of fish.

	Empty	PhytoP	ZooP	Eury	Mysids	Chaob	FW Invert	Worm	Snail	Grass Shrimp	Crabs	Mac	Veg	Detritus	Sed	Uniden OM	Fish Eggs	Fish
STS-5	1																	
STS-6				1														
STS-7			1	1														
STS-8				1														
STS-9	1																	

Appendix C: All Data

Table C-1. Attributes of biota (species, weight, sex, age, % water), carbon and nitrogen isotope values (δ), and mercury concentrations (log_{10}[Hg] on a μg g^{-1} wet wt and dry wt basis). Abb: gaspereau (GS), herring (HR), mummichog (MC), sucker (SK), dace (DC), striped bass (SB), lamprey (Lam), smooth flounder (SF), juvenile rainbow smelt (SMS), rainbow smelt (SM), tomcod (TC), trout (TRT), juvenile winter flounder (WFS), winter flounder (FL), double crested cormorant egg white (CW) and egg yolk (CY), eel (EEL), stickleback (STS), sand shrimp (CR), soft-shell clams (MA), deposit-feeding clams (MAC), oyster (OY), ribbed mussels (RM), sediment (SED), suspended sediments (SPM).

Sample	Wt	Length		Age			%	[Hg] μg/g wet wt			Avg.		log_{10}	[Hg] μg/g dry wt			Avg		log_{10}
id	g	cm	Sex	y	δ15N	δ13C	H2O	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]
GS-1	299.8	27.4	female+	7			81.2	0.073	0.081	0.079	0.078	0.004	-1.108	0.389	0.432	0.422	0.414	0.022	-0.383
GS-2	208.7	25.4	male	4			91.2	0.066	0.061	0.061	0.063	0.003	-1.202	0.754	0.692	0.694	0.713	0.035	-0.147
GS-3	220.4	25.5	female+	4			77.9	0.039	0.045	0.059	0.048	0.010	-1.319	0.178	0.206	0.267	0.217	0.045	-0.664
GS-4	198.7	25.5	female+	4			76.2	0.052	0.061	0.053	0.055	0.005	-1.258	0.218	0.257	0.222	0.232	0.022	-0.634
GS-5	175.3	24	female+	3			77.3	0.054	0.055	0.058	0.056	0.002	-1.255	0.238	0.241	0.256	0.245	0.010	-0.611
GS-6	177	--	female+	3	12.57	-20.09	76.2	0.066	0.071	0.065	0.067	0.003	-1.174	0.275	0.298	0.272	0.282	0.014	-0.550
GS-7	245.8	30.3	female+	5	12.67	-20.25	78.6	0.061	0.061	0.062	0.061	0.001	-1.213	0.284	0.285	0.289	0.286	0.003	-0.544
GS-8	235.3	28.1	female+	5	13.05	-20.24	78.3	0.062	0.063	0.065	0.063	0.001	-1.199	0.285	0.291	0.299	0.292	0.007	-0.535
GS-9	203.6	28.6	male	5	12.83	-20.41	77.8	0.081	0.068	0.070	0.073	0.007	-1.137	0.364	0.305	0.315	0.328	0.032	-0.484
GS-10	343.7	31.7	female+	8	12.92	-19.99	75.8	0.088	0.088	0.090	0.089	0.001	-1.053	0.364	0.362	0.371	0.366	0.005	-0.437
HR-12	225.2	28	female+	5			71.32	0.037	0.042	0.034	0.038	0.004	-1.426	0.127	0.148	0.117	0.131	0.016	-0.884
HR-13	102	24.1	male	3	12.47	-22.00	73.5	0.024	0.026	0.024	0.025	0.001	-1.611	0.089	0.096	0.092	0.093	0.004	-1.034
HR-14	162.2	27.5	female+	4	12.68	-20.69	73.6	0.037	0.032	0.035	0.035	0.003	-1.459	0.141	0.122	0.132	0.132	0.010	-0.881
HR-15	161.9	28.4	female+	5	12.88	-20.19	69.4	0.054	0.044	0.046	0.048	0.005	-1.320	0.176	0.143	0.149	0.156	0.018	-0.806
HR-17	168	28.1	female+	5	12.67	-20.61	74.3	0.037	0.039	0.038	0.038	0.001	-1.423	0.144	0.151	0.147	0.147	0.004	-0.833
HR-18	163.4	27.5	male	4	12.86	-20.51	73.4	0.028	0.032	0.032	0.031	0.002	-1.512	0.107	0.120	0.120	0.116	0.007	-0.937
HR-19	152.3	24.6	female+	4			71.7	0.031	0.034	0.026	0.030	0.004	-1.521	0.111	0.118	0.091	0.107	0.014	-0.972
HR-20	190.6	26.2	male	4			68.8	0.037	0.039	0.041	0.039	0.002	-1.410	0.119	0.125	0.130	0.125	0.006	-0.904
HR-7	160.9	27.8	female+	4	12.59	-20.44	73.9	0.024	0.026	0.024	0.025	0.001	-1.611	0.090	0.098	0.094	0.094	0.004	-1.027
HR-8	162.1	27.5	male	4			61.4	0.005	0.004	0.005	0.005	0.000	-2.337	0.012	0.012	0.012	0.012	0.000	-1.924

Table C-1 continue: Attributes of biota, δ15N and δ13C values, and mercury levels.

