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Mercury in yellow perch (*Perca flavescens*) from Lake St. Francis and nearby tributaries of the St. Lawrence River

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ABSTRACT

Mercury accumulation in fish is a substantial problem in northern temperate regions. Highly variable levels of mercury have been measured in fish from the St. Lawrence River. Here, I used stable isotopes of carbon ($\delta^{13}C$) as tracers of energy source to distinguish food webs of Lake St. Francis (a section of the St. Lawrence River near Cornwall, Ontario) from those of surrounding tributaries and coastal wetlands. I investigated the role of stable isotopes of nitrogen ($\delta^{15}N$) as estimates of trophic position, and I compared mercury accumulation in yellow perch (*Perca flavescens*) from Lake St. Francis and the tributaries and coastal wetlands nearby. Since wetlands and tributaries were thought to be the major sites of methylmercury production, I predicted that fish feeding in tributaries would be more contaminated with mercury than fish of the same size or trophic level that are deriving energy from Lake St. Francis.

Several components of the food webs of Lake St. Francis and its tributaries and coastal wetlands were sampled for mercury and/or stable isotope analyses (dissolved inorganic carbon (DIC), particulate organic matter (POM), zooplankton, benthic invertebrates, and yellow perch). Differences between systems were observed in the $\delta^{13}C$ values of DIC (Lake St. Francis: -1.08 ± 0.10‰; tributaries: -8.90 ± 0.24‰), POM (Lake St. Francis: -26.00 ± 0.28‰; tributaries: -30.41 ± 0.43‰), zooplankton (Lake St. Francis: -21.53 ± 0.59‰; tributaries: -25.81 ± 0.68‰), benthic invertebrates (Lake St. Francis: -17.54 ± 0.25‰; tributaries: -29.24 ± 0.82‰) and yellow perch (Lake St. Francis: -15.66 ± 0.22‰; tributaries: -24.24 ± 0.34‰). Therefore, $\delta^{13}C$ values could potentially be used to distinguish between

food webs of Lake St. Francis and of tributaries and wetlands.

Contrary to existing literature where nitrogen isotopes indicate trophic position, $\delta^{15}N$ seemed to be an indicator of energy source in tributaries. This was clear since $\delta^{15}N$ values in tributaries were positively correlated with $\delta^{13}C$ ($r=0.525$, $p<0.001$), but not with estimates of fish size such as length ($r=0.265$, $p=0.567$), age ($r=0.141$, $p=0.256$) or weight ($r=0.254$, $p=0.100$). Accordingly, no relationship between log Hg and $\delta^{15}N$ was observed in yellow perch feeding in tributaries and wetlands ($r^2=0.01$, $p=0.50$). However, log Hg was positively related to $\delta^{15}N$ in yellow perch from Lake St. Francis that were caught in the summer of the year 2000 ($r^2=0.32$, $p<0.005$).

Log Hg increased with length, age and weight of yellow perch ($r^2=0.31$, 0.37, and 0.32 respectively; $p<0.005$). The relationships were scattered and differed between sampling years for length and age ($p\leq0.01$). However, for a given age, length or weight, log Hg levels were the same in fish from both systems ($p>0.5$ in all cases), not supporting the initial prediction. The high variability in mercury levels indicates that factors other than fish size and source of food (tributaries and wetlands or Lake St. Francis) are affecting mercury accumulation in yellow perch.

RÉSUMÉ

L'accumulation du mercure dans les poissons est un problème important dans les régions tempérées de l'hémisphère Nord. Des niveaux variables de mercure ont été mesurés dans les poissons du fleuve Saint-Laurent. Dans cette étude, des isotopes stables de carbone ($\delta^{13}C$) ont été utilisés comme indicateurs de sources d'énergie afin de différencier les chaînes alimentaires du lac Saint-François (une section du fleuve Saint-Laurent près de Cornwall (Ontario)), de celles des tributaires et des zones humides adjacents. Le rôle des isotopes stables d'azote ($\delta^{15}N$) comme indicateurs de position trophique a été étudié. De plus, l'accumulation de mercure dans les perchaudes (*Perca flavescens*) du lac Saint-François a été comparée à celles des perchaudes se nourrissant dans les tributaires et zones humides environnants. Croyant que les zones humides et les tributaires étaient des sites importants de production de methylmercure, j'avais prédit que les perchaudes se nourrissant dans ces systèmes seraient plus contaminées en mercure que des perchaudes de même taille ou d'un même niveau trophique se nourrissant dans le lac Saint-François.

Des échantillons de carbone inorganique dissout (CID), de matière organique particulaire (MOP), et de consommateurs dans ces systèmes ont été soumis à des analyses de mercure et/ou d'isotopes stables. Des signaux $\delta^{13}C$ différents ont été mesurés entre les systèmes pour le CID (lac Saint-François: -1.08 ± 0.10‰; tributaires: -8.90 ± 0.24‰), pour la MOP (lac Saint-François: -26.00 ± 0.28‰; tributaires: -30.41 ± 0.43‰) pour des consommateurs tels le zooplancton (lac Saint-François: -21.53 ± 0.59‰; tributaires: -25.81 ± 0.68‰), les invertébrés benthiques (lac Saint-François: -17.54 ± 0.25‰; tributaires: -29.24 ±

0.82‰) et les perchaudes (lac Saint-François: -15.66 ± 0.22‰; tributaires: -24.24 ± 0.34‰). Les signaux de $\delta^{13}C$ peuvent donc potentiellement servir d'indicateurs d'énergie pour différencier les organismes se nourrissant dans le lac Saint-François de ceux s'alimentant dans les tributaires et zones humides.

Contrairement aux études antérieures ayant démontré que $\delta^{15}N$ peut servir d'indicateur de position trophique, les signaux $\delta^{15}N$ des perchaudes des tributaires et zones humides semblaient plutôt être des indicateurs de source d'énergie. Chez ces poissons, les valeurs de $\delta^{15}N$ étaient positivement corrélées à celles de $\delta^{13}C$ ($r=0.525$, $p<0.001$) et non aux mesures de taille des perchaudes telles la longueur ($r=0.265$, $p=0.567$), l'âge ($r=0.141$, $p=0.256$) et la masse ($r=0.254$, $p=0.100$). Conséquemment, aucune relation n'a été détectée entre les concentrations de mercure (log Hg) et $\delta^{15}N$ chez les perchaudes des tributaires et des zones humides ($r^2=0.01$, $p=0.50$). Par contre, une relation positive a été observée entre log Hg et $\delta^{15}N$ des perchaudes se nourrissant dans le lac Saint-François et prises en l'année 2000 ($r^2=0.32$, $p<0.005$).

J'ai observé des corrélations positives entre les niveaux de mercure et la longueur, l'âge et la masse des perchaudes ($r^2=0.31$, 0.37, et 0.32 respectivement; $p<0.005$). L'accumulation de mercure avec la longueur et l'âge des perchaudes était différente selon l'année d'échantillonage ($p\leq0.01$). Les niveaux de mercure des perchaudes de mêmes longueur, âge ou masse étaient similaires entre les deux systèmes ($p>0.5$ dans tous les cas), ne supportant pas la prédiction initiale. La variabilité observée des niveaux de mercure indique que des facteurs autre que les mesures de taille ou de source d'énergie (tributaires et zones humides ou lac Saint-François) régissent l'accumulation de mercure chez les perchaudes.

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1. INTRODUCTION

This section is divided into four subsections. The first one will provide a very brief overview of the mercury cycle (Figure 1), certain factors affecting levels of mercury in fish will be presented, and the accumulation of mercury and its toxicity to humans and wildlife will be discussed. Following the mercury subsection, the use of stable isotopes of carbon and nitrogen in the characterization of food webs and of contaminant accumulation will be reviewed. The third and fourth subsections of the introduction present a description of Lake St. Francis, a segment of the St. Lawrence River near Cornwall, Ontario as well as the rationale for this study.

1.1. MERCURY

Mercury (Hg) is a highly toxic metal that accumulates and biomagnifies in organisms. It is a global pollutant that can exist in several interchangeable physical and chemical forms: elemental mercury (Hg^0), a liquid at room temperature and the only metal with a vapor pressure, inorganic mercury (Hg^{2+}), and mercury bound to organic material such as methylmercury (CH_3Hg^+), dimethylmercury and ethylmercury.

1.1.1. Mercury cycle

Even though extensive literature exists on the mercury cycle, certain processes are still poorly understood, such as the way mercury is transformed in the environment or the factors governing its accumulation in organisms (Morel et al., 1998).

Most of the mercury in the atmosphere is in the elemental form (Lindqvist et al., 1991) where it has a residence time of approximately one year (Fitzgerald and Mason, 1997). Long range transport allows atmospheric mercury to reach even remote areas, potentially traveling thousands of kilometers from source areas before being deposited to land and water (Lindqvist, 1994). It has been estimated that anthropogenic inputs of mercury to the atmosphere have tripled over the last century (Mason et al., 1994), with chlor-alkali factories, metal smelters, waste incinerators, and the burning of peat and coal as major point sources (Lindqvist et al., 1991). Natural emissions of mercury arise from volcanic activity, geological mineral deposits, forest fires, degassing from the ocean, as well as through the photoreduction of Hg^{2+}, and the biological formation of Hg^0 or dimethylmercury (Lindqvist et al., 1991; Rasmussen, 1994). Some scientists believe that 50% of the mercury in the atmosphere comes from anthropogenic origins, and the remainder comes from natural and/or recycled mercury.

Before falling back to land and water surfaces primarily by wet, but also by dry deposition (Morel et al., 1998), Hg^0 is thought to be slowly oxidized to Hg^{2+}, which is a more soluble form of mercury. Conventionally, most researchers believe that this is the most abundant form of mercury in precipitation, however, a recent study by Van Loon (2001) showed that Hg^0 could be the predominant form. Methylmercury typically is a small fraction of total mercury in precipitation. Values ranging from 0.37 to 6% are reported in the literature (reviewed by Downs et al., 1998) for methylmercury in precipitation. Once in aquatic systems, inorganic mercury can be reduced back to the volatile elemental form by solar radiation (Amyot et al., 1994, 1997) or by microorganisms (Mason et al., 1995).

Other than atmospheric deposition, runoff from the watershed can be a source of

mercury to aquatic systems, and mercury enters the systems bound to humic material (Driscoll et al., 1995). Sediment-bound mercury, in the insoluble HgS (cinnabar) form, can also be a significant source to the water column, as mercury linked to sulfide in HgS can be oxidized, releasing Hg^{2+} into the water column (Björnberg et al., 1988).

The amount of methylmercury in water is the net sum of methylation and demethylation processes. Most methylmercury production occurs in anoxic waters and sediments, although evidence exists that methylmercury production could occur in oxic waters (e.g., Compeau and Bartha, 1985; Morel et al., 1998). Microorganisms, such as sulfate-reducing bacteria, are thought to be the principal methylators of mercury (Compeau and Bartha, 1985).

Photodegradation of methylmercury has been observed in lake water (Sellers et al., 1996), and when compared to demethylation by microorganisms (Misra, 1992), the former is probably the most important pathway of degradation in low mercury, oxic waters (Morel et al., 1998).

1.1.2. Factors affecting mercury levels in fish

1.1.2.1. *Environmental factors*

Net mercury methylation has been found to be a major determinant of mercury concentrations in fish (Porcella, 1994). In addition, mercury burdens in fish have been inversely associated with certain environmental parameters, such as pH (McMurtry et al.,1989; Cope et al., 1990; Gilmour and Henry, 1991; Haines et al., 1992, 1994; Watras et al., 1994; Rose et al., 1999; Scheuhammer and Graham, 1999), hardness (Hanten et al., 1998;

McMurtry et al., 1989), alkalinity (Spry and Weiner, 1991; Hanten et al., 1998) and selenium levels (Rudd et al., 1980; Turner and Rudd, 1983; Bjerregaard et al., 1999).

On the other hand, positive relationships have been observed between mercury and variables such as aluminum levels (Driscoll et al.,1995), temperature (Bodaly et al., 1993; Harris and Bodaly, 1998), and the size of the watershed (McMurtry et al., 1989). The percentage of coastal wetlands in the drainage basin (Driscoll et al., 1995) and the creation of reservoirs (Hall et al., 1998; Tremblay et al., 1998; Bodaly and Fudge, 1999) have also been associated with elevated mercury levels in fish. In the absence of point sources, the atmosphere is a major source of mercury to aquatic systems. Atmospheric deposition to a seepage lake (no inputs or outputs) in Wisconsin was sufficient to account for all the mercury found in fish from the lake (Porcella, 1994).

Confounding relationships have been observed between dissolved organic carbon (DOC) or colour and mercury levels in fish. Mercury concentrations in perch (*Perca fluviatilis*) were positively related to the colour of seepage and low pH lakes in Russia (Haines et al., 1992; 1994). Results from a larger study in the same region showed no relationship between mercury levels in perch and water color in high-pH lakes (Haines et al., 1994). In Adirondack lakes, Driscoll et al. (1995) observed increasing mercury levels in yellow perch (*Perca flavescens*) with increasing DOC concentrations, except in lakes with very high DOC levels, where the bioavailability of methylmercury was decreased. Positive relationships have also been reported between DOC and mercury levels in lake trout (*Salvelinus namaycush*) from Ontario lakes (McMurtry et al.,1989), in fish from Swedish forest lakes (Lindqvist et al., 1991), and in standardized 30-g yellow perch from Wisconsin

lakes (Watras et al., 1998). Contrary to these studies, negative relationships between mercury in yellow perch and DOC or color have been reported in Michigan (Grieb et al., 1990) and Wisconsin seepage lakes (Cope et al., 1990).

Like the relationship with DOC, conflicting trends were seen between mercury levels in fish and lake size. Results of McMurtry et al. (1989) showed a positive relationship between the area of lakes in Ontario and levels of mercury in lake trout. Another study by Rose et al. (1999) showed a positive relationship between lake size and mercury levels in largemouth bass (*Micropterus salmoides*) from Massachusetts. On the other hand, a negative relationship was observed by Bodaly et al. (1993) for mercury levels in fish of varying trophic levels in lakes of various sizes in northwestern Ontario.