Sample	Wt	Length		Age			%	[Hg] µg/g wet wt			Avg.		log_{10}	[Hg] µg/g dry wt			Avg		log_{10}
id	g	cm	Sex	y	δ15N	δ13C	H2O	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]
HR-9	114.2	26.6	male	4	12.67	-20.47	73.2	0.050	0.045	0.045	0.047	0.003	-1.331	0.188	0.166	0.168	0.174	0.012	-0.759
MC-21	17.1	11.1	female		12.15	-16.44	75.4	0.101			0.101		-0.996	0.410			0.410		-0.387
MC-22	13.8	10.3	female		12.87	-17.01	77.2	0.089			0.089		-1.051	0.390			0.390		-0.408
MC-23	21	12	female		12.81	-19.69	81.9	0.080	0.073	0.088	0.081	0.007	-1.094	0.444	0.404	0.486	0.444	0.041	-0.352
MC-24	11.6	10.1	male		13.40	-18.64	78.4	0.065	0.058	0.000	0.041	0.036	-1.388	0.299	0.268	0.000	0.189	0.165	-0.723
MC-25	6	8	female		8.90	-15.03	78.2	0.030	0.033	0.031	0.031	0.002	-1.509	0.136	0.150	0.141	0.142	0.007	-0.846
MC-26	12.9	10.4	male		14.00	-18.72	78.4	0.074	0.064	0.061	0.066	0.007	-1.177	0.344	0.296	0.284	0.308	0.032	-0.511
MC-27	15.6	10.3	male		13.39	-17.90	78.6	0.053	0.052	0.000	0.035	0.030	-1.455	0.249	0.245	0.000	0.165	0.143	-0.784
MC-28	10.4	9.8	male		11.68	-16.60	73.1	0.014	0.012	0.000	0.009	0.008	-2.059	0.051	0.047	0.000	0.032	0.028	-1.489
SK-1	46.1	17.3	female	1	11.52	-31.41	79.6	0.820	0.791	0.896	0.836	0.054	-0.078	4.018	3.879	4.393	4.097	0.266	0.612
SK-2	24	13.6	male	1	10.26	-24.66	79.2	0.405	0.232	0.188	0.275	0.115	-0.561	1.947	1.118	0.902	1.322	0.551	0.121
SK-3	44	17	female	1			72.5	0.255	0.206	0.175	0.212	0.040	-0.674	0.927	0.749	0.636	0.771	0.147	-0.113
SK-4	38.2	16.1	female	1	9.89	-31.81	79.4	0.192	0.173	0.191	0.185	0.011	-0.732	0.932	0.840	0.927	0.900	0.052	-0.046
SK-5	28.2	14.4	female	1	10.95	-31.28	79.6	0.486	0.461	0.458	0.468	0.015	-0.329	2.382	2.260	2.245	2.296	0.075	0.361
SK-6	28.4	15.3	female	1	9.56	-33.57	80.3	0.170	0.162	0.175	0.169	0.006	-0.771	0.865	0.824	0.889	0.860	0.033	-0.066
SK-7	23	13.8	male	1	10.31	-27.67	79.7	0.223	0.205	0.215	0.214	0.009	-0.669	1.099	1.010	1.059	1.056	0.044	0.024
SK-8	9.9	10	female	1	10.77	-25.60	79.3	0.078	0.115	0.105	0.099	0.019	-1.004	0.374	0.557	0.505	0.479	0.094	-0.320
DC-1	0.4178	3.6	inden				89.8	0.059			0.059		-1.229	0.578			0.578		-0.238
DC-2	0.2487	3.3	inden				95.8	0.089			0.089		-1.051	2.119			2.119		0.326
DC-3	0.2802	3.3	inden				93.6	0.068			0.068		-1.167	1.063			1.063		0.026
DC-4	0.2875	3.5	inden				93.6	0.064			0.064		-1.194	1.000			1.000		0.000
DC-5	0.3407	3.5	inden				97.1	0.066			0.066		-1.180	2.276			2.276		0.357
DC-6	0.2212	3.1	inden				93.6	0.046			0.046		-1.337	0.719			0.719		-0.143
DC-7	0.275	3.2	inden				91.8	0.061			0.061		-1.215	0.744			0.744		-0.128
DC-8	0.303	3.5	inden		10.03	-25.26	93.6	0.085			0.085		-1.071	1.328			1.328		0.123
DC-9	0.2362	3.1	inden				93.6	0.101			0.101		-0.996	1.578			1.578		0.198
DC-10	0.357	3.5	inden				93.6	0.054			0.054		-1.268	0.844			0.844		-0.074

Table C-1 continue: Attributes of biota, δ15N and δ13C values, and mercury levels.

Sample	Wt	Length		Age			%	[Hg] µg/g wet wt			Avg.		log_{10}	[Hg] µg/g dry wt			Avg		log_{10}
id	g	cm	Sex	y	δ15N	δ13C	H2O	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]
SB-1	28.2	15.2	immature	1	12.92	-19.34	90	0.097			0.097		-1.013	0.970			0.970		-0.013
SB-19	32.8	15.7	immature	1	13.18	-17.05	73	0.076	0.077		0.077		-1.116	0.282	0.285		0.284		-0.547
SB-20	45.7	17	male	1	13.66	-17.55	73.1	0.140	0.122	0.110	0.124	0.015	-0.908	0.521	0.452	0.407	0.460	0.057	-0.337
SB-2	36.4	16.2	immature	1	13.97	-18.47	78	0.100	0.096	0.081	0.092	0.010	-1.035	0.455	0.436	0.368	0.420	0.046	-0.377
SB-5	33.2	16	immature	1	13.16	-20.94	82.9	0.092			0.092		-1.036	0.538			0.538		-0.269
SB-12	237.6	28.5	male	2	13.96	-17.81	69.2	0.293	0.307	0.312	0.304	0.010	-0.517	0.951	0.997	1.013			
SB-9	177.8	25.6	female	2	13.80	-18.54	75.7	0.106	0.125	0.154	0.128	0.024	-0.893	0.436	0.512	0.632	0.527	0.099	-0.278
SB-15	219.2	27.6	female	2	13.25	-21.63	60.9	0.335	0.287	0.251	0.291	0.042	-0.536	0.857	0.734	0.641	0.744	0.108	-0.129
SB-14	223.4	27.8	male	2	13.11	-20.20	82	0.131	0.136	0.124	0.130	0.006	-0.885	0.728	0.753	0.690	0.724	0.032	-0.140
SB-11	234.3	28	male	2	12.90	-19.82	80.2	0.216	0.247	0.204	0.223	0.022	-0.653	1.093	1.246	1.032	1.124	0.110	0.051
SB-16	252	29.3	male	2	13.40	-20.58	78.9	0.493	0.469	0.447	0.470	0.023	-0.328	2.336	2.223	2.117	2.225	0.110	0.347
SB-3	258.3	29.5	male	2	13.34	-20.44	80.4	0.238	0.262	0.236	0.245	0.014	-0.610	1.216	1.335	1.206	1.252	0.072	0.098
SB-17	258.4	28.5	female	2	13.49	-17.14	73.2	0.300	0.256	0.288	0.281	0.022	-0.551	1.118	0.955	1.073	1.049	0.084	0.021
SB-8	264.3	29.7	male	2	13.85	-19.66	79.7	0.222	0.190	0.178	0.196	0.023	-0.707	1.092	0.934	0.877	0.967	0.111	-0.014
SB-4	275.4	30	female	2	13.06	-17.50	77.7	0.290	0.361	0.305	0.319	0.038	-0.496	1.302	1.621	1.368	1.430	0.168	0.155
SB-10	285.5	30	female	2	13.86	-16.69	74.1	0.215	0.229	0.264	0.236	0.025	-0.627	0.832	0.884	1.018	0.911	0.096	-0.040
SB-18	802	49	female	4	13.39	-17.98	72.9	0.339	0.327	0.333	0.333	0.006	-0.477	1.252	1.207	1.228	1.229	0.023	0.090
SB-6	2222.9	58.2	female	5	15.09	-15.35	93.5	0.389	0.345	0.396	0.377	0.027	-0.424	5.985	5.308	6.085	5.792	0.423	0.763
SB-7	2395	58.2	female	5	14.59	-17.01	72.6	0.252	0.222	0.222	0.232	0.017	-0.635	0.920	0.809	0.809	0.846	0.064	-0.073
LAM			inden		13.45	-17.83	66.4	0.718	0.751	0.675	0.714	0.038	-0.146	2.136	2.234	2.009	2.126	0.113	0.328
SF-1	116	20.6	female	4	12.82	-18.97	74.5	0.054	0.061	0.066	0.060	0.006	-1.221	0.212	0.238	0.257	0.236	0.022	-0.628
SF-2	86	18.1	female	3	13.36	-19.40	74.5	0.061	0.067	0.000	0.043	0.037	-1.370	0.239	0.263	0.000	0.167	0.145	-0.776
SF-3	148.3	21.6	female	5	12.37	-20.04	75.9	0.040	0.045	0.038	0.041	0.003	-1.389	0.166	0.185	0.158	0.169	0.014	-0.771
SF-4	166.4	22.5	female	5	13.22	-19.90	75.5	0.075	0.067	0.078	0.073	0.005	-1.134	0.307	0.275	0.317	0.300	0.022	-0.523
SF-5	57.3	15.9	male	3	11.40	-21.52	72	0.046	0.032	0.037	0.038	0.007	-1.418	0.163	0.114	0.132	0.136	0.024	-0.865
SMS-13	0.89	5.8	immature	1	13.61	-21.19	78.4	0.055			0.055		-1.260	0.255			0.255		-0.594
SMS-14	0.89	5.6	immature	1	13.91	-20.74	78.7												

Table C-1 continue: Attributes of biota, δ15N and δ13C values, and mercury levels.

Sample	Wt	Length		Age			%	[Hg] µg/g wet wt			Avg.		log_{10}	[Hg] µg/g dry wt			Avg		log_{10}
id	g	cm	Sex	y	δ15N	δ13C	H2O	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]
SMS-18	0.99	5.6	immature	1			79.7	0.016			0.016		-1.807	0.077			0.077		-1.115
SMS-19	1.39	6.3	immature	1	9.82	-25.26	79.4	0.041			0.041		-1.388	0.198			0.198		-0.702
SMS-17	1.41	6.5	immature	1	13.71	-21.06	76.9	0.019			0.019		-1.723	0.082			0.082		-1.087
SMS-20	1.47	6.5	immature	1			75.5	0.013			0.013		-1.898	0.052			0.052		-1.287
SMS-11	1.57	6.9	immature	1	13.78	-19.60	77.9	0.026			0.026		-1.585	0.118			0.118		-0.929
SMS-15	1.85	7.1	immature	1	12.32	-19.67	80.6	0.029			0.029		-1.536	0.150			0.150		-0.823
SMS-12	2.01	7	immature	1	13.41	-20.54	80.6	0.029			0.029		-1.538	0.149			0.149		-0.825
SMS-16	2.4	7.3	immature	1	13.61	-20.37	77.3	0.034			0.034		-1.463	0.152			0.152		-0.819
SMS-9	3.24	8	immature	2	12.23	-20.19	79.4	0.025			0.025		-1.600	0.122			0.122		-0.914
SMS-5	3.59	8.5	immature	2	12.47	-19.64	77.9	0.039			0.039		-1.414	0.175			0.175		-0.758
SMS-6	3.69	8.5	immature	2	12.21	-20.34	81.4	0.027			0.027		-1.571	0.144			0.144		-0.840
SMS-2	4.1	8.5	immature	2	12.47	-19.97	78.9	0.028			0.028		-1.550	0.133			0.133		-0.875
SMS-3	4.27	8.9	immature	2	12.76	-19.75	79	0.029			0.029		-1.530	0.140			0.140		-0.853
SMS-10	4.58	8.9	immature	2	11.63	-20.75	76.7	0.182	0.154	0.232	0.189	0.039	-0.723	0.779	0.662	0.996	0.812	0.169	-0.090
SMS-1	4.66	9.1	immature	2	12.23	-19.50	79.3	0.041			0.041		-1.387	0.198			0.198		-0.703
SMS-8	4.76	8.9	immature	2	12.39	-20.15	79.7	0.039			0.039		-1.405	0.194			0.194		-0.713
SMS-7	4.84	9	immature	2	12.11	-20.02	80.8	0.020			0.020		-1.696	0.105			0.105		-0.979
SMS-4	5.4	9.9	immature	2	12.45	-19.34	79.6	0.064			0.064		-1.195	0.313			0.313		-0.504
sm-13	26.9	18.9	male	2+	13.82	-18.14	75.2	0.070	0.055	0.080	0.068	0.013	-1.166	0.280	0.222	0.323	0.275	0.051	-0.561
sm-19	27.9	16.9	male	2+	12.92	-18.37	76.3	0.025	0.044	0.028	0.033	0.010	-1.488	0.107	0.186	0.119	0.137	0.042	-0.863
sm-17	31.5	18.2	male	2+	14.00	-17.13	68.4	0.040			0.040		-1.403	0.125			0.125		-0.903
sm-22	34.6	18.2	male	2+	14.23	-17.65	77	0.025	0.029	0.031	0.028	0.003	-1.548	0.109	0.126	0.135	0.123	0.013	-0.909
SM-25	36.2	18.1	female+	2+			81.6	0.020	0.022	0.016	0.019	0.003	-1.711	0.108	0.121	0.089	0.106	0.016	-0.976
SM-27	38.1	17.8	male	2+			77.8	0.019	0.017	0.016	0.017	0.002	-1.760	0.087	0.076	0.072	0.078	0.008	-1.107
sm-18	40.2	19.1	male	2+	13.70	-17.88	71.8	0.038	0.035	0.037	0.037	0.002	-1.436	0.135	0.124	0.131	0.130	0.005	-0.886
sm-12	40.4	18.3	female	2+			77												
sm-6	41.5	18.6	female+	2+	13.64	-16.40	77	0.078	0.054		0.066		-1.181	0.337	0.237		0.287		-0.543

Table C-1 continue: Attributes of biota, δ15N and δ13C values, and mercury levels.