1.1.2.2. *Biological factors*

Several studies have reported positive relationships between fish length and mercury levels in muscle tissue (Brouard et al., 1994; Futter, 1994; Mills et al., 1994; Lalonde, 1998; Scheuhammer and Graham, 1999). In addition to this endpoint, weight and age have also been correlated to mercury levels in fish. All three variables were positively related to mercury in yellow perch from Adirondack lakes (Simonin, et al., 1994; Driscoll et al., 1995). Ion et al. (1997) found a significant positive relationship between mercury and age of yellow perch from the St. Lawrence River, but not with length or weight. On the other hand, fish length and weight were stronger predictors of mercury levels in fish than age, in a study conducted by Grieb et al. (1990). Mercury concentrations in pike (*Esox lucius*), roach (*Rutilus rutilus*) and perch increased with length and weight of the fish in eight forest lakes in

Sweden (Lindqvist et al., 1991). Francis et al. (1998) reported a positive relationship between mercury and length or weight of the common carp (*Cyprinus carpio*) and of the channel catfish (*Ictalurus punctatus*). Age and length were positively related to mercury levels in a variety of fish species from Connecticut lakes (Neumann and Ward, 1999; Ward and Neumann, 1999) as well as in brook trout (*Salvelinus fontinalis*) and five nonsalmonid sport fish from Maine, (Stafford and Haines,1997).

Growth rate has been negatively associated with mercury levels in fish. In faster growing fish, mercury concentrations are diluted by the higher rate of muscle formation relative to the rate of uptake of mercury (Lindqvist et al., 1991; Driscoll et al., 1995).

Seasonality is another factor influencing fish contaminant burdens. Spring levels of mercury in fish are generally higher than summer or fall levels (Lindqvist, et al., 1991; Ward and Neumann, 1999). Potential explanations for this variation in mercury levels include: potentially enhanced methylation due to warming temperatures and lower dissolved oxygen levels, increased feeding rates in spring and early summer, greater inputs of mercury from runoff after spring rains, changes in consumption of food and prey items with season, as well as increased levels of protein per unit muscle in spring due to depletion of lipid reserves after winter and spawning periods (Ward and Neumann, 1999).

1.1.2.3. *Food web structure*

Food web structure is another major factor that can influence mercury levels in fish; the highest levels are found in top trophic level fish of the longest food webs (Cabana and Rasmussen, 1994; Cabana et al., 1994; Futter,1994). The length of the pelagic food chain

was a major factor influencing the variability of mercury in lake trout from lakes in the St. Lawrence River system (Cabana et al., 1994). These authors showed that lake trout from lakes without the opossum shrimp (*Mysis relicta*) or forage fish had the lowest mercury burdens. In lakes where *Mysis* was present but where forage fish were absent, mercury levels were intermediate. Highest mercury levels in lake trout were seen in lakes where both *Mysis* and forage fish were present. In another study, the probability of encountering mercury levels exceeding 0.5 μg/g wet weight in a lake trout of a give size was empirically predicted to be eight times higher in lakes where forage fish were present, as opposed to lakes where forage fish were absent (Futter, 1994).

1.1.3. Accumulation of mercury

The form of mercury that biomagnifies through food webs is methylmercury. In phytoplankton, inorganic mercury ($HgCl_2$) and methylmercury (CH_3HgCl) accumulate passively at the same rate. Both have similar octanol-water partition coefficients, or K_{ow} (3.3 for $HgCl_2$ and 1.7 for CH_3HgCl; e.g., Mason et al., 1996) and can pass through cellular membranes (Mason et al., 1996). At higher trophic levels, methylmercury is assimilated more efficiently than inorganic mercury, the greatest discrimination between the two forms of mercury occurring between phytoplankton and zooplankton (Mason et al., 1996). In phytoplankton, methylmercury tends to accumulate in the cytoplasm, while the inorganic mercury is associated with cellular membranes, which are not assimilated by zooplankton. The net result is an increased proportion of methylmercury in zooplankton.

Watras and Bloom (1992) and Watras et al. (1998) observed that bioconcentration

factors (log ($[Hg]_{organism}$ / $[Hg]_{water}$)) for methylmercury were higher than those for total or inorganic mercury for phytoplankton, zooplankton and fish. The bioconcentration factors for methylmercury increased by approximately 0.5 log units (i.e., 3X) between trophic levels, indicating that methylmercury biomagnified. The proportion of methylmercury to total mercury increased from approximately 5% in water, to 15% in phytoplankton, to 30% in zooplankton, to more than 90% in fish (Watras and Bloom, 1992). These proportions increased with acidification, possibly due to increased supply of methylmercury at the base of the food chain (Watras and Bloom, 1992). Similar figures were reported by Becker and Bigham (1995). Several other studies have shown that methylmercury is the predominant (> 90%) form of mercury in fish tissues (Becker and Bigham, 1995; Wagemann et al., 1997; Francis et al., 1998; Watras et al., 1998; Hammerschmidt et al., 1999; Scheuhammer and Graham, 1999).

Although previous studies have shown that the proportion of methylmercury to total mercury in water is generally below 10% (Fitzgerald and Clarkson, 1991; Stober et al., 1995), recent studies have found that proportions can be much higher, as much as 55% in wetlands (St. Louis et al., 1994; Lean and Holmes, 2000; Holmes, unpublished). The closer to the source of methylmercury production (i.e., the closer to wetland areas), the higher the proportion of methylmercury to total mercury seems to be in the water.

The accumulation of mercury in different components of food webs has been investigated by various researchers. Watras et al. (1998) found that methylmercury biomagnified by a factor of 1.6 between microseston and zooplankton and by a factor of 4 between zooplankton and fish. Similarly, Bargagli et al. (1998) observed increasing

concentrations of mercury through successive trophic levels which included: phytoplankton, zooplankton, benthic invertebrates, fish, seabirds, piscivorous penguins and predatory birds and Weddell seals (*Leptonychotes weddellii*).

The biomagnification of mercury poses a threat to humans and wildlife, as mercury levels can exceed consumption guidelines set to protect against adverse health effects in higher trophic level organisms. Mercury levels in 7% of yellow perch sampled from Adirondack lakes exceeded the 1 μg/g wet weight guideline of the U.S. Food and Drug Administration (Simonin et al., 1994; Driscoll et al., 1995). Several recent studies have reported mercury levels in fish (especially piscivorous species) that exceed the Canadian mercury guideline of 0.5 μg/g wet weight set by Health and Welfare Canada (1990) to protect humans consuming fish (e.g., Kidd et al., 1995b; Lalonde, 1998; Rose et al., 1999; Scheuhammer and Graham, 1999; Ward and Neumann, 1999).

1.1.4. Toxicity of mercury

Elemental mercury is the main form of mercury to which humans are occupationally exposed (WHO, 1976) but this contributes little to the accumulated mercury in their tissues. Human accumulation of mercury occurs mainly through the consumption of fish (WHO, 1990; Clarkson, 1997). Since methylmercury constitutes the near totality of mercury in fish tissues, it is this form that is of most interest from a human perspective. Methylmercury is a neurotoxicant, selectively affecting the central nervous system (Clarkson, 1997). Because of the high affinity of methylmercury to SH containing groups, it is found in tissues that have high levels of thiol-containing molecules. They range from lower-weight molecules, such as

cysteine and glutathione, to higher-weight molecules, like proteins (Clarkson, 1997).

Methylmercury can cross the blood-brain barrier which can potentially cause serious damage to both developing and adult brains. The most vulnerable period for methylmercury damage is during brain development (i.e., prenatal and possibly early postnatal stages) (Spyker et al., 1972; WHO 1990; Rodier, 1994). During the prenatal stage, methylmercury inhibits basic cellular processes such as cellular division and migration of neurons (Sager et al., 1982; Burbacher et al., 1990), altering neuronal development and resulting in brain size and architecture changes (WHO, 1990). In the adult brain, methylmercury causes inhibition of protein synthesis as well as a loss of neuron numbers in the cerebellum and the visual cortex (WHO, 1990; Clarkson, 1997). Some effects of exposure include tremors, ataxia (loss of coordination), and constriction of the visual field (reviewed in Langford and Ferner, 1999). Methylmercury can also have deleterious effects on wildlife such as piscivorous birds and mammals (reviewed in Wolfe et al., 1998). These include brain lesions, degeneration of the spinal chord, as well as malfunctioning of the central nervous system. According to the Canadian Tissue Residue Guidelines for methylmercury, aquatic organisms should not exceed levels of 0.033 mg/kg wet weight in order to protect Canadian wildlife consuming fish or shellfish from any toxicological effects (Environment Canada, 2000).

1.2. STABLE ISOTOPES

Isotopic compositions are measured as the ratio of the two most abundant nuclides of an element, one form being more predominant than the other (Clark and Fritz, 1997). The two stable forms of carbon and nitrogen are ^{12}C and ^{13}C, and ^{14}N and ^{15}N respectively. The natural

terrestrial abundance of ^{12}C and ^{13}C is 98.89 and 1.11%, respectively. For terrestrial nitrogen, 99.63% is in the form of ^{14}N, while the remaining 0.37% occur as ^{15}N (Ehleringer and Rundel, 1988).

Absolute isotope ratios are difficult to measure precisely and require sophisticated equipment. To circumvent this problem, the apparent isotopic ratio of a sample is measured simultaneously with that of a known reference (Clark and Fritz, 1997) and is expressed in the delta notation: $\delta X\ (‰) = [(R_{sample}/ R_{standard})-1] \times 1000$, where X is ^{13}C or ^{15}N and R is the corresponding ratio $^{13}C/^{12}C$ or $^{15}N/^{14}N$. Positive δ values indicate an enrichment of the heavy isotope, while negative δ values indicate a decrease in heavy isotope content (and a concurrent increase in the amount of light isotopes) in the sample relative to the reference. Currently, Vienna Pee Dee Belemnite (VPDB) is the accepted reference for carbon, and has a $^{13}C/^{12}C$ abundance ratio of 0.01237 (Clark and Fritz, 1997). N_2 in air is the accepted reference for nitrogen isotope analysis, with a $^{15}N/^{14}N$ abundance ratio of 0.003677 (Clark and Fritz, 1997).

1.2.1. Fractionation

Isotope fractionation is the process where the ratio of heavy to light isotope is altered. Because the two isotopes differ in mass, their physical and chemical properties vary slightly, and they react at different rates. Fractionation can occur during physicochemical reactions where forward and backward reaction rates are the same. Physical changes of state and chemical transformations are examples of such reactions (Clark and Fritz, 1997). Fractionation can also occur during kinetic reactions where the forward reaction is favored, such as diffusion through a concentration gradient or during biologically mediated reactions

like photosynthesis (Clark and Fritz, 1997).

Fractionation during photosynthesis occurs due to the preferential uptake of $^{12}CO_2$ by photosynthetic organisms. The isotopic ratio of plants varies according to the photosynthetic pathway used to fix carbon dioxide (Bender, 1971). Plants utilizing the C_3 pathway have carbon signatures ($\delta^{13}C$) that are on average 20‰ lighter than the source of CO_2. This is caused by the discrimination against $^{13}CO_2$ by the enzyme ribulose bisphosphate carboxylase (Rubisco) (Park and Epstein, 1960). A series of three or four steps (depending on the photosynthetic pathway) and their corresponding fractionation results in depleted carbon signatures in plants compared to the source of carbon (Clark and Fritz, 1997). Atmospheric CO_2 has $\delta^{13}C$ values around -7‰ while C_3 plants have characteristic signatures averaging around -27‰ (Clark and Fritz, 1997). C_4 plants have heavier $\delta^{13}C$ signatures, ranging from -9 to -14‰ (Ehleringer and Rundel, 1988), averaging values of -12.5‰ (Clark and Fritz, 1997). These values are more enriched than those of C_3 plants because of the presence of an extra enzyme, PEP carboxylase, that provides more CO_2 to Rubisco for fixation (reviewed in Clark and Fritz, 1997). Plants utilizing the Crassulacean acid metabolism (CAM) cycle have a wide range of isotopic compositions, but are usually intermediate between C_3 and C_4 plants (Clark and Fritz, 1997). Aquatic plants also have a wide range of isotopic carbon signatures (-8 to -30‰) that depends on the photosynthetic pathway used, as well as the inorganic carbon taken up (CO_2 or bicarbonate HCO_3^-) (Ehleringer and Rundel, 1988). Other factors affecting the carbon signature of aquatic photosynthetic organisms include latitude (Goericke and Fry, 1994), water temperature (Goericke and Fry, 1994), and flow conditions (Finlay et al., 1999).

1.2.2. Carbon isotopes and food webs

After photosynthesis, little fractionation of carbon isotope ratios occurs during food assimilation (DeNiro and Epstein, 1978; Rau et al., 1983). Fractionation is usually between 0 and 1‰ from one trophic level to the next (Peterson and Fry, 1987). France and Peters (1997) have found that enrichment in ^{13}C in aquatic food webs was ecosystem-specific: fractionation between trophic levels in food webs varied from 0.2‰ in freshwater, to 0.5‰ in estuaries, to 0.8‰ for coastal waters, to 1.1‰ in the open ocean. This small increase in $\delta^{13}C$ between trophic levels could be associated with a greater loss of ^{12}C during respiration (DeNiro and Epstein, 1978; Rau et al., 1983).

The lack of, or very small, trophic fractionation has enabled researchers to use stable isotopes to trace carbon from food sources in aquatic food webs. Several researchers have investigated the contribution of allochthonous versus autochthonous carbon in food webs (Peterson and Fry, 1987; Lester et al., 1995; Finlay et al., 1999). Others have distinguished benthic from planktonic energy sources with $\delta^{13}C$ (Laane et al., 1990; Hecky and Hesslein, 1995; France, 1995a,c; McCarthy et al., 1997). Benthic algae are more enriched in ^{13}C (i.e., their isotopic ratio is more positive) compared to planktonic algae (France, 1995a) because of a difference in water velocity (Finlay et al., 1999) that affects the boundary layer of aquatic plants, and therefore the rate of diffusion of carbon for photosynthesis (Keeley and Sandquist, 1992). The carbon pool is finite, and as carbon becomes limiting in the boundary layer, benthic algae no longer discriminate between carbon isotopes and must assimilate normally rejected ^{13}C (Keeley and Sandquist, 1992; Hecky and Hesslein, 1995).