Sample	Wt	Length		Age			%	[Hg] µg/g wet wt			Avg.		log10	[Hg] µg/g dry wt			Avg		log10
id	g	cm	Sex	y	δ15N	δ13C	H2O	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]
SM-26	41.7	18.1	male	2+			77	0.029	0.029		0.029		-1.545	0.124	0.124		0.124		-0.907
sm-9	42.4	19	female+	2+	13.96	-17.30	77	0.052	0.053		0.052		-1.282	0.224	0.230		0.227	0.005	-0.644
sm-4	42.5	19.7	male	2+	13.67	-16.94	77	0.058	0.055	0.066	0.059	0.006	-1.228	0.250	0.237	0.285	0.257	0.025	-0.590
sm-8	47.7	19.8	female+	2+	13.65	-17.55	74.3	0.048	0.060	0.065	0.058	0.009	-1.239	0.187	0.233	0.253	0.224	0.034	-0.649
sm-21	50.1	19.7	female+	2+	13.17	-15.89	68.6	0.031	0.034	0.037	0.034	0.003	-1.469	0.099	0.108	0.118	0.108	0.010	-0.965
SM-24	51.3	22	male	2+	14.00	-21.40	73.7	0.025	0.030	0.041	0.032	0.008	-1.495	0.095	0.114	0.156	0.122	0.031	-0.915
sm-2	55.6	21.3	female+	2+	13.29	-17.77	66.4	0.027	0.021	0.029	0.025	0.004	-1.594	0.079	0.062	0.085	0.076	0.012	-1.121
sm-20	81.5	23	female+	2+	15.07	-15.80	76.3	0.092	0.131	0.097	0.107	0.021	-0.972	0.389	0.551	0.409	0.450	0.089	-0.347
TC-62	11.1	11.4	male	1	14.40	-19.65	77.3	0.071	0.065	0.050	0.062	0.011	-1.209	0.313	0.286	0.218	0.272	0.049	-0.565
TC-66	13.5	12.3	female	1	13.15	-20.22	77.3	0.031	0.029	0.032	0.030	0.002	-1.518	0.137	0.126	0.139	0.134	0.007	-0.874
TC-64	15	12.5	female	1	13.68	-19.23	78.5	0.025	0.021	0.020	0.022	0.002	-1.661	0.114	0.098	0.093	0.102	0.011	-0.993
TC-60	17.3	13.2	female	1	13.80	-18.50	75.9	0.028	0.036		0.032		-1.498	0.116	0.147		0.132		-0.880
TC-61	18.4	13.6	male	1	14.13	-18.47	75.8	0.036	0.033	0.034	0.034	0.001	-1.469	0.147	0.134	0.140	0.140	0.006	-0.852
TC-65	20.6	13.9	female	1	13.49	-19.91	80.8	0.045	0.032	0.037	0.038	0.006	-1.422	0.232	0.167	0.193	0.197	0.033	-0.705
TC-63	23.5	14.8	female	1	14.50	-18.71	76	0.006	0.044	0.044	0.031	0.022	-1.509	0.025	0.181	0.181	0.129	0.090	-0.889
TC-56	26	14.8	male	1	13.81	-18.75	76	0.036	0.054		0.045		-1.347	0.150	0.225		0.188		-0.727
TC-69	27.9	16.1	male	1	13.90	-17.10	78.2	0.035	0.039	0.038	0.037	0.002	-1.432	0.161	0.177	0.172	0.170	0.008	-0.770
TC-42	31	17.9	female	1			65	0.020	0.033	0.034	0.029	0.008	-1.537	0.057	0.095	0.097	0.083	0.022	-1.081
TC-21	50.7	19.1	female	2	14.97	-18.10	77	0.055	0.056	0.059	0.057	0.002	-1.246	0.241	0.242	0.257	0.247	0.009	-0.608
TC-24	51.3	22	male	2	13.94	-16.20	80.7	0.060	0.061	0.061	0.061	0.001	-1.218	0.309	0.315	0.316	0.314	0.004	-0.504
TC-22	53	19.2	female	2	14.48	-16.96	77.3	0.027	0.030	0.036	0.031	0.005	-1.513	0.117	0.130	0.159	0.135	0.021	-0.869
TC-49	55.3	19	male	2	13.36	-17.86	79.8	0.042	0.037	0.040	0.040	0.002	-1.403	0.207	0.183	0.197	0.196	0.012	-0.708
TC-36	58.1	19.2	male	2	15.28	-16.41	75.5	0.056	0.068	0.045	0.056	0.012	-1.251	0.229	0.278	0.182	0.229	0.048	-0.640
TC-48	61.2	20.1	female	2	13.14	-18.48	78.1	0.090	0.098		0.094		-1.029	0.409	0.446		0.427		-0.369
TC-47	69.5	20.8	female	2	14.54	-17.70	77	0.076	0.074	0.074	0.074	0.001	-1.130	0.328	0.320	0.320	0.322	0.005	-0.492
TC-45	71.5	21.7	female	2	14.23	-15.05	76.1	0.076	0.082	0.073	0.077	0.005	-1.115	0.317	0.344	0.303	0.321	0.020	-0.493
TC-44	101.8	24	male	2	14.34	-15.59	82.4	0.082	0.063	0.061	0.069	0.012	-1.163	0.466	0.358	0.347	0.390	0.066	-0.409

Table C-1 continue: Attributes of biota, δ15N and δ13C values, and mercury levels.

Sample	Wt	Length		Age			%	[Hg] µg/g wet wt			Avg.		log_{10}	[Hg] µg/g dry wt			Avg		log_{10}
id	g	cm	Sex	y	δ15N	δ13C	H2O	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]
TC-43	149.6	29.1	male	3	14.65	-17.86	80.8	0.413	0.297	0.328	0.346	0.060	-0.461	2.151	1.547	1.708	1.802	0.313	0.256
TRT-1					10.55	-25.00	76.2	0.064	0.069	0.067	0.067	0.003	-1.177	0.267	0.289	0.282	0.279	0.011	-0.554
WF-22	103.8	21.4	female	A	11.95	-19.00	80	0.114	0.157	0.142	0.138	0.022	-0.862	0.570	0.784	0.709	0.688	0.109	-0.163
WF-26	91.1	19.9	male	A	12.22	-18.27	79	0.076	0.041	0.060	0.059	0.017	-1.230	0.361	0.196	0.284	0.280	0.082	-0.552
WF-27	94.9	21.6	female	A	13.11	-17.09	79.3	0.033	0.033	0.032	0.033	0.001	-1.487	0.159	0.158	0.154	0.157	0.003	-0.803
WF-28	115.5	20	female	A	12.76	-17.42	79.7	0.084	0.076	0.083	0.081	0.004	-1.092	0.414	0.374	0.409	0.399	0.022	-0.399
WF-31	115.1	21.8	female	A	11.76	-19.71	78.4	0.057	0.062	0.062	0.060	0.003	-1.221	0.263	0.285	0.286	0.278	0.013	-0.556
WF-32	87.8	19.8	male	A	13.17	-18.60	74.4	0.022			0.022		-1.658	0.086			0.086		-1.066
WF-36	45.2	15.6	male	A	11.72	-19.72	79.7	0.077	0.051	0.060	0.063	0.013	-1.202	0.381	0.251	0.297	0.310	0.066	-0.509
WF-37	201.3	25.8	female	A	12.25	-18.70	79.7		0.135	0.145	0.140	0.007	-0.854		0.666	0.714	0.690	0.034	-0.161
WF-38	42.9	15	male	A	11.69	-18.24	78.4	0.040	0.044	0.043	0.042	0.002	-1.375	0.184	0.203	0.198	0.195	0.010	-0.710
WF-40	9.2	-	immature	J	12.69	-19.08	79.7	0.033	0.031	0.035	0.033	0.002	-1.482	0.162	0.152	0.173	0.162	0.011	-0.790
WF-41	5.1	-	immature	J	13.00	-18.36	76.9	0.036			0.036		-1.447	0.154			0.154		-0.811
WFS-1	4.6	6.8	immature	J	11.83	-21.90	78.9	0.041			0.041		-1.391	0.193			0.193		-0.715
WFS-2	10.06	8.2	immature	J	12.90	-21.73	79.3	0.026			0.026		-1.590	0.124			0.124		-0.906
WFS-3	4.25	6.2	immature	J	12.74	-20.81	81.8												
WFS-4	3.85	6	immature	J	12.69	-20.27	85.2	0.046			0.046		-1.337	0.311			0.311		-0.507
WFS-5	8.89	7.7	immature	J	12.63	-20.50	79.6	0.013			0.013		-1.880	0.065			0.065		-1.190
WFS-6	10.25	8.2	immature	J	12.35	-21.19	83.3	0.018			0.018		-1.754	0.105			0.105		-0.977
WFS-7	6.89	7.4	immature	J			81.2												
WFS-8	9.5	8.2	immature	J	12.09	-21.60	80.5	0.017			0.017		-1.779	0.085			0.085		-1.069
WFS-9	4.35	6.1	immature	J	13.01	-20.06	79.9	0.036			0.036		-1.441	0.180			0.180		-0.745
WFS-10	3.86	5.9	immature	J	12.49	-22.27	79.6	0.031			0.031		-1.504	0.154			0.154		-0.813
GW-1	22.9	52.6			16.23	-18.85	98.82	0.024	0.039	0.025	0.029	0.009	-1.532	2.007	3.324	2.133	2.488	0.727	0.396
GW-10	29.1	56			16.45	-19.72	98.7	0.025	0.032	0.032	0.030	0.004	-1.526	1.905	2.487	2.482	2.292	0.334	0.360
GW-2	31.8	60			15.96	-18.00	98.9	0.067	0.053	0.000	0.040	0.035	-1.397	6.089	4.847	0.000	3.645	3.218	0.562
GW-3		55.2			16.43	-18.21	98.5	0.022	0.043	0.062	0.042	0.020	-1.374	1.453	2.886	4.110	2.816	1.330	0.450

Table C-1 continue: Attributes of biota, δ15N and δ13C values, and mercury levels.