Stable isotopes of carbon were used by Magnusson et al. (1999) to investigate the

contribution of C_3 and C_4 plants to a terrestrial food web in the Amazonian savanna. C_4 grasses were much more enriched in ^{13}C than the C_3 shrubs, bushes, and vines present in the study area (-13.4 ± 0.27 and -30.4 ± 1.3‰, respectively).

Carbon isotopes have also been used to study the transport of sewage-contaminated sediments (Bachtiar et al., 1996) and the incorporation of sewage in aquatic food webs (Spies et al., 1989). The isotopic composition of sewage matter is consistently enriched relative to sediments or particulate organic matter (POM).

Carbon isotopes can only be useful when there is no overlap between the isotopic ratios of the carbon sources (France, 1995b; 1996). Otherwise, distinguishing between energy sources is impossible and their contribution to food webs can not be determined. This was the case in a study conducted by France (1995b), where a compilation of published measurements of $\delta^{13}C$ values for attached algae (ranging from -40 to -20‰, with a mean of -29 ± 4‰), completely overlapped with those for terrestrial leaf litter (mean of -28 ± 1‰). The contribution of these two energy sources to consumers such as invertebrates and fish could not be assessed in the majority of cases. The scope for using stable isotopes of carbon as tracers of the incorporation of forest detritus into aquatic food webs is therefore limited (France, 1996).

1.2.3. Nitrogen isotopes and food webs

Contrary to carbon isotopes, stable isotopes of nitrogen can be used as a continuous measure of trophic position (Cabana and Rasmussen, 1994). Irrespective of age or habitat (Minigawa and Wada, 1984), the isotopic composition of nitrogen becomes consistently

enriched in ^{15}N by an average of 3 to 5‰ (Peterson and Fry, 1987) from prey to predator along food webs (e.g. DeNiro and Epstein, 1981; Minigawa and Wada, 1984).

Conventional studies of trophic structure relied on observation or on the examination of stomach contents to assign trophic levels to organisms. However, this method is time consuming, and only provides a short-term estimate of what is ingested. Seasonal or spatial variability in prey items is not taken into account. In addition, certain prey items, like zooplankton and insect larvae, can be digested and not easily distinguished from detritus (Bitterlich and Gnaiger, 1984). Stable isotopes provide a time-integrated measure of what is digested and assimilated over a period of months to years for populations that grow slowly (Hesslein et al., 1993). They circumvent the problems of empty stomachs and unidentifiable prey items. Because of this, nitrogen isotopes were found to be more reliable than stomach content analysis to identify trophic positions (Kidd, 1996).

The consistent enrichment in $\delta^{15}N$ between an organism and its prey is a result of the preferential excretion of ^{14}N during metabolic processes (Gaebler et al., 1966). Minigawa and Wada (1984) observed that guppies excreted ammonia that was depleted in ^{15}N compared to their diet, supporting the hypothesis that the increase in $\delta^{15}N$ in animal tissues is generated by the excretion of lighter nitrogen. Similarly, Steele and Daniel (1978) found that the isotopic composition of urine from cows was lighter than that of their diet, while $\delta^{15}N$ signatures in milk and blood were enriched. To preserve mass balance, the depleted $\delta^{15}N$ of urine was offset by an enrichment of ^{15}N elsewhere in the cow.

Different animal tissues can have varying fractionation of $\delta^{15}N$, an important factor to consider when performing food web investigations. DeNiro and Epstein (1981) found that the

enrichment between diet and animal $\delta^{15}N$ varied from 2‰ in the pancreas, to 5.8‰ in the brain of mice. Pinnegar and Polunin (1999) measured the nitrogen composition in various tissues (e.g., whole fry, white muscle, red muscle, heart and liver) of juvenile rainbow trout (*Oncorhynchus mykiss*). Of all tissues analyzed, $\delta^{15}N$ of white muscle was the least variable, and was deemed the most suitable tissue for use in ecological studies of trophic interactions.

Minigawa and Wada (1984) determined that, aside from the $\delta^{15}N$ signal of the diet, the isotopic composition of nitrogen in animals was dependent upon the $\delta^{15}N$ value of the nitrogen source, as little fractionation occurs during assimilation of nitrogen when the nutrient source is limited (Wada and Hattori, 1976) (see below). The authors found that the $\delta^{15}N$ of primary producers (and the rest of the food web) from the East China Sea was much lighter (near 0‰) than the $\delta^{15}N$ of primary producers and corresponding food webs from other systems, such as the Bearing Sea and Lake Ashinoko (+5.6 and +5.0‰, respectively). The primary producers from the East China Sea were marine blue green algae and their signature indicated that they fixed atmospheric nitrogen ($\delta^{15}N$ near 0‰), while the phytoplankton from the Bearing Sea and Lake Ashinoko consisted mostly of diatoms assimilating inorganic nitrogen with enriched $\delta^{15}N$ values. Similarly, Estep and Vigg (1985) observed the incorporation of isotopically light nitrogen originating in blue green algae fixing atmospheric nitrogen into the food web of Lahontan Reservoir.

As discussed earlier, other than the type of nitrogen being assimilated, the availability of nitrogen is another factor influencing the nitrogen signal at the base of food webs. When nitrogen is limiting, the $\delta^{15}N$ of algae reflects the signal of the source of nitrogen, as discrimination against ^{15}N is nonexistant. However, in non-limiting conditions, a large

fractionation occurs during assimilation of nitrogen, as algae preferentially incorporate the lighter ^{14}N into their cellular proteins (Wada and Hattori, 1976). Fertilization of a river in the Kuparuk River, Alaska with nitrogen (0‰) and phosphorus caused a fractionation of about 9‰ during nitrogen assimilation by algae, a difference that could be detected higher up the food web from insects to fish (Peterson et al., 1993).

In addition to the use of fertilizers, sewage discharges and atmospheric deposition have an impact on background signatures of nitrogen (e.g., Broman et al., 1992; McClelland et al. 1997), thereby affecting the $\delta^{15}N$ in organisms up the food chain. Sewage-derived nitrogen is usually isotopically distinct from other sources of nitrogen. Spies et al. (1989) and Tucker et al.(1999) reported that sewage-derived nitrogen was lighter than nitrogen from marine systems. The incorporation of nitrogen from sewage into marine primary producers and consumers was observed in these studies. The contribution of sewage-derived nitrogen to the food webs decreased with distance from sewage inputs (Tucker et al., 1999). On the other hand, McClelland et al. (1997) as well as Fry (1999) observed that nitrogen signatures at the base of the food web (primary producers and consumers) increased with inputs of nitrogen wastewater. In certain cases, the enrichment could be detected through the food web up to piscivorous fish (Hansson et al., 1997).

Cabana and Rasmussen (1996) demonstrated that the nitrogen signatures of primary consumers across various lakes increased with the human population density of the watershed, likely due to the heavy composition of sewage. The authors attributed the enriched isotopic composition of sewage nitrogen to the high trophic positioning of humans and therefore of their excreted nitrogen. Enrichment was also attributed to the preferential loss of the lighter

nitrogen isotope during ammonification and subsequent volatilization of nitrogen. This would result in a more positive (or enriched) nitrogen value for sewage. The researchers showed that anthropogenic impacts accounted for most (68%) of the variation in $\delta^{15}N$ at the base of the food web, which in turn explained a large proportion of the between-lake variability in $\delta^{15}N$ of walleye (*Stizostedion vitreum*) and yellow perch (70 and 30% respectively).

In order to compare food chain length or to assess the trophic level of specific consumers between systems, a correction for the differences in the baseline $\delta^{15}N$ is necessary (Cabana and Rasmussen, 1996; Vander Zander et al.,1997; Vander Zanden and Rasmussen, 1999). Measuring an organism's $\delta^{15}N$ relative to that of a long-lived primary consumer (like a unionid mussel) of the same system was shown to provide an estimate of trophic position that can be used to correct for $\delta^{15}N$ variation among systems (Cabana and Rasmussen, 1996; Vander Zander et al., 1997). The $\delta^{15}N$ of primary consumers like unionid mussels are less variable temporally than the $\delta^{15}N$ of primary consumers which have a short nitrogen turnover time (i.e. minutes versus weeks). The former are therefore better choices for the correction of baseline $\delta^{15}N$ prior to among-site comparisons in trophic structure (Cabana and Rasmussen, 1996).

1.2.4. Food web characterization with multiple stable isotopes

The combined use of carbon and nitrogen isotopes, as tracers of carbon sources and an indicator of trophic position respectively, has enabled ecologists to trace the flow of energy and to investigate the trophic structure of food webs. Many researchers have conducted studies where both carbon and nitrogen isotopes were used in tandem (Spies et al., 1989; Fry,

1991, 1999, et al., 1999; Hesslein et al., 1991; Hobson and Welch, 1992; Kling et al., 1992; Gu et al., 1994,1996a,b, 1997; Doucett et al., 1996; Keough et al., 1996; Kwak and Zedler, 1997; Kidd et al, 1999; Takai and Sakamoto, 1999; Vander Zanden and Rasmussen, 1999; Vander Zanden et al., 1999; Yoshii et al., 1999; Harvey and Kitchell, 2000; Mbongwe, 2000; Pastershank, 2001). In studies where trophic interactions are difficult to observe, hypothetical ones have been generated from lists of species present in the system, and by extrapolating feeding behaviors of organisms from one system to another (Kling et al.,1992). However, trophic interactions generated this way can be inaccurate. For example, Kling et al. (1992) showed, with the combined used of carbon and nitrogen isotopes, that the food-web structure of macrozooplankton in lakes can vary considerably between systems, even when the zooplankton community compositions are similar. It was shown that in most lakes, the copepod *Heterocope* was herbivorous, contrary to original beliefs that *Heterocope* was a predator of *Diaptomus*, a herbivorous copepod.

1.3. STABLE ISOTOPES AND CONTAMINANTS IN FOOD WEBS

For little over a decade, researchers have been using stable isotopes of nitrogen as a continuous measure of trophic position to quantitatively investigate the accumulation of contaminants such as organochlorines and trace metals in freshwater and marine food webs.

1.3.1. Organochlorines

Broman et al. (1992) and Rolff et al. (1993) estimated *in situ* biomagnification of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) with $\delta^{15}N$ in two

food webs from the Northern Baltic. The three most toxic PCDD/F isomers (i.e., 2,3,7,8-TCDD, 2,3,4,7,8-PnCDF, and 1,2,3,7,8-PnCDD) biomagnified and were positively related to $\delta^{15}N$. Contrary to the findings of these studies, no PCDD/F congener appeared to be correlated with $\delta^{15}N$ in organisms from the Gulf of the Farallones National Marine Sanctuary (Jarman et al., 1997). Sample size was very small in this last study, and no statistical analysis was conducted.

Jarman et al. (1996) conducted another study in the same region, and examined the relationship between trophic position ($\delta^{15}N$) and several organochlorines such as total dichlorodiphenyltrichloroethane (∑DDT), total polychlorinated biphenyls (∑PCB), total chlordane (∑CHL), total hexachlorocyclohexane (∑HCH) and hexachlorobenzene (HCB). In their study, all organochlorines were positively correlated with $\delta^{15}N$, with concentrations increasing from invertebrates to fish, to birds and finally to the northern sea lion.

Campbell et al. (2000) did not find a significant correlation between $\delta^{15}N$ and the concentration of six major groups of organochlorines (toxaphene (chlorobornanes), ∑DDT, ∑PCBs, ∑CHL, dieldrin, and ∑HCH) in organisms from the subalpine Bow Lake. Interestingly, carbon source (pelagic or benthic), as indicated by $\delta^{13}C$, was a very good predictor of contaminant levels. Organochlorines were more efficiently transferred in the pelagic than in the benthic food web. Pelagic organisms had greater contaminant burdens as well as higher lipid content than did benthic organisms. As carbon signatures of lipids are light (DeNiro and Epstein, 1977), pelagic organisms had correspondingly more depleted isotopic compositions than their benthic counterparts. These tendencies were reflected by a negative correlation between $\delta^{13}C$ and contaminant levels in organisms.

Positive relationships between $\delta^{15}N$ and lipophilic organochlorines were observed in organisms of pelagic food webs in Lake Ontario (Kiriluk et al., 1995), Lake Baikal (Kucklick et al., 1996), Lake Laberge (Kidd et al., 1995a) and Peter Lake, Northwest Territories (Kidd et al., 1998b). In all studies, lipid was found to be a key predictor of contaminant accumulation. Kidd et al. (1998a,b) showed that the slopes of the relationships between log organochlorine concentrations and $\delta^{15}N$ for several fish species from subarctic lakes increased with the lipophilicity of the compounds. This indicates the greater bioaccumulation of the more lipophilic organochlorines.

Positive correlations between organochlorine concentrations ($\sum$PCB, $\sum$CHL, $\sum$DDT, and toxaphene) and $\delta^{15}N$ in the walrus (*Odobenus rosmarus*) have been presented by Muir et al. (1995). In the Great Lakes, higher concentrations of organochlorines (PCBs and HCB) were measured in waterfowl from the Great Lakes feeding on zebra mussels (*Dreissena polymorpha*) compared to those consuming macrophytes (Mazak et al., 1997). The former were also more enriched in nitrogen composition.

Results from these studies show that nitrogen isotopes, as a continuous measure of trophic position, can sometimes be used to predict organochlorine accumulation in aquatic food webs. Vander Zanden and Rasmussen (1996) found that organochlorine concentrations in lake trout were better predicted with models using nitrogen isotopes than those based on discrete measures of trophic position, such as those conducted by Rasmussen et al. (1990) and Bentzen et al. (1996).