Sample	Wt	Length		Age			%	[Hg] µg/g wet wt			Avg.		log_{10}	[Hg] µg/g dry wt			Avg		log_{10}
id	g	cm	Sex	y	δ15N	δ13C	H2O	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]
GW-5	28	63			16.04	-20.03	98.7	0.038	0.039	0.012	0.030	0.015	-1.524	2.922	3.030	0.959	2.304	1.166	0.362
GW-	25.4	58.6			16.58	-19.47	98.7	0.025	0.032	0.032	0.030	0.004	-1.526	1.905	2.487	2.482	2.292	0.334	0.360
GW-7		58			15.99	-18.80	98.7	0.025	0.021	0.023	0.023	0.002	-1.641	1.908	1.600	1.762	1.756	0.154	0.245
GW-8	29.2	60			16.62	-19.23	98.7	0.025	0.024	0.024	0.024	0.001	-1.617	1.915	1.846	1.808	1.856	0.055	0.269
GW-9	24.5	56.4			16.88	-25.15	98.7	0.024	0.018	0.025	0.022	0.004	-1.648	1.862	1.381	1.946	1.730	0.305	0.238
GY-1	7.4	52.6			14.87	-22.84	60.5	0.119	0.080	0.113	0.104	0.021	-0.983	0.301	0.203	0.286	0.263	0.053	-0.580
GY-10	8.3	56			14.90	-23.14	57.1	0.112	0.117	0.096	0.108	0.011	-0.965	0.261	0.273	0.224	0.253	0.026	-0.598
GY-2	6.5	60			14.97	-22.28	58.5	0.138	0.102	0.059	0.100	0.040	-1.001	0.333	0.246	0.142	0.240	0.095	-0.619
GY-3		55.2			15.07	-21.99	61.8	0.130	0.156	0.132	0.139	0.014	-0.856	0.340	0.408	0.346	0.365	0.038	-0.438
GY-5	7.5	63			15.33	-23.51	51.6	0.121	0.107	0.101	0.110	0.010	-0.960	0.250	0.221	0.209	0.227	0.021	-0.645
GY-6	7.7	58.6			15.08	-22.96	57.1	0.128	0.124	0.104	0.119	0.013	-0.926	0.298	0.289	0.242	0.277	0.030	-0.558
GY-7		58			15.02	-22.58	57.1	0.109	0.104	0.083	0.099	0.014	-1.006	0.254	0.242	0.193	0.230	0.032	-0.638
GY-8	8.5	60			18.04	-22.95	57.1	0.117	0.124	0.102	0.114	0.011	-0.942	0.273	0.288	0.238	0.266	0.026	-0.575
GY-9	6.3	56.4			15.63	-22.93	53.2	0.080	0.073	0.051	0.068	0.015	-1.167	0.171	0.156	0.109	0.145	0.032	-0.838
EEL-1	242	55.5	M?	8	12.78	-17.98	74.2	0.045	0.051	0.049	0.048	0.003	-1.316	0.174	0.198	0.190	0.187	0.012	-0.727
EEL-2	756.1	71		10	9.58	-22.23	58.7	0.031	0.033	0.038	0.034	0.004	-1.469	0.075	0.080	0.092	0.082	0.009	-1.084
EEL-3	424.1	62	M?	9			64.8	0.081	0.091	0.075	0.082	0.008	-1.084	0.230	0.259	0.213	0.234	0.023	-0.631
EEL-4	528.3	63.5		9	13.51	-22.62	60.8	0.238	0.240	0.255	0.244	0.009	-0.612	0.607	0.612	0.651	0.623	0.024	-0.205
EEL-5	293.9	55.5	M?	8	13.26	-19.99	72.7	0.073	0.067	0.061	0.067	0.006	-1.174	0.267	0.245	0.223	0.245	0.022	-0.610
EEL-6	621.4	71		10	14.99	-17.72	69.2	0.276	0.308	0.301	0.295	0.017	-0.530	0.896	1.000	0.977	0.958	0.055	-0.019
EEL-7	534.4	68		9			65.4	0.093	0.075	0.105	0.091	0.015	-1.041	0.269	0.217	0.303	0.263	0.044	-0.580
EEL-8	549.1	66.5		9	13.96	-20.94	67.3	0.148	0.127	0.151	0.142	0.013	-0.848	0.453	0.388	0.462	0.434	0.040	-0.362
STS-1	1.1503	4	inden		13.51	-21.54	70.3	0.417			0.417		-0.380	1.405			1.405		0.148
STS-10	0.5217	3.1	inden		14.03	-21.95	70.3	0.019			0.019		-1.720	0.064			0.064		-1.193
STS-2	1.2915	4.4	inden		13.89	-22.51	75	0.359			0.359		-0.445	1.436			1.436		0.157
STS-3	0.4553	3	inden		12.71	-21.39	56.5	0.014			0.014		-1.845	0.033			0.033		-1.484
STS-4	0.9876	4	inden		13.21	-22.35	72	0.013			0.013		-1.887	0.046			0.046		-1.335

Table C-1 continue: Attributes of biota, δ15N and δ13C values, and mercury levels.

Sample	Wt	Length		Age			%	[Hg] µg/g wet wt			Avg.		log_{10}	[Hg] µg/g dry wt			Avg		log_{10}
id	g	cm	Sex	y	δ15N	δ13C	H2O	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]
STS-5	0.8255	3	inden		13.53	-21.77	70.1	0.029			0.029		-1.536	0.097			0.097		-1.012
STS-6	0.9206	4.1	inden		8.37	-23.28	66.6	0.031			0.031		-1.514	0.092			0.092		-1.038
STS-7	0.8282	3.5	inden		13.29	-21.89	75.3	0.009			0.009		-2.053	0.036			0.036		-1.445
STS-8	0.4964	3.1	inden		12.81	-23.06	76.5	0.195			0.195		-0.711	0.828			0.828		-0.082
STS-9	0.8066	3.4	inden				70.3	0.012			0.012		-1.935	0.039			0.039		-1.408
STS-9	0.8066	3.4	inden				70.3	0.045			0.045		-1.346	0.152			0.152		-0.819
CR-10	0.7321	>5			12.34	-19.82	79.4	0.012			0.012		-1.927	0.057			0.057		-1.241
CR-11	0.5929	4 to 5					82.5	0.034			0.034		-1.466	0.195			0.195		-0.710
CR-12	0.142	3 to 4			11.01	-23.21	76.5	0.020			0.020		-1.698	0.085			0.085		-1.069
CR-13	0.3353	3 to 4	immature		10.81	-22.95	90	0.027			0.027		-1.566	0.272			0.272		-0.566
CR-14	2.8815	>5	female		12.84	-19.42	81	0.006			0.006		-2.247	0.030			0.030		-1.525
CR-15	2.6734	>5	female		13.39	-19.69	81.2												
CR-16	2.7995	>5	female		12.99	-18.36	79.7	0.010			0.010		-2.022	0.047			0.047		-1.329
CR-17	2.5447	>5			12.67	-17.54	75	0.008			0.008		-2.106	0.031			0.031		-1.504
CR-2	0.7347	>5			11.32	-19.89	86.7	0.012			0.012		-1.936	0.087			0.087		-1.060
CR-3	0.8514				12.04	-20.09	78.2	0.017			0.017		-1.763	0.079			0.079		-1.101
CR-4	0.3305	4 to 5			11.19	-22.54	50.7	0.022			0.022		-1.662	0.044			0.044		-1.355
CR-6	0.6559	>5			12.75	-20.08	79.8	0.019			0.019		-1.720	0.094			0.094		-1.026
CR-7	0.4722	4 to 5			11.95	-20.51	79.1	0.019			0.019		-1.728	0.090			0.090		-1.048
CR-8	0.577				10.79	-22.85	77.5	0.032			0.032		-1.495	0.142			0.142		-0.848
CR-9	0.6066				12.36	-20.16	75	0.008			0.008		-2.100	0.032			0.032		-1.498
MA-15		6.8	25.6		9.83	-22.64	89.4	0.020			0.020		-1.708	0.185			0.185		-0.734
MA-16		5.9	18.9		9.38	-23.44	89.8	0.018			0.018		-1.748	0.175			0.175		-0.757
MA-2		6.8	31.9		13.36	-22.05	87.5	0.016			0.016		-1.802	0.126			0.126		-0.899
MA-21		5.8	16.7					0.158			0.158		-0.800	0.158			0.158		-0.800
MA-23		4.7	11.3				79.4	0.022			0.022		-1.661	0.106			0.106		-0.975
MA-26		2.1	1.2				83.4	0.036			0.036		-1.445	0.216			0.216		-0.665

Table C-1 continue: Attributes of biota, δ15N and δ13C values, and mercury levels.