1.3.2. Mercury

Aside from organochlorines, several studies have used nitrogen isotopes to investigate mercury biomagnification in a variety of organisms from marine and freshwater food webs (Yoshinaga et al., 1992; Cabana and Rasmussen, 1994; Kidd et al., 1995b; Jarman et al., 1996; Atwell et al., 1998; Camusso et al., 1998; Thompson et al., 1998; Bearhop et al., 2000; Pastershank, 2001). The findings of these studies are summarized in Table 1. In most cases, positive relationships were observed between trophic position ($\delta^{15}N$) and mercury concentrations, illustrating the biomagnification of mercury through food webs.

The lack of relationship between $\delta^{15}N$ and mercury in the feathers of great skua and northern fulmar in the study conducted by Thompson et al. (1998) was due to an uncoupling of the two variables. The nitrogen composition of feathers represented the diet at the time of feather growth, while the mercury levels corresponded to the body pool of mercury accumulated up to the time of feather growth.

Nitrogen isotopes can be used in the modeling of mercury accumulation in food webs (Kidd et al., 1995b). In studies where regression analyses were performed between log mercury and $\delta^{15}N$ (Table 1; Yoshinaga et al., 1992; Kidd et al., 1995b; Jarman et al., 1996; Atwell et al., 1998; Pastershank, 2001), slopes of the relationships ranged from 0.15 to 0.48, except for one study where the slope was 0.043 but the regression was not significant (Pastershank, 2001).

1.4. THE ST. LAWRENCE RIVER (LAKE ST. FRANCIS)

Lake St. Francis is an enlarged section of the St. Lawrence River approximately 230

km^2 near Cornwall, Ontario. Most of the water in Lake St. Francis originates from the Great Lakes, while the tributaries are only minor contributors to the water budget (Yang et al., 1996). In 1995-1996, the mean annual discharge of the St. Lawrence River at Cornwall was 7370 m^3/s (from Rondeau et al., 2000).

Elevated concentrations of mercury in the sediments near Cornwall have previously been reported and associated with point sources of contamination (Sloterdijk et al., 1991). High levels of mercury in the sediments and their subsequent contribution to elevated mercury levels in fish were the principal reasons why this region was designated an area of concern by the International Joint Commission in 1985 (IJC, 1985).

1.5. RATIONALE

Strikingly different isotopic signatures of dissolved inorganic carbon (DIC) between the St. Lawrence River and its tributaries and coastal wetlands have been reported in previous studies (Yang et al., 1996; Barth et al., 1998; Barth and Veizer, 1999). Focusing specifically on results regarding the St. Lawrence River system near Cornwall, Yang et al. (1996) presented $\delta^{13}C_{DIC}$ values of -0.4 and -1.5‰ in fall 1991 and spring 1992 respectively, while the $\delta^{13}C_{DIC}$ in the Raquette River, a tributary on the south side of the St. Lawrence River (see Figure 1) was -11.1‰. Similarly, Barth et al. (1998) reported 'Main Channel' St. Lawrence River values of $\delta^{13}C_{DIC}$ ranging from -1.8 to 0.3‰, while wetlands and tributaries such as Cooper Marsh and Hoople Creek have $\delta^{13}C_{DIC}$ values from -11.3 to -5.6‰, and from -13.7 to -10.5‰, respectively. The sampling sites for the study of Barth et al. (1998) were visited from four to six times between July, 1994 and April, 1996. Results of more extensive

sampling of these locations are reported in Barth and Veizer (1999). In the study of Barth and Veizer (1999), the sites were visited twice a month from May to December, 1995 and from April to June, 1996. The isotopic compositions of DIC ranged from -1.7 to 2.2‰ in the 'Main Channel', from -12.3 to -2.6‰ in Cooper Marsh and from -13.7 to -8.2‰ in Hoople Creek. Seasonal trends were apparent in all these studies. As photosynthesis preferentially takes up ^{12}C, $\delta^{13}C_{DIC}$ values become progressively more enriched in ^{13}C from spring to fall (Yang et al., 1996).

The depleted $\delta^{13}C_{DIC}$ signatures in these tributaries and coastal wetlands were attributed to bacterial respiration and decomposition of organic matter, as well as influx of isotopically light ground and soil water. On the other hand, the more enriched $\delta^{13}C_{DIC}$ signatures observed in the St. Lawrence River water were essentially those of water from the Great Lakes. The long residence time of water in the Great Lakes allows isotopic equilibrium between dissolved CO_2 and the atmosphere to take place (Yang et al., 1996; Barth and Veizer, 1999).

I postulated that the isotopic difference between the DIC in the Main Channel of the St. Lawrence River (Lake St. Francis) and that of its tributaries and coastal wetlands should be preserved in the food webs supported by these energy sources. This distinction enabled me to compare the accumulation of contaminants such as mercury between these systems, as most of the mercury accumulation in fish originates from the diet (Rodgers, 1994; Hall et al., 1997; Harris and Bodaly, 1998).

The objectives of this study were: 1) to determine if stable isotopes of carbon could be used to distinguish food webs of Lake St. Francis from those of its surrounding tributaries and

wetlands near Cornwall, Ontario; 2) to determine if stable isotopes of nitrogen were estimates of trophic position; and 3) to compare the accumulation of mercury between fish from a) Lake St. Francis and b) its surrounding tributaries and coastal wetlands.

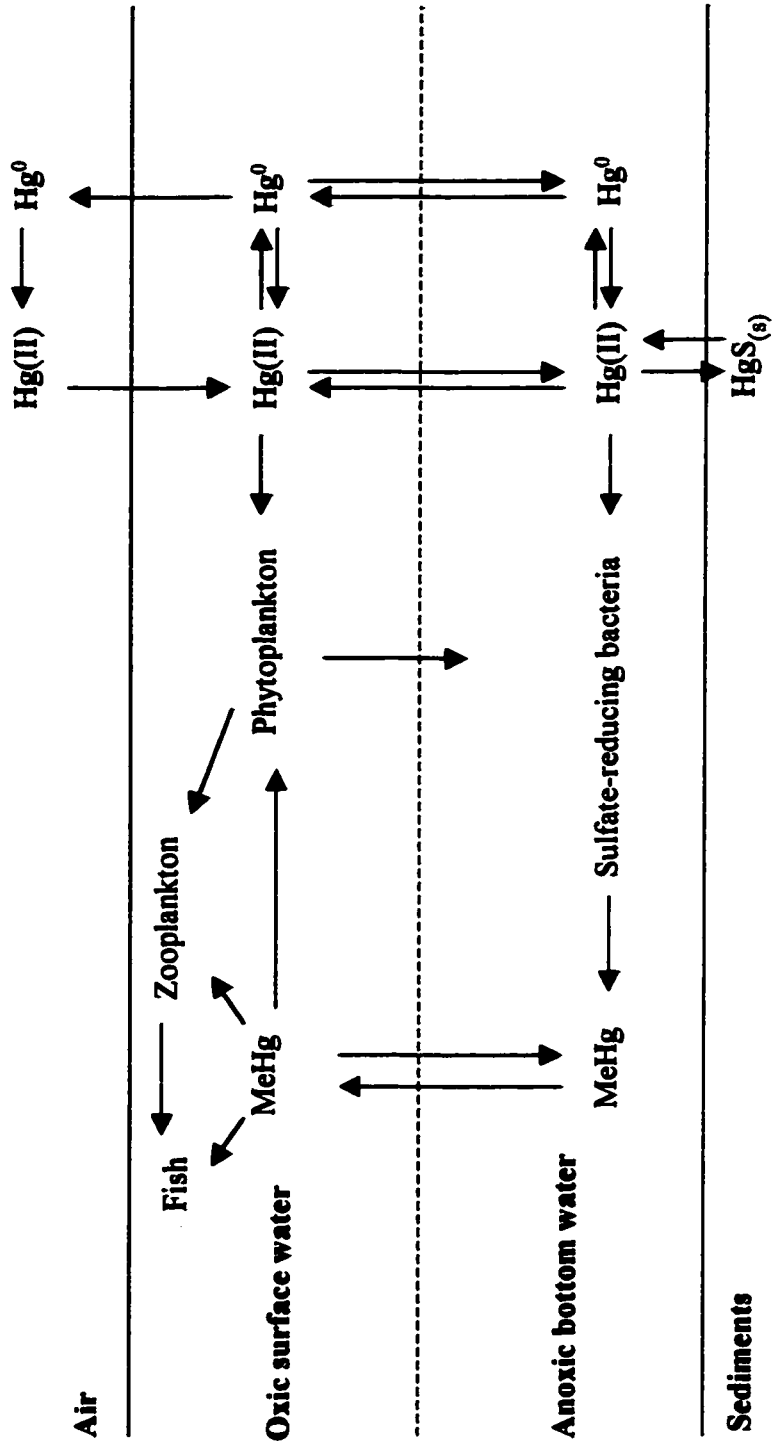
Bacterial respiration and the decomposition of organic matter have been demonstrated as important processes in the tributaries and wetlands of Lake St. Francis (Yang et al., 1996; Barth and Veizer, 1999). These two processes are known to positively affect the supply of mercury available for methylation (Driscoll et al., 1995) as well as methylation itself (Bodaly et al., 1984). In addition, methylmercury levels in water from wetlands have previously been shown to be high (Lean and Holmes, 2000; Holmes, unpublished). Therefore, I proposed that tributaries and coastal wetlands along the shores of Lake St. Francis are a greater source of methylmercury to the water and subsequent food web than is the main channel of the St. Lawrence River. I predicted that, for a given size or trophic level, fish relying on energy from the St. Lawrence River (Lake St. Francis) would have lower mercury concentrations than those deriving energy from wetlands or tributaries.

To test this, several components of the food webs of Lake St. Francis and its tributaries and coastal wetlands were sampled for mercury and stable isotope analyses. Yellow perch (*Perca flavescens* Mitchill) was the chosen fish species because of its abundance and its fisheries importance to man. This species inhabits a variety of habitats and is readily available to commercial and recreational fishermen (Scott and Crossman, 1973) therefore making it an important test species to do among system comparisons.

Table 1.1. Summary of recent studies investigating the accumulation of Hg in organisms with $\delta^{15}N$ (‰). Slopes of regressions between log Hg vs $\delta^{15}N$ are in bold.

Relationship between Hg and $\delta^{15}N$	Organisms	Study area	Source
positive correlation between Hg (μg/g ww) and $\delta^{15}N$ (r=0.89)	lake trout	seven Ontario and Quebec lakes differing in food chain length	Cabana and Rasmussen (1994)
Hg (μg/g dw) increases with $\delta^{15}N$ from phytoplankton to bivalve to gastropod	macroalgae, bivalves, gastropods, fish	marine region outside the Sacca del Canarin lagoon in the river Po delta, Italy	Camusso et al. (1998)
no relationship due to uncoupling of Hg and $\delta^{15}N$	feathers of great skua and northern fulmar	Foula, Shetland	Thompson et al. (1998)
relatively minor positive relationship between Hg (μg/g dw) and $\delta^{15}N$	feathers and blood of great skua, stomach regurgitates	two colonies from Foula, Shetland, and St Kilda archipelago, Western Isles	Bearhop et al. (2000)
log Hg (μg/g ww)=**0.205**($\delta^{15}N$)-0.709	insects, crustaceans fish, shellfish, reptiles, birds, mammals	Papua, New Guinea	Yoshinaga et al. (1992)
log Hg (μg/g ww) vs $\delta^{15}N$ between lakes (species pooled): slopes range from **0.17 to 0.48** yellow perch (lakes pooled): log Hg (μg/g ww)=**0.15**($\delta^{15}N$)-2.16	lake trout, burbot, walleye, northern pike, white sucker, lake cisco, lake whitefish, yellow perch	six Northwestern Ontario lakes	Kidd et al. (1995b)
slope of log Hg (μg/g ww) vs $\delta^{15}N$: **0.32** (slope converted from ln Hg to log Hg from data in Table 2 and Figure 3 of Jarman et al. (1996))	invertebrates, fish, birds, marine mammals	Gulf of the Farallones, California, USA	Jarman et al. (1996)
log Hg (μg/g dw)=**0.2**($\delta^{15}N$)-3.33	POM, invertebrates, marine birds, marine mammals	Lancaster Sound, Northwest Territories	Atwell et al. (1998)
log Hg (μg/g ww)=**0.043**($\delta^{15}N$)-1.26 non-significant regression (r^2=0.03)	sediments, sand shrimp, 4 types of bivalves, rainbow smelt, tomcod, stickleback, winter flounder, striped bass	Miramichi River Estuary, New Brunswick	Pastershank (2001)

Figure 1.1. Biogeochemical cycle of mercury in aquatic systems (modified from Morel et al., 1998).


Air
Oxic surface water
Anoxic bottom water
Sediments
Hg(II)
Hg0
Hg(II)
Hg0
Hg(II)
Hg0
HgS(s)
Phytoplankton
Zooplankton
Fish
MeHg
MeHg
Sulfate-reducing bacteria

2. MATERIALS AND METHODS

2.1. Study Sites

All sampling was conducted in Lake St. Francis and its associated tributaries, from 44°58'N 74°77'W to 45°10'N 74°20'W. A number of sampling sites were situated at the Raquette, St. Regis, Grass, and Raisin Rivers, in Grey's Creek, in a wetland area called the Snye, in 14 sites on Lake St. Francis, as well as at several sites in Cooper Marsh and surrounding canals (Figure 2.1, Table 2.1).

2.2. Sample collection

Dissolved inorganic carbon (DIC), particulate organic matter (POM), zooplankton, benthic invertebrates and yellow perch (*Perca flavescens* Mitchill) were collected between June and November, 1999 and from June to September, 2000 (see Table 2.1).

2.2.1. *DIC*

In June and August, 1999, three water samples per site were collected approximately 50 cm below the surface in 2L plastic or in 100 ml amber glass bottles, leaving no head space. The samples were put in coolers and brought back to the laboratory, and within 8 hours, the water was filtered using 1.2μm (GF/C) or 0.7μm (GF/F) glass fiber filters to reduce bacterial activity that could alter the carbon signature of DIC. Water samples were then stored at 4°C in air tight amber glass bottles, pending stable isotope analysis.

2.2.2. *POM*

Triplicate water samples were collected approximately 50 cm below the water surface with 2 L plastic bottles. In the laboratory, POM was collected from these water samples by filtration through 'pretreated' 1.2μm GF/C glass fiber filters. Prior to filtration, filters were put in a 500°C oven for 4 hours to remove any traces of organic carbon, rinsed with deionized water under slight vacuum and dried at 60°C for 2 hours, and weighed. Filters containing the POM were stored at -20°C until isotope analysis of carbon and nitrogen.

2.2.3. *Zooplankton and plant material*

Composite zooplankton samples were collected by combining multiple hauls of a 150μm mesh zooplankton net. Zooplankton samples were frozen at -20°C until carbon and nitrogen isotope analysis. Plant material and detritus were also collected by the net and were not separated from the zooplankton.

2.2.4. *Benthic invertebrates*

Benthic invertebrates were collected with an Ekman dredge between June and August, 2000. In the field, organisms were manually removed from the sediments and were put in clean glass bottles with a bit of river water, permitting a clearing of gut contents. The bottles were put in a 4°C refrigerator over night. The following day, invertebrates were sorted according to coarse taxa and frozen at -20°C until carbon and nitrogen isotope analyses. Sub-samples of benthic invertebrates collected were preserved in 95% ethanol for identification purposes.

2.2.5. *Yellow perch*

Yellow perch were collected by angling and gill nets, killed with a blow to the head, put in plastic bags on ice, and brought back to the laboratory where total length (cm), weight (g) and sex were recorded. The characteristics of every fish are presented in Appendix A. Approximately 10 scales from every fish were removed from below the lateral line, near the area where the tip of the pectoral fin touches the body for age determination (Jearld, 1983). The left operculum was also removed for this purpose and age determination was conducted according to a method described by LeCren (1947). The fish were then stored in plastic bags at -20°C until mercury and stable isotope analyses.

2.2.5.1. Age determination

The age of each fish was based upon the observation of multiple scales and of the operculum from the left side of the fish (Jearld, 1983; LeCren, 1947). Both structures were examined separately by two people. Readings between the two observers concurred in 87% of cases. Fish with scales showing only one winter annulus were assigned to the 1+ age class, while those with 2 annuli were called 2+, etc. (Jearld, 1983).

2.2.5.2. Stomach contents

The stomachs of some fish were removed and contents were separated according to coarse taxa and frozen for stable isotope analyses. A sub-sample of prey items was preserved with 95% ethanol for identification purposes.

2.3. Stable Isotope Analysis

Carbon and nitrogen signatures are reported in the δ notation, as the parts per thousand deviation from a standard. Standards for carbon and nitrogen were Vienna Pee Dee Belemnite and N_2 in air, respectively.

All stable isotope analyses were performed at the G.G. Hatch Isotope Laboratory in the Earth Science Department at the University of Ottawa.

2.3.1. *DIC in water*

The DIC in the water samples collected in 1999 was extracted by acidifying the water samples with 85% H_3PO_4, thereby converting all inorganic carbon to CO_2. The resulting carbon dioxide was purified under vacuum, through various cold traps of liquid nitrogen and -80°C ethanol, and sealed in a pyrex breakseal. Isotopic composition of the CO_2 was measured with a triple collector VG SIRA 12 mass spectrometer. Precision of analyses was ± 0.10‰.

2.3.2. *POM, zooplankton and plant material, benthic invertebrates and fish*

Filters containing POM were dried at 60°C for 2 hours. Excess filter was cut with a scalpel and the remaining filter with POM was rolled up with stainless steel forceps and put in a 12x5 mm tin capsule (Elemental Microanalysis Ltd., supplied by Iso-mass Scientific Inc., Alberta, Canada) for carbon and nitrogen stable isotope analysis. Frozen benthic invertebrates, zooplankton and fish muscle samples were lyophilized with a Freeze Dryer 3 Model 75200 (Labconco Corporation, Missouri, U.S.) and powdered with a mortar and

pestle. Powdered samples were put in 3.5x5 mm tin capsules (Elemental Microanalysis Ltd., supplied by Iso-mass Scientific Inc., Alberta, Canada) for carbon and nitrogen isotope analyses.

As loss of material and variation in $\delta^{15}N$ (Bunn et al., 1995) due to acidification was a concern, samples of POM, zooplankton and benthic invertebrates were not acidified to remove carbonates. For two sites, enough of the amphipod *Gammarus fasciatus* was collected and half of the organisms were acidified for comparison purposes. Acidified samples were put 1N HCl for 2 hours, rinsed with deionized water, frozen and then prepared for stable isotope analysis exactly like the other samples.

Isotopic compositions of POM, zooplankton, benthic invertebrates and fish were determined by combustion (combustion-reduction for nitrogen) on a CE Elemental analyzer followed by GC gas separation and subsequent analysis by Continuous-Flow on a Finnigan MAT Delta^{plus} IRMS. Precision of routine analyses of both isotopes was ± 0.20‰. Laboratory standards for carbon (USGS-24, NBS-21, and IAEA-CH-6), and nitrogen (IAEA-N-1, IAEA-N-2, and USGS-25), as well as a sample of acetanilide (run as an unknown) were run approximately every ten samples to minimize instrument variation.

2.4. Mercury analysis

All glassware and previously used polypropylene conical tubes were washed, submerged overnight in a 10% (v/v) HNO_3 acid bath, then rinsed three times with deionized water and left to air-dry prior to mercury analysis.

2.4.1. *Sample preparation*

One day prior to analysis, fish were transferred from -20°C to 4°C to thaw overnight. The following day, triplicate samples of dorsal muscle (approximately 0.25 - 0.50 g) were removed with a scalpel and teflon-coated forceps and put in acid-washed 50 ml Pyrex tubes. Dissecting tools were thoroughly rinsed with deionized water between each fish.

Digestion of tissues was performed according to the method outlined in Armstrong and Uthe (1971) and Wagemann et al. (1997). Tissues were digested with 5 ml of 4:1 (v/v) H_2SO_4:HNO_3 at 90°C for 2 hours. The samples were then left to cool for a few minutes, after which 15 ml of 6% $KMnO_4$ was added. Tubes were covered with parafilm and left overnight. The following morning, approximately 15 drops of 30% H_2O_2 were added to the samples until the solution was clear. Samples were diluted to 25 ml with deionized water, mixed well and poured into 15 ml polypropylene conical tubes.

2.4.2. *Mercury measurements*

Total mercury concentrations in all fish collected in 1999 and in 9 fish collected in 2000 were determined by cold vapor atomic absorbance spectrometry (CVAAS) using a CETAC - 6000A Mercury Analyzer (CETAC Technologies Inc., Nebraska, U.S.). A 10% (w/v) $SnCl_2$ and 7% (v/v) HCl solution was the reducing agent, as recommended in the M-6000A Mercury Analyzer Operator's Manual (1997). Total mercury levels in the remaining fifty-two fish collected in 2000 were measured by cold vapor atomic fluorescence spectrometry (CVAFS) with a Tekran Series 2600 Mercury Analysis System, as the M-6000A Mercury Analyzer was not operational. The samples were diluted 30 more times for analysis

on this machine because of its higher sensitivity. The reducing agent was a solution of 3% (w/v) $SnCl_2$ and 7% (v/v) HCl, as suggested in the Series 2600 Analytical Guide, Rev: 1.03 (1999). All total mercury concentrations are reported on a μg/g wet weight basis.

2.4.3. *Quality control*

For every analytical run (of seven to ten fish, in triplicate), one procedural blank, as well as five standards were used to generate a six point calibration curve. Standards were prepared by making stock solutions of mercury (0.75, 3.75, 2.5, 50 and 75 ng/ml) in 4:1 (v/v) H_2SO_4:HNO_3. The original mercury standard solution used to prepare these stock solutions was a VWR brand 1000 ppm Atomic Absorption Standard (Lot # A7045027, VWR Scientific Products, Pennsylvania, U.S.).

Procedural blanks, internal spikes and certified reference material were used for quality assurance/quality control. Procedural blanks, consisting only of 4:1 (v/v) H_2SO_4:HNO_3, were analyzed approximately every ninth fish sample. Internal spikes were run every sixth to ninth fish sample. For these samples, 5 ml of the 2.5 ng/ml mercury standard was added to a fourth replicate of a particular fish instead of the regular, mercury-free acid mixture. One sample of certified reference material DORM-II (dogfish muscle from the Institute for National Measurement Standards, National Research Council Canada, Ottawa, ON, Canada) was analyzed approximately every sixth fish sample.

Standards for the calibration curves, procedural blanks, internal spikes and certified reference material were subjected to the same digestion procedure as all fish samples.

Average mercury recovery (± standard error) in DORM-II was 88.3 ± 3.5% and 80.8

± 7.2% respectively, for the CETAC M-6000A and the Tekran Series 2600 mercury analyzers. The accepted mercury concentrations in DORM-II is 4.64 μg/g ± 0.26 (Institute for National Measurement Standards, National Research Council Canada, Ottawa, ON, Canada).

Method detection limits of analyses (3 times the standard deviation of procedural blanks in a particular run * the dilution factor) averaged 0.757 ppb for the CETAC M-6000A Mercury Analyzer and 0.713 ppb for the Tekran Series 2600 Mercury Analysis System.

Mercury recoveries of spiked samples averaged (± standard error) 109.4 ± 3.3% and 126.4 ± 4.8% for the CETAC M-6000A and the Tekran Series 2600 mercury analyzers, respectively.

2.5. Statistical analyses

All statistical analyses were performed with SYSTAT® 10 for Windows® (2000). Rejection of the null hypothesis occurred when $p<0.05$.

A Scheirer-Ray-Hare extension of the Kruskall-Wallis test (a two-way nonparametric ANOVA, Sokal and Rohlf, 1995, pp. 445-447) was performed to determine if the $\delta^{13}C$ values of DIC differed between sampling dates as well as between Lake St. Francis and tributaries/ wetlands. Pearson correlations were performed between carbon signatures of DIC and various organisms to determine if carbon signatures were preserved up food webs. When assumptions were not met, Spearman rank correlations were performed. Mann-Whitney U tests (non-parametric t-tests) were conducted to determine if $\delta^{13}C$ and $\delta^{15}N$ values of POM differed between Lake St. Francis and tributaries/wetlands.

A discriminant function analysis was performed to separate an initial 34 fish into two groups (Lake St. Francis and tributaries) based on their carbon signature. The initial fish used in this analysis were those caught using a fishing line (i.e., not gill net) that were certainly feeding in Lake St. Francis and those that were known to be caught far upstream in tributaries to ensure that they were not feeding in Lake St. Francis (e.g., Grass and Raisin River fish). These initial fish are identified in Table 2.1 and also in Appendix A. The analysis resulted in the equation of a line cutting across the cluster of points, fish on one side of the line being from Lake St. Francis while those on the other side of the line were classified as tributary fish. Using this discriminant function, the remaining 68 fish were then assigned to one of the two groups. Mann-Whitney U tests were used to compare average length, age, and weight of fish from the two groups. Within the two groups of yellow perch, Pearson correlations were performed between fish nitrogen and carbon signatures, and between fish nitrogen signatures and size estimates. Spearman rank correlations were performed in cases where assumptions were not met.

Since two mercury analyzers were used to determine mercury levels in muscle tissue, triplicate samples of seven fish (except one fish, run in duplicate) were run on both machines to determine if biases existed between analytic methods. Mercury concentrations from one analyzer were regressed against those from the second analyzer. A slope of unity and an intercept of 0 indicate an absence of bias between the two machines. As the slope estimate could been biased due to measurement error on the independent variable, a model II major axis regression was performed instead of a regular model I linear regression (Sokal and Rohlf, 1995). Mercury concentrations were log-transformed to reduce heteroscedasticity.

General Linear Model was used to determine if growth rates (slopes of the length vs age relationships) differed between energy sources (Lake St. Francis and tributaries). Length was set as the dependent variable, age was the independent variable and source was the categorical variable. A principal component analysis was performed to extract a variable (factor 1) that would factor out the effect of fish size. General Linear Model was then used to compare fish $\delta^{15}N$ between the two systems while correcting for variations in fish size. Fish $\delta^{15}N$ was the dependent variable, factor 1 was the independent variable and source was the categorical variable.