Sample	Wt	Length		Age			%	[Hg] µg/g wet wt			Avg.		log_{10}	[Hg] µg/g dry wt			Avg		log_{10}
id	g	cm	Sex	y	δ15N	δ13C	H2O	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]
MA-27		7.9	48.9		9.74	-22.61	94	0.026			0.026		-1.590	0.429			0.429		-0.368
MA-28		7.6	41.6		8.08	-24.15	93.1	0.028			0.028		-1.552	0.406			0.406		-0.391
MA-33		6.5	22.1		9.69	-23.79													
MA-33					9.24	-23.22													
MA-4		6.5	20.4		9.10	-23.13													
MA-4					10.05	-22.69													
MA-40		3.3	3.9		8.73	-24.41	90.4	0.021			0.021		-1.683	0.216			0.216		-0.665
MA-5		7.8	44.8		9.28	-22.90													
MAC-1					7.50	-19.66													
MAC-1					8.50	-20.19													
MAC-2					10.01	-18.32													
MAC-2					10.37	-18.55													
MAC-3	0.0923	27			8.84	-23.65	90.6	0.016			0.016		-1.783	0.175			0.175		-0.757
MAC-4	0.0554	27			13.64	-22.02	92.6	0.034			0.034		-1.472	0.456			0.456		-0.341
MAC-5	0.0164	21			10.11	-17.53		0.105			0.105		-0.977	0.105			0.105		-0.977
MAC-6	0.0496	20			9.92	-17.48	87.3	0.096			0.096		-1.019	0.754			0.754		-0.122
MAC-8	0.0146	15.5			8.23	-24.15	90.4	0.031			0.031		-1.511	0.321			0.321		-0.493
MAC-9	0.0202	13			10.21	-19.18	89.1	0.176			0.176		-0.755	1.613			1.613		0.208
MAC-10	0.037	12			8.92	-18.79	94.1	0.052			0.052		-1.285	0.879			0.879		-0.056
MAC-7	0.0251	23.5						0.023			0.023		-1.643	0.023			0.023		-1.643
MAC-S					7.53	-23.36													
MAC-S					7.90	-23.38													
MAC-S					7.56	-23.69													
OY-1					10.08	-24.45		0.049			0.049		-1.308	0.049			0.049		-1.308
OY-1					10.36	-24.75		0.049			0.049		-1.308	0.049			0.049		-1.308
OY-10		62			9.21	-25.20	94.5	0.067			0.067		-1.176	1.211			1.211		0.083
OY-2					8.10	-27.78		0.056			0.056		-1.249	0.056			0.056		-1.249

Table C-1 continue: Attributes of biota, δ15N and δ13C values, and mercury levels.

Sample	Wt	Length		Age			%	[Hg] µg/g wet wt			Avg.		log_{10}	[Hg] µg/g dry wt			Avg		log_{10}
id	g	cm	Sex	y	δ15N	δ13C	H2O	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]
OY-3		79			9.53	-24.39	93.5	0.020			0.020		-1.690	0.314			0.314		-0.503
OY-4		113			9.16	-24.27	86.5	0.036			0.036		-1.448	0.264			0.264		-0.578
OY-5		103			9.41	-28.10	71	0.015			0.015		-1.835	0.050			0.050		-1.298
OY-6		84			9.93	-25.22	93.6	0.026			0.026		-1.593	0.399			0.399		-0.399
OY-7		89			8.70	-26.63	95.4	0.021			0.021		-1.688	0.446			0.446		-0.350
OY-8		56					95.9	0.023			0.023		-1.639	0.560			0.560		-0.252
OY-9		76			10.89	-25.44	91.1	0.018			0.018		-1.751	0.200			0.200		-0.700
RM-1					8.09	-25.11													
RM-10		42			8.34	-23.74	91.7												
RM-2		61			8.16	-25.67	94.2		0.012		0.012		-1.930		0.203		0.203		-0.693
RM-2		61			8.07	-24.79	91.7	0.194	0.200		0.197		-0.706	2.334	2.371		2.352		0.372
RM-3		50			8.61	-24.39	86												
RM-4		56			9.33	-23.26	92												
RM-4		56					91.7		0.201		0.201		-0.696		2.425		2.425		0.385
RM-5		58			9.74	-24.72	91.9		0.185		0.185		-0.733		2.286		2.286		0.359
RM-6		59			9.51	-24.57	91.9		0.046		0.046		-1.335		0.571		0.571		-0.244
RM-7		55					91.7		0.038		0.038		-1.424		0.453				
RM-8		56					93.4		0.016		0.016		-1.791		0.245		0.245		-0.610
RM-20					11.22	-18.49	92.6		0.188		0.188		-0.725		2.546		2.546		0.406
SED-1					3.39	-27.96													
SED-2					3.17	-27.72													
SED-3					3.51	-27.73													
SED-4							59.0	0.056	0.056	0.052	0.055			0.136	0.136	0.127	0.133		
SED-5																			
SED-6							59.3	0.062	0.056	0.050	0.056			0.152	0.138	0.123	0.138		
SED-8					2.83	-27.75													
SED-9							59.4	0.081	0.056	0.053	0.063			0.199	00.138	0.131	0.152		

Table C-1 continue: Attributes of biota, δ15N and δ13C values, and mercury levels.