General Linear Models were also used to determine which variables were predictors of mercury concentrations in fish from both sources. Mercury concentrations were log-transformed to improve normality and homogeneity of variance of residuals. Highly correlated variables such as length, weight and age were not used together in the same regression. In certain analyses, factor 1was used in place of age, length or weight in General Linear Models. Log Hg was the dependent variable, while nitrogen, and estimates of size (age, length, weight or factor 1) were set as independent variables. When comparing between tributaries and Lake St. Francis, the source was used as a categorical variable. Similarly, year and sex were categorical variables when comparing differences between years, and sexes. If no significant differences in the rate of mercury accumulation existed between categorical variables (i.e., if the slopes of log Hg vs the dependent variables were similar between categorical variables), the data were pooled and a model I linear regression was performed. A model II reduced major axis regression was performed when investigating the relationship between nitrogen signatures and mercury concentrations since the slope estimate was a

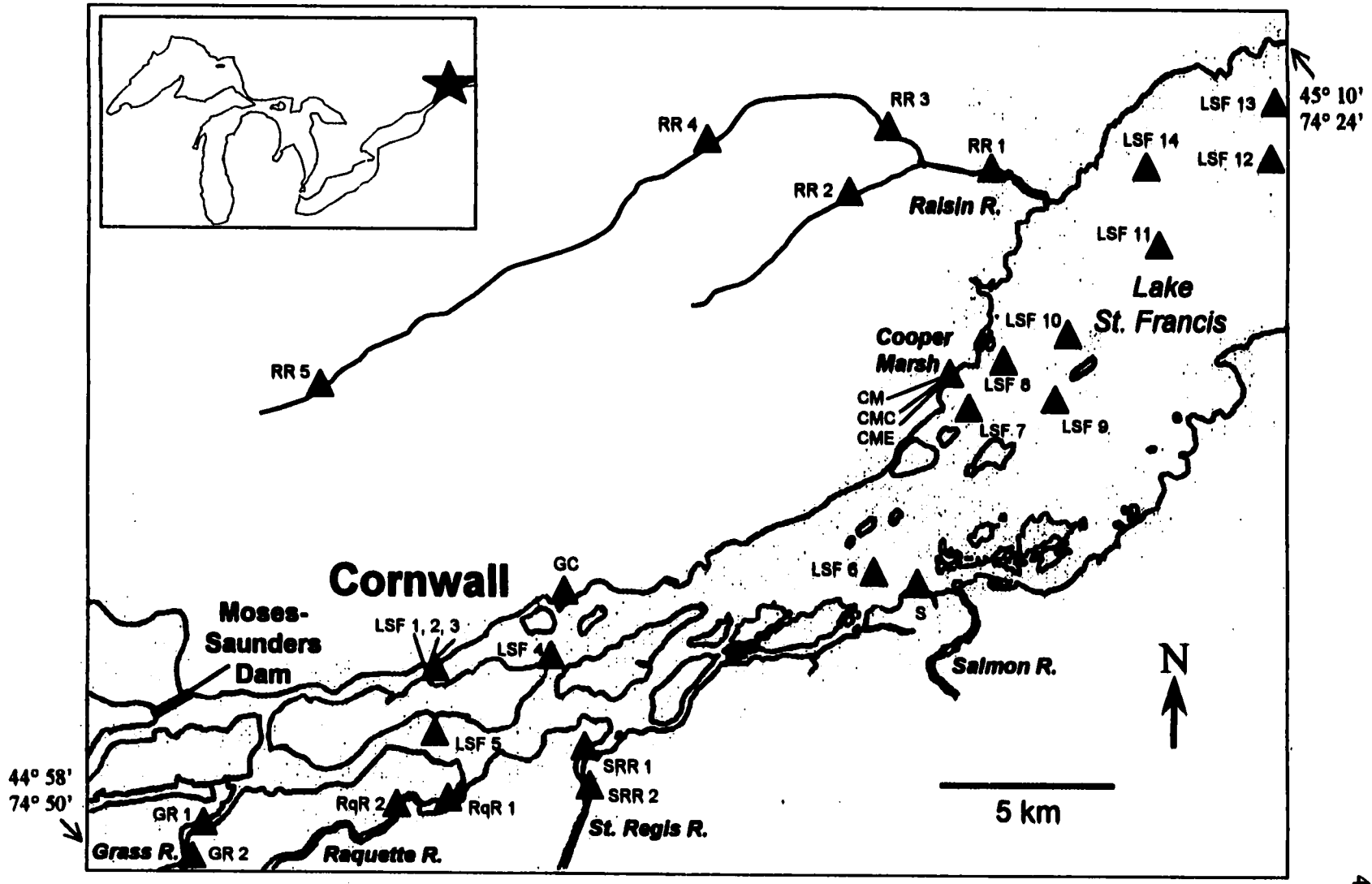
variable of interest and could have been biased due to measurement error on the independent variable (nitrogen signatures) (Sokal and Rohlf, 1995).

Table 2.1. Number of samples collected at different locations in Lake St. Francis and its nearby tributaries and wetlands. Fish samples in bold were used in a discriminant function analysis to classify fish into tributaries or Lake St. Francis based on their carbon signatures.

Date	Location	DIC	POM	Zooplankton	Benthic invertebrates	Fish
06/02/99	Cooper Marsh	3	3			
	Grey's Creek	2	3			
	Lake St. Francis 1	3	3			
	Lake St. Francis 2	3	3			
	Lake St. Francis 3	3	3			
	Lake St. Francis 4	3	3			
	Lake St.Francis 5	3	3			
	Lake St.Francis 6	3	3			
	Raisin River 3	3	3			
	Raquette River 1	3	3			
	St. Regis River 1	3	3			
	The Snye	3	3			
08/11/99	Grey's Creek	3	3			
	Lake St. Francis 1	3	3	1		
	Lake St. Francis 2	3	3			
	Lake St. Francis 3	3	3	1		
	Lake St. Francis 4	3	3	1		
	Lake St. Francis 5	3	3			
	Raquette River 1	3	3	1		
	St. Regis River 1	3	3	1		
08/13/99	Cooper Marsh	3	3			
	Raisin River 2	3	3	1		
	Raisin River 4	3	3			
	Raisin River 5	3	3	1		
08/28/99	Cooper Marsh canal					**7**
	Cooper Marsh canal entrance					**6**
	Lake St. Francis 8					**1**
09/17/99	Lake St. Francis 7					**1**
09/28/99	Grass River 1					**5**
	Lake St. Francis 14					**10**
	Raquette River 2					**5**
	St. Regis River 2					**6**

Date	Location	DIC	POM	Zooplankton	Benthic invertebrates	Fish
06/12/00	Grey's Creek		2			
	Lake St. Francis 1		3			
	Lake St. Francis 2		3	1		
	Lake St. Francis 3		3		2 taxa	
	Lake St. Francis 4		3			
	Raquette River 1		1			
07/19/00	Cooper Marsh canal entrance					1
07/25/00	Lake St. Francis 14				1 taxon from 1 fish stomach	6
08/09/00	Cooper Marsh canal					8
	Cooper Marsh canal entrance					1
08/22/00	Raisin River 1				1	1
08/23/00	Raquette River 1				1	
09/20/00	Grass River 2					10
	Raquette River 2					11
	St. Regis River 2					10
09/23/00	Lake St. Francis 9					3
	Lake St. Francis 10					3
	Lake St. Francis 11					2
	Lake St. Francis 12					1
	Lake St. Francis 13					4

Figure 2.1. Map showing the location of sampling sites in Lake St. Francis and its nearby tributaries and wetlands near Cornwall, Ontario. CM = Cooper Marsh; CMC = Cooper Marsh canal; CME = Cooper Marsh canal entrance; GC = Grey's Creek; GR = Grass River; LSF = Lake St. Francis; RqR = Raquette River; RR = Raisin River; S = The Snye; SRR = St. Regis River


RR 4
RR 3
RR 1
RR 2
Raisin R.
RR 5
LSF 13
LSF 14
LSF 12
45° 10'
74° 24'
LSF 11
Lake
St. Francis
LSF 10
Cooper
Marsh
LSF 8
CM
CMC
CME
LSF 7
LSF 9
Cornwall
GC
LSF 6
S
Moses-
Saunders
Dam
LSF 1, 2, 3
LSF 4
Salmon R.
N
LSF 5
SRR 1
SRR 2
St. Regis R.
44° 58'
74° 50'
GR 1
RqR 2
RqR 1
5 km
Grass R.
GR 2
Raquette R.

3. RESULTS

3.1. Carbon isotopes as tracers of energy sources

A statistical analysis testing the effects of location and sampling date on $\delta^{13}C_{DIC}$ was conducted for samples collected in both June and August 1999 which are shown in Figure 3.1. Carbon signatures of DIC from Lake St. Francis sites were significantly enriched (by approximately 8‰) than those from sampling sites in tributaries and wetlands (Scheirer-Ray-Hare extension of the Kruskall-Wallis test: H=39.00, n=53 df=1, $p<0.001$). Although not statistically significant, August values tended to be more enriched in ^{13}C than June values, especially in Lake St. Francis (H=2.38, n=53, df=1, $p>0.05$).

For a given sampling month, the carbon signatures of POM were significantly related to the isotopic composition of DIC (Spearman rank correlations, June 1999: $r=0.60$, $p<0.001$, n=35; August 1999: $r=0.72$, $p<0.001$, n=36), even though seasonal variations were more pronounced for POM (Figure 3.2). In addition, the $\delta^{13}C$ of zooplankton were significantly correlated to the $\delta^{13}C$ of POM (Spearman rank correlation, August 1999: $r_{POM\text{-}zooplankton}= 0.86$, $p=0.03$, n=7). The $\delta^{13}C$ of benthic invertebrates were not significantly correlated to the $\delta^{13}C$ of POM (Spearman rank correlation, August 1999: $r_{POM\text{-}benthic\ invertebrates}= 0.60$, $p>0.2$, n=5).

The carbon signatures of Lake St. Francis POM, zooplankton, and benthic invertebrates were more enriched in their $\delta^{13}C$ values relative to tributary and wetland sampling sites. Average $\delta^{13}C$ values of POM in Lake St. Francis were approximately 4‰ more enriched in ^{13}C than $\delta^{13}C$ values of POM from tributaries (Lake St. Francis:-26.00 ± 0.28‰; tributaries: -30.41 ± 0.43‰) (Mann-Whitney U test: U=1444.5, n=79, df=1, $p<0.005$)

(Figure 3.2). Like POM, the $\delta^{13}C$ values of zooplankton collected in August 1999 were about 4‰ heavier in Lake St. Francis (-21.53 ± 0.59‰) than in tributaries (-25.81 ± 0.68‰) (Table 3.1). One exception to this trend is the zooplankton sample taken in Lake St. Francis during the 2000 sampling season, which was lighter (-31.38‰) than all other samples taken in 1999. No statistical analysis comparing the mean $\delta^{13}C$ value of zooplankton between systems was attempted because of the low sample size (n=4 in tributaries, n=3 in Lake St. Francis).

Samples of *Gammarus fasciatus* acidified with 1N HCl had lighter carbon and nitrogen isotopic compositions than non-acidified samples (Table 3.2). Since acidification did not affect the pattern observed between Lake St. Francis and tributary benthic invertebrates, yet altered the isotopic composition of carbon and nitrogen (Table 3.2), only non-acidified values were considered.

Differences in the carbon signals between the two systems were more pronounced in benthic invertebrates than in POM or zooplankton. Average tributary benthos $\delta^{13}C$ values were more than 10‰ lighter than those in Lake St. Francis benthos (tributaries: -29.24 ± 0.82‰; Lake St. Francis:-17.54 ± 0.25‰; Table 3.3). No statistical analysis comparing the mean $\delta^{13}C$ value of benthic invertebrates between systems was attempted due to the low sample size (n=2 in tributaries, n=3 in Lake St. Francis).

Initial classification of a training set of fish based on their $\delta^{13}C$ resulted in the following discriminant function: $Z=12.143+0.605(\delta^{13}C)$. The carbon signatures of the fish from tributaries and wetlands did not overlap with those of Lake St. Francis fish. Accordingly, there was 0% misclassification when the discriminant function was used to classify the fish from the training set. Following this, the discriminant function was employed to categorize

the remainder of the fish into one of two groups. The 'cut off' value determining which system a particular fish was assigned to was where Z = 0 (i.e., when $\delta^{13}C$ = -20.07‰). Fish with $\delta^{13}C$ lower than -20.07‰ were classified as tributary fish, while those with $\delta^{13}C$ greater than -20.07‰ were assigned to the Lake St. Francis group. This resulted in 61 individuals classified as Lake St. Francis fish, and 41 fish assigned to the tributaries and wetlands group (Figure 3.3). Relationships between variables such as nitrogen and carbon isotopic ratios, size estimates, and mercury concentrations for all 102 fish from both systems were similar to the trends observed when considering only the 34 fish of the training set used in the initial discriminant analysis.

Benthic organisms, especially *Gammarus fasciatus*, were the major prey items found in the stomachs of the yellow perch that were examined. Lake St. Francis fish were, on average, slightly older (Mann-Whitney U test: U=1654, n=102, df=1, p=0.004), longer (U=1914.5, n=102, df=1, p<0.005) and heavier (U=1963, n=102, df=1, p<0.005) than yellow perch from the tributaries and wetlands group (Table 3.4).

A summary of the differences in mean (± SE) $\delta^{13}C$ values between DIC, POM, zooplankton, benthic invertebrates and yellow perch of Lake St. Francis and tributaries/ wetlands is presented in Figure 3.4. For zooplankton, only samples from the 1999 sampling season were included in the calculation of the mean as only a single sample from one location was taken in the year 2000.

3.2. Nitrogen isotopes as estimates of trophic position

The $\delta^{15}N$ values of fish from tributaries spanned approximately 4.8‰, ranging from

10.3 to 15.07‰. Values from Lake St. Francis only spanned 3.2‰, with $\delta^{15}N$ ranging from 13.15 to 16.36‰ (Figure 3.3). No significant relationship was observed between nitrogen composition and age, total length or weight of yellow perch feeding in tributaries (Figure 3.5). However, these three variables were positively related to $\delta^{15}N$ in Lake St. Francis fish. A principal component analysis was performed to factor out the correlation between age, weight, and length of fish. Appendix B shows the results of the analysis. Only one factor (factor 1) was retained, as it was the only factor with an eigenvalue greater than one (Manly, 1998). The test scores of factor 1 were used in subsequent statistical tests. This variable was not significantly correlated with $\delta^{15}N$ in tributary fish, in contrast to the positive correlation observed between factor 1 and $\delta^{15}N$ in Lake St. Francis fish (tributaries: Spearman rank correlation $r=0.21$, $p=0.17$, $n=41$; Lake St. Francis: Pearson correlation $r=0.48$, $p<0.005$, $n=61$).

A strong positive correlation was observed between nitrogen and carbon signatures of yellow perch in tributaries and wetlands (Pearson correlation: $r= 0.525$, $p<0.001$, $n=41$) but no relationship existed between these two variables in Lake St. Francis fish (Pearson correlation: $r= 0.005$, $p=0.967$, $n=61$) (Figure 3.3).

Considering the range in $\delta^{15}N$ values, there was little overlap between the nitrogen signatures of fish from the two systems (Figure 3.3). After controlling for variations in fish size, nitrogen signatures were significantly lower in tributary fish compared to Lake St. Francis fish (source term: $n=102$, $df=1$, F-ratio=64.16, $p<0.005$). This difference was observable in lower trophic level organisms such as POM, zooplankton, and benthic invertebrates. The $\delta^{15}N$ signals of all organisms are summarized in Figure 3.6. Only

zooplankton from the 1999 sampling season were included and fish $\delta^{15}N$ were not corrected for variations in fish size. The $\delta^{15}N$ signals of POM were significantly lighter in tributaries than in Lake St. Francis (Mann-Whitney U test: U=1209.5, n=79, df=1, $p<0.005$; Figures 3.6 and 3.7). No statistical analyses were attempted to compare mean $\delta^{15}N$ values of zooplankton and benthic invertebrates between systems because of the low sample size (zooplankton: n=4 in tributaries, n=3 in Lake St. Francis; benthic invertebrates: n=2 in tributaries, n=3 in Lake St. Francis). Average zooplankton $\delta^{15}N$ values from 1999 were similar in tributaries and in Lake St. Francis (tributaries: 4.85 ± 0.42‰; Lake St. Francis: 5.34 ± 0.95‰; Table 3.1, Figure 3.6). As for benthic invertebrates, samples from Lake St. Francis had more enriched $\delta^{15}N$ values than samples from tributaries (tributaries: 6.59 ± 0.77‰; Lake St. Francis: 10.22 ± 1.11‰; Table 3.3, Figure 3.6). The individual invertebrate taxa had varying $\delta^{15}N$, as seen in Table 3.3. The leech collected in June 2000 from Lake St. Francis had a very enriched $\delta^{15}N$ value of 12.39‰.

3.3. Mercury

In all analyses, mercury concentrations were log-transformed (log Hg) to improve normality and homogeneity of variance of residuals. Error bars are not shown for log Hg concentrations in Figures 3.8 to 3.12 to reduce the amount of information presented on each figure and to facilitate the observation of trends. The standard errors of log Hg concentrations were on average 0.025 log units, 12 out of 102 fish having standard errors ≥0.05 log units and only 1 of them having a standard error >0.1 log units.

3.3.1. Mercury accumulation with $\delta^{15}N$

Results of the General Linear Models testing the effects of nitrogen on log Hg concentrations, with source (tributaries or Lake St. Francis), year, and sex as categorical variables are summarized in Table 3.5. Statistics of the linear regressions are shown in the text. The relationship between log Hg and $\delta^{15}N$ differed between systems. No relationship between log Hg and $\delta^{15}N$ existed for fish in tributaries ($n=41$, $r^2=0.01$, RMS=0.04, $p=0.56$) (Figure 3.8). However, a significant relationship was seen in Lake St. Francis fish ($n=61$, $r^2=0.23$, RMS=0.04, $p<0.005$).

Mercury accumulated differently between years in Lake St. Francis fish, but not in fish from tributaries, as dictated by the interaction terms of the General Linear Models for both systems. Consequently, a separate linear regression was performed for each sampling year for Lake St. Francis fish. A significant positive relationship between log Hg and $\delta^{15}N$ was observed in Lake St. Francis fish from the 2000 sampling season, but not for fish caught in 1999 (Figure 3.8) (1999: $n=30$, $r^2=0.02$, RMS=0.02, $p=0.50$; 2000: $n=31$, $r^2=0.32$, RMS=0.05, $p<0.005$). There was one outlier in the linear regression for fish sampled in 2000. However, the coefficients of the regression with the outlier removed were still within the estimates of the original regression. The outlier was therefore not greatly affecting the regression and thus was not removed. The linear regression (model II, reduced major axis) of log Hg and $\delta^{15}N$ of yellow perch caught in the summer of 2000 yielded: log Hg ($\mu g/g$ ww) = $-5.81+0.35\delta^{15}N$ ($n=31$, $r^2=0.32$, RMS=0.05, $p<0.005$). No effect of sex was detected on log Hg levels in fish sampled from either Lake St. Francis or tributaries and wetlands.

3.3.2. Mercury accumulation with size variables

Table 3.6 summarizes the results of the General Linear Models testing the effects of size variables on log Hg in fish, with source, year, and sex as categorical variables. Mercury concentrations were positively related to age ($n=102$, $r^2=0.31$, RMS=0.03, $p<0.005$), length ($n=102$, $r^2=0.37$, RMS=0.03, $p<0.005$) and weight ($n=102$, $r^2=0.32$, RMS=0.05, $p<0.005$) (Figures 3.9 to 3.11). Slopes and intercepts of the relationships between log Hg and age, length or weight were not significantly different between locations.

To test whether the lack of significant differences between systems was caused by other variables obscuring the relationship, effects of year and of sex were tested among systems. Mercury accumulated differently between years with length and age, but not with weight. No effect of sex was detected on log Hg levels in fish. There was substantial variation of log Hg levels in fish, as indicated by the scatter of data points around the regression lines, especially for the relationship between log Hg and age of fish (Figures 3.9 to 3.11). Mercury levels ranged from approximately 0.06 μg/g ww to greater than 0.3 μg/g ww within the 2 and 3 year old age class (Figure 3.10). Mercury concentrations were higher in fish that grew more slowly, growth rates decreasing with fish age (1999: $n=41$, $r^2=0.16$, RMS=0.02, $p=0.009$; 2000: $n=61$, $r^2=0.33$, RMS=0.04, $p<0.005$) (Figure 3.12). However, relationships between length and age of yellow perch were similar in both systems, supporting the assumption that yellow perch from the two systems grew at the same rate (age * source term: $n=102$, $df=1$, F-ratio=0.04, $p=0.84$).

The assumption of independence of residuals was violated for all General Linear Model tests that were conducted. There was high autocorrelation, indicating that there could

be subgroups of fish more correlated with each other than with the rest of the fish in the group. An attempt to reduce the autocorrelation was made by including other variables (sex, machine, year of sampling) into the General Linear Models but none of them rectified the problem.

3.3.3. Analytical method effect

Log Hg levels estimated by cold vapor atomic fluorescence spectrometry (Tekran Series 2600 analyzer) were regressed against those estimated by cold vapor atomic absorbance spectrometry (CETAC M-6000A analyzer). The slope of the relationship was 1.045(± 0.127) (n=20, RMS=0.0123, r^2= 0.73, $p<0.005$) and was not significantly different from a slope of 1, as expected if there is no bias between the two analytical methods (Figure 3.13). The intercept was 0.069(± 0.126) and was not significantly different from 0 (t=-0.666, p=0.514). In some cases, all replicates of some fish were above the 1:1 line while all replicates of others were below the line. Although there was no consistent difference between mercury estimates of both analyzers, there seemed to be more variation in estimates of the Tekran Series 2600 compared to those of the CETAC M-6000A. In the worst case, for a given fish, the difference in average log Hg between the two analyzers was 0.12 log units. Quality control measures such as the recovery of mercury in SRM and in spiked samples were slightly lower and more variable for the Tekran Series 2600 than those of the CETAC M-6000A (see Methods section on quality control).

Table 3.1. Values of $\delta^{13}C$ (‰) and $\delta^{15}N$ (‰) for zooplankton samples collected at sites in tributaries and in Lake St. Francis. Each $\delta^{13}C$ and $\delta^{15}N$ value is one estimate of several organisms pooled together. Means ± SE for both systems are shown for August, 1999 samples.

Location	Date	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)
Tributaries			
St. Regis River 1	08/11/99	-24.28	4.95
Raquette River 1	08/11/99	-25.79	4.08
Raisin River 2	08/13/99	-27.59	6.01
Raisin River 5	08/13/99	-25.59	4.38
Mean ± SE (n=4)		-25.81 ± 0.68	4.86 ± 0.42
Lake St. Francis			
Lake St. Francis 1	08/11/99	-22.71	3.45
Lake St. Francis 3	08/11/99	-21.03	6.31
Lake St. Francis 4	08/11/99	-20.86	6.27
Mean ± SE (n=3)		-21.53 ± 0.59	5.34 ± 0.95
Lake St. Francis 2	06/12/00	-31.38	1.65

Table 3.2. Effects of acid washing with 1N HCl on $\delta^{13}C$ (‰) and $\delta^{15}N$ (‰) values of the amphipod *Gammarus fasciatus* from Lake St. Francis. Approximately ten organisms per location were pooled to obtain single $\delta^{13}C$ and $\delta^{15}N$ values.

Location	$\delta^{13}C$ (‰)			$\delta^{15}N$ (‰)		
	no treatment	acid treatment	difference	no treatment	acid treatment	difference
Lake St. Francis[1]	-17.48	-18.55	-1.07	9.53	8.29	-1.24
Lake St. Francis 3	-18.00	-19.81	-1.81	8.75	7.43	-1.32

[1]This sample was taken from the stomach of a fish caught in Lake St. Francis 14.

Table 3.3. Values of $\delta^{13}C$ (‰) and $\delta^{15}N$ (‰) for different benthic invertebrates from sites in tributaries and in Lake St. Francis. Except for the leech sample where only one organism was used, approximately ten organisms were pooled to obtain single $\delta^{13}C$ and $\delta^{15}N$ values for each site.

Location	Taxa	Date	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)
Tributaries				
Raquette River 1	Ephemeroptera (mayfly)	08/23/00	-28.42	5.82
Raisin River 1	*Gammarus fasciatus*	08/22/00	-30.07	7.36
Mean ± SE (n=2)			-29.24 ± 0.82	6.59 ± 0.77
Lake St. Francis				
Lake St. Francis 3	*Gammarus fasciatus*	06/12/00	-18.00	8.75
Lake St. Francis[1]	*Gammarus fasciatus*	07/25/00	-17.48	9.53
Lake St. Francis 3	leech	06/12/00	-17.15	12.39
Mean ± SE (n=3)			-17.54 ± 0.25	10.22 ± 1.11

[1]This sample was taken from the stomach of a fish caught in Lake St. Francis 14.

Table 3.4. Mean ± SE length (cm), weight (g), age (yrs) and total Hg concentration (μg/g ww) in yellow perch from Lake St. Francis and tributaries and wetlands near Cornwall, Ontario. Ranges are in brackets.

	n	Length (cm)	Weight (g)	Age (yrs)	Hg (μg/g ww)
Tributaries	41	16.02 ± 0.35 (12.10-20.10)	46.16 ± 5.84 (17.76-93.56)	2.5 ± 0.2 (1-5)	0.16 ± 0.01 (0.07-0.34)
Lake St. Francis	61	18.88 ± 0.41 (12.20-26.0)	84.01 ± 3.42 (16.52-214.30)	3.3 ± 0.2 (1-9)	0.22 ± 0.02 (0.07-0.70)

Table 3.5. Results for each term of the General Linear Models examining the relationship between log Hg (μg/g ww) in yellow perch and $\delta^{15}N$ (‰), feeding location (source), sampling year, and sex. df = degrees of freedom

	Term	n	df	F-ratio	p
Source					
	$\delta^{15}N$	102	1	13.67	<0.005
	Source	102	1	8.95	0.004
	$\delta^{15}N$*source	102	1	8.92	0.004
Year					
Tributaries	$\delta^{15}N$	41	1	0.12	0.74
	Year	41	1	1.27	0.27
	$\delta^{15}N$*year	41	1	0.90	0.35
Lake St. Francis	$\delta^{15}N$	61	1	9.52	0.003
	Year	61	1	4.68	0.03
	$\delta^{15}N$*year	61	1	4.94	0.03
Sex					
Tributaries	$\delta^{15}N$	41	1	0.05	0.82
	Sex	41	1	0.46	0.50
	$\delta^{15}N$*sex	41	1	0.39	0.54
Lake St. Francis	$\delta^{15}N$	61	1	16.80	<0.005
	Sex	61	1	0.33	0.56
	$\delta^{15}N$*sex	61	1	0.38	0.54

Table 3.6. Results for each term of the General Linear Models testing for effects of categorical variables (source (tributaries/wetlands and Lake St. Francis); source and sampling year; source and sex) on the relationship between log Hg (μg/g ww) and size estimates (length, age and weight) of yellow perch. df= degrees of freedom

Categorical variables	Size estimate	Term	n	df	F-ratio	p
Source						
	Length	Length	102	1	25.15	<0.005
		Source	102	1	0.0009	0.98
		Length*source	102	1	0.0003	0.99
	Age	Age	102	1	37.68	<0.005
		Source	102	1	0.87	0.35
		Age*source	102	1	0.20	0.65
	Weight	Weight	102	1	18.17	<0.005
		Source	102	1	0.13	0.71
		Weight*source	102	1	0.08	0.78
Year and source						
	Length	Length	102	1	22.95	<0.005
		Year	102	1	2.13	0.15
		Source	102	1	0.13	0.72
		Length*year	102	1	4.57	0.04
		Length*source	102	1	0.30	0.58
	Age	Age	102	1	29.13	<0.005
		Year	102	1	1.37	0.24
		Source	102	1	0.28	0.60

Categorical variables	Size variable	Term	n	df	F-ratio	p
Year and source		Age*year	102	1	8.49	<0.005
		Age*source	102	1	0.25	0.62
	Weight	Weight	102	1	14.45	<0.005
		Year	102	1	0.31	0.58
		Source	102	1	0.22	0.64
		Weight*year	102	1	1.72	0.19
		Weight*source	102	1	0.002	0.96
Sex and source						
	Length	Length	102	1	22.20	<0.005
		Sex	102	1	0.06	0.80
		Source	102	1	0.03	0.87
		Length*sex	102	1	0.01	0.91
		Length*source	102	1	0.01	0.90
	Age	Age	102	1	35.34	<0.005
		Sex	102	1	2.41	0.12
		Source	102	1	0.29	0.59
		Age*sex	102	1	3.15	0.08
		Age*source	102	1	0.001	0.96
	Weight	Weight	102	1	36.09	<0.005
		Sex	102	1	0.14	0.71
		Source	102	1	0.64	0.42
		Weight*sex	102	1	0.82	0.36
		Weight*source	102	1	3.65	0.06

Figure 3.1. Mean (± SE) $\delta^{13}C$ (‰) of DIC from various locations in Lake St. Francis and tributaries and wetlands, in June and August, 2000. Error bars not shown if smaller than symbol size. Sample sizes: n=3 except for Grey's Creek in June, 2000, where n=2. RqR1 = Raquette River 1; SRR1 = St. Regis River 1; S = The Snye; GC = Grey's Creek; CM = Cooper Marsh; RR2 = Raisin River 2; RR3 = Raisin River 3; RR4 = Raisin River 4; RR5 = Raisin River 5