Sample id	Wt g	Length cm	Sex	Age y	δ15N	δ13C	% H2O	[Hg] µg/g wet wt (n=1)	(n=2)	(n=3)	Avg. [Hg]	stdev	log_{10} [Hg]	[Hg] µg/g dry wt (n=1)	(n=2)	(n=3)	Avg [Hg]	stdev	log_{10} [Hg]
SED-10					3.71	-27.94													
SED from Strawberry Marsh					2.49	-25.88													
SPM from the Miramichi River Estuary					3.58	-25.68													
SPM from the Northwest Miramichi					1.43	-27.09													
SPM from the Northwest Miramichi				1.30	1.18	-28.23													
SPM from the Southwest Miramichi					1.78	-27.00													
SPM from the Northwest Miramichi (-acid)					3.48	-27.91													
SPM from the Northwest Miramichi (-acid)					-1.18	-28.23													
Chaoborus from SM-7					7.15	-22.43													
crab from TC-44					10.48	-18.81													
Eurytemora from STS-7					9.36	-22.03													
Eurytemora from STS-8					10.00	-23.42													
Eurytemora from STS-3					8.47	-23.26													
Eurytemora from STS-10					9.10	-22.00	60.8												
Eurytemora from STS-2					9.32	-22.36	64.1												
Eurytemora from Estuarine Water					10.62	-22.35													
Eurytemora from Estuarine Water					9.81	-23.16													
Ichthyoplankton from Estuarine Water					14.29	-21.43													
Ichthyoplankton from Estuarine Water					13.91	-21.95													
Ichthyoplankton from Estuarine Water					13.05	-21.81													
lobster larvae from Estuarine Water					8.67	-21.06													
Mysids from SB-20					9.32	-21.81													
Mysids from Estuarine Water					8.57	-23.23													
oligochaete from sediment					11.63	-23.61													
polychaetes from SF-1					9.48	-21.55													
polychaetes from SF-3					9.42	-19.31													

Table C-1 continue: Attributes of biota, δ15N and δ13C values, and mercury levels.

Sample id	Wt g	Length cm	Sex	Age y	δ15N	δ13C	% H2O	[Hg] µg/g wet wt (n=1)	(n=2)	(n=3)	Avg. [Hg]	stdev	log_{10} [Hg]	[Hg] µg/g dry wt (n=1)	(n=2)	(n=3)	Avg [Hg]	stdev	log_{10} [Hg]
polychaetes from WFS-6					9.79	-21.89													
Polychaete-1 (no acid wash)					10.58	-21.36													
Polychaete-2 (no acid wash)					11.09	-21.80													
AP-10					7.52	-23.57													
AP-2					5.32	-23.64													
AP-3					6.40	-26.05													
AP-4					6.88	-23.02													
AP-5					5.93	-25.88													
AP-9					7.17	-24.60													
AP-9					5.87	-23.30													
AP-3-N					8.54	-23.18													
Fresh Water:																			
RB-1					5.75	-33.46													
RB-1					6.72	-28.58													
RE-2					7.22	-22.18													
RE-2-N					8.19	-22.16													
MI-3					10.10	-24.33													
MI-3-N					10.84	-24.21													
M-2					7.28	-16.24													
M-2					5.69	-19.54													
M-2-N					7.72	-20.41													
Estuarine sea grass:																			
EG-1-N					7.47	-12.31													
EG-2-N					7.93	-13.83													
EG-1					6.44	-11.58													
EG-2					7.63	-11.29													
EG-2					5.80	-11.44													

Table C-1 continue: Attributes of biota, δ15N and δ13C values, and mercury levels.

Sample id	Wt g	Length cm	Sex	Age y	δ15N	δ13C	% H2O	[Hg] µg/g wet wt (n=1)	(n=2)	(n=3)	Avg. [Hg]	stdev	log_{10} [Hg]	[Hg] µg/g dry wt (n=1)	(n=2)	(n=3)	Avg [Hg]	stdev	log_{10} [Hg]
brown algae																			
AS-2-N					7.74	-16.69													
AS-1-N					7.70	-17.40													
AS-2					7.69	-17.34													
AS-1					7.43	-16.61													
Marine Samples:																			
P-155-N					5.47	-23.79													
P-156-N					7.11	-17.55													
P-156					7.06	-17.21													
P-157-N					6.67	-21.96													
P-157					7.10	-22.58													
P-158-N					6.21	-16.02													
P-178-N					5.90	-20.43													
P-178					6.42	-21.19													
P- 178					6.42	-21.19													
P- 156					7.06	-17.21													
P -157					7.10	-22.58													
P-156-N					6.73	-17.61													
Z-SC-1317-N					7.47	-24.40													
Z-SC-1319-N					7.74	-23.85													
Z-SC-1320-N					7.56	-23.98													
Z-SC-1321-N					8.17	-23.99													
Z-SC-1323-N					7.27	-24.85													
Z-SC-1323-N					7.32	-24.35													
Z-SC-1387-N					8.59	-23.07													
Z-SC-1310-N					7.18	-24.47													
Z-SC-1310-N					7.53	-24.21													

Table C-1 continue: Attributes of biota, δ15N and δ13C values, and mercury levels.

Sample	Wt	Length		Age			%	[Hg] µg/g wet wt			Avg.		log_{10}	[Hg] µg/g dry wt			Avg		log_{10}
id	g	cm	Sex	y	δ15N	δ13C	H2O	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]	(n=1)	(n=2)	(n=3)	[Hg]	stdev	[Hg]
Z-SC-1304					7.39	-21.92													
Z-SC-1301					7.29	-24.05													
Z-SC-1302					7.92	-24.63													
Z-SC-1202					16.47	-20.02													
Z-SC-1308					8.41	-22.19													
Z-SC-1309					8.25	-23.30													
Z-SC-1320					8.55	-23.98													
Z-SC-1323					7.71	-24.26													
Z-SC-1310					7.70	-25.07													

Appendix D: A plot of all $\delta^{15}N$ and $\delta^{13}C$ values.

Figure Headings

Figure 1. A plot of $\delta^{15}N$ and $\delta^{13}C$ values for 348 freshwater, marine and estuarine samples. Abb: gaspereau (GS), herring (HR), mummichog (MC), sucker (SK), age-1 striped bass (SB-1), age-2 striped bass (SB-2), age-3+ striped bass (SB-3+), smooth flounder (SF), juvenile rainbow smelt (SMS), age-1rainbow smelt (SM-1), age-2 rainbow smelt (SM-2), age-3+ rainbow smelt (SM-3+), age-1 tomcod (TC-1), age-2 tomcod (TC-2), age-3+ tomcod (TC-3+), juvenile winter flounder (WF-0), age-1+ winter flounder (WF-1), double crested cormorant egg white (White) and egg yolk (YOLK), eel (EEL), stickleback (sts), sand shrimp (CR), soft-shell clams (MA), deposit-feeding clams (MAC), oyster (OY), polychaetes (PO), ribbed mussels (RM), Eel grass (EG), benthic algae (AS), marine phytoplankton (PP), estuarine zooplankton (ZP), amphipod (AP)sediment (SED), suspended particulate matter from the South west Miramichi River (SW), Northwest Miramichi River (NW), Estuarine Waters (EW),.

FIGURE 1.