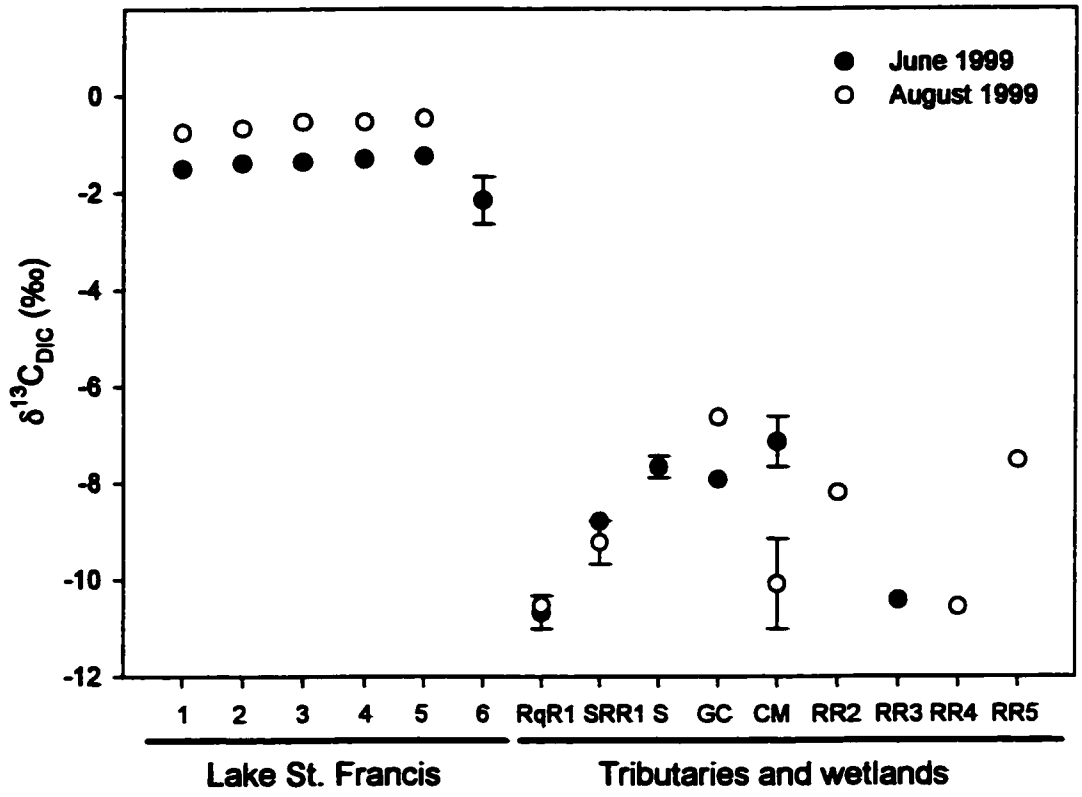

June 1999
August 1999
0
-2
-4
-6
-8
-10
-12
$\delta^{13}C_{DIC}$ (‰)
1
2
3
4
5
6
RqR1
SRR1
S
GC
CM
RR2
RR3
RR4
RR5
Lake St. Francis
Tributaries and wetlands

Figure 3.2. Mean (± SE) $\delta^{13}C$ (‰) of POM from various locations in Lake St. Francis and tributaries and wetlands. Error bars not shown if smaller than symbol size. See Table 2.1 for sample sizes. Abbreviations for sampling locations are the same as in Figure 3.1.

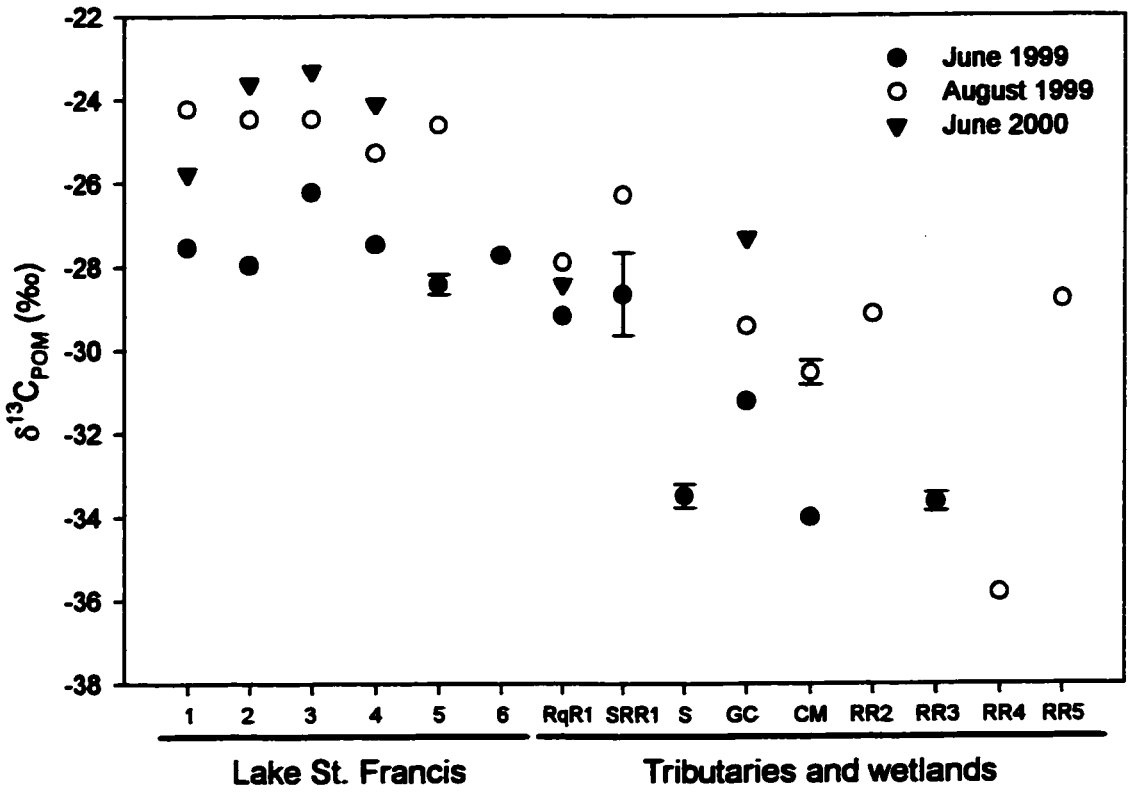

-22
-24
-26
-28
-30
-32
-34
-36
-38
$\delta^{13}C_{POM}$ (‰)
June 1999
August 1999
June 2000
1
2
3
4
5
6
RqR1
SRR1
S
GC
CM
RR2
RR3
RR4
RR5
Lake St. Francis
Tributaries and wetlands

Figure 3.3. Relationships between $\delta^{15}N$ (‰) and $\delta^{13}C$ (‰) for yellow perch from tributaries (n=41) and from Lake St. Francis (n=61). The dashed line represents the discriminant function [$Z=12.143+0.605(\delta^{13}C)$] with which individual fish were assigned to one group or another. Pearson correlation coefficients and corresponding p-values are shown for both groups of fish.

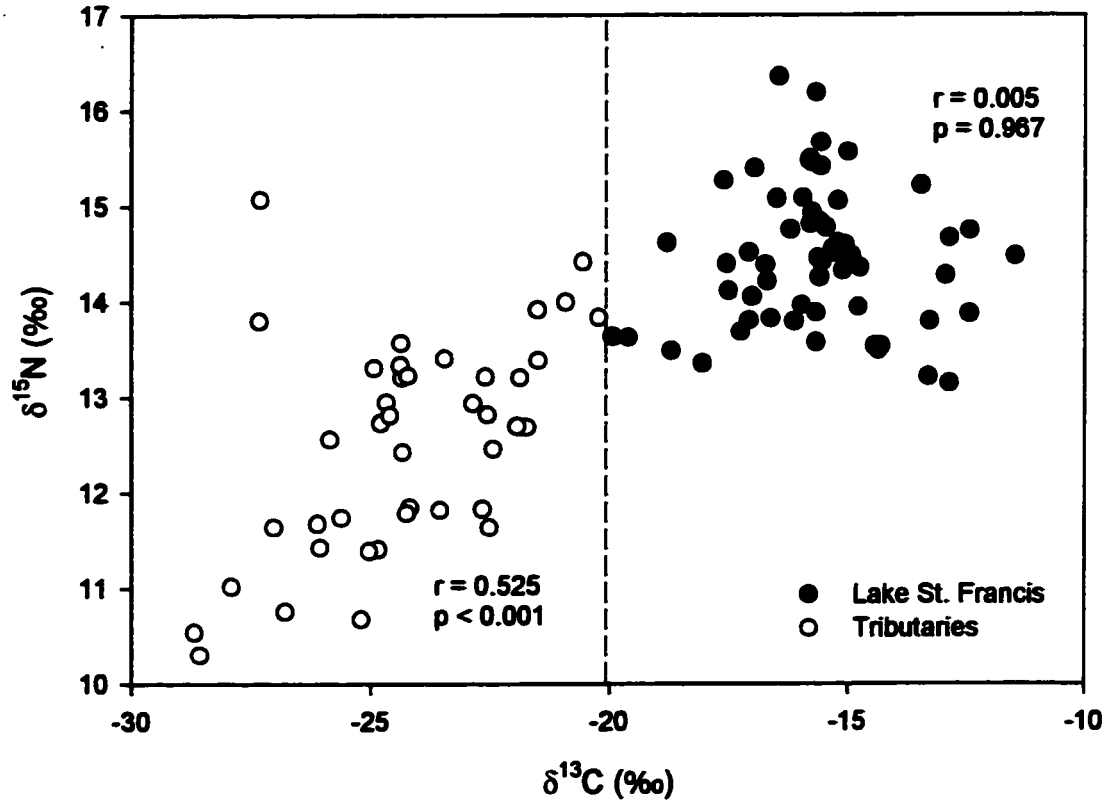

17
16
15
14
13
12
11
10
-30
-25
-20
-15
-10
δ15N (‰)
δ13C (‰)
r = 0.005
p = 0.967
r = 0.525
p < 0.001
Lake St. Francis
Tributaries

Figure 3.4. Relationship between mean (± SE) $\delta^{13}C$ (‰) of DIC (Lake St. Francis: n=33; tributaries: n=38), POM (Lake St. Francis: n=37; tributaries: n=42), zooplankton (Lake St. Francis: n=3; tributaries: n=4), benthic invertebrates (Lake St. Francis: n=3; tributaries: n=2), and yellow perch (Lake St. Francis: n=61; tributaries: n=41) from Lake St. Francis and from tributaries and wetlands. Only zooplankton samples from the 1999 sampling season were included in the calculation of the mean. Error bars not shown if smaller than symbol size.

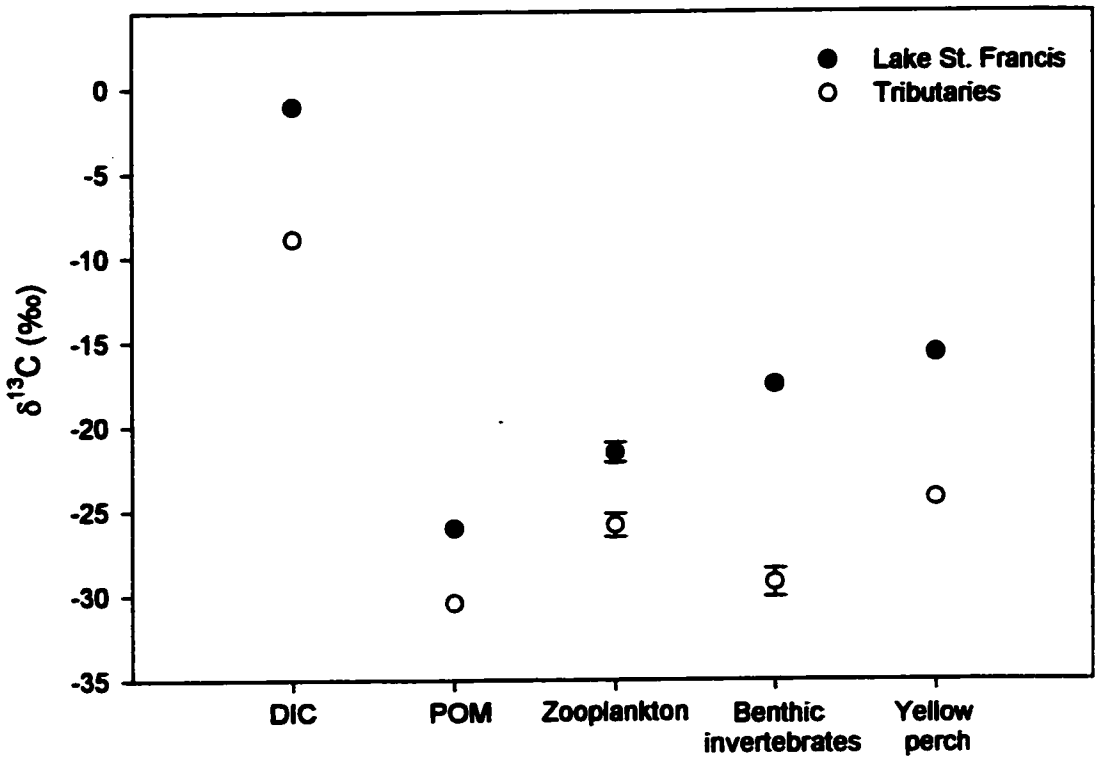

Lake St. Francis
Tributaries
0
-5
-10
-15
-20
-25
-30
-35
δ13C (‰)
DIC
POM
Zooplankton
Benthic invertebrates
Yellow perch

Figure 3.5. Relationships between $\delta^{15}N$ (‰) and length (cm), age (yrs) and weight (g) for yellow perch from tributaries (n=41) and from Lake St. Francis (n=61). Pearson correlation coefficients and corresponding p-values are shown for the relationship between $\delta^{15}N$ and length, while Spearman rank correlation coefficients and corresponding p-values are shown for the relationships between $\delta^{15}N$ and age, and between $\delta^{15}N$ and weight.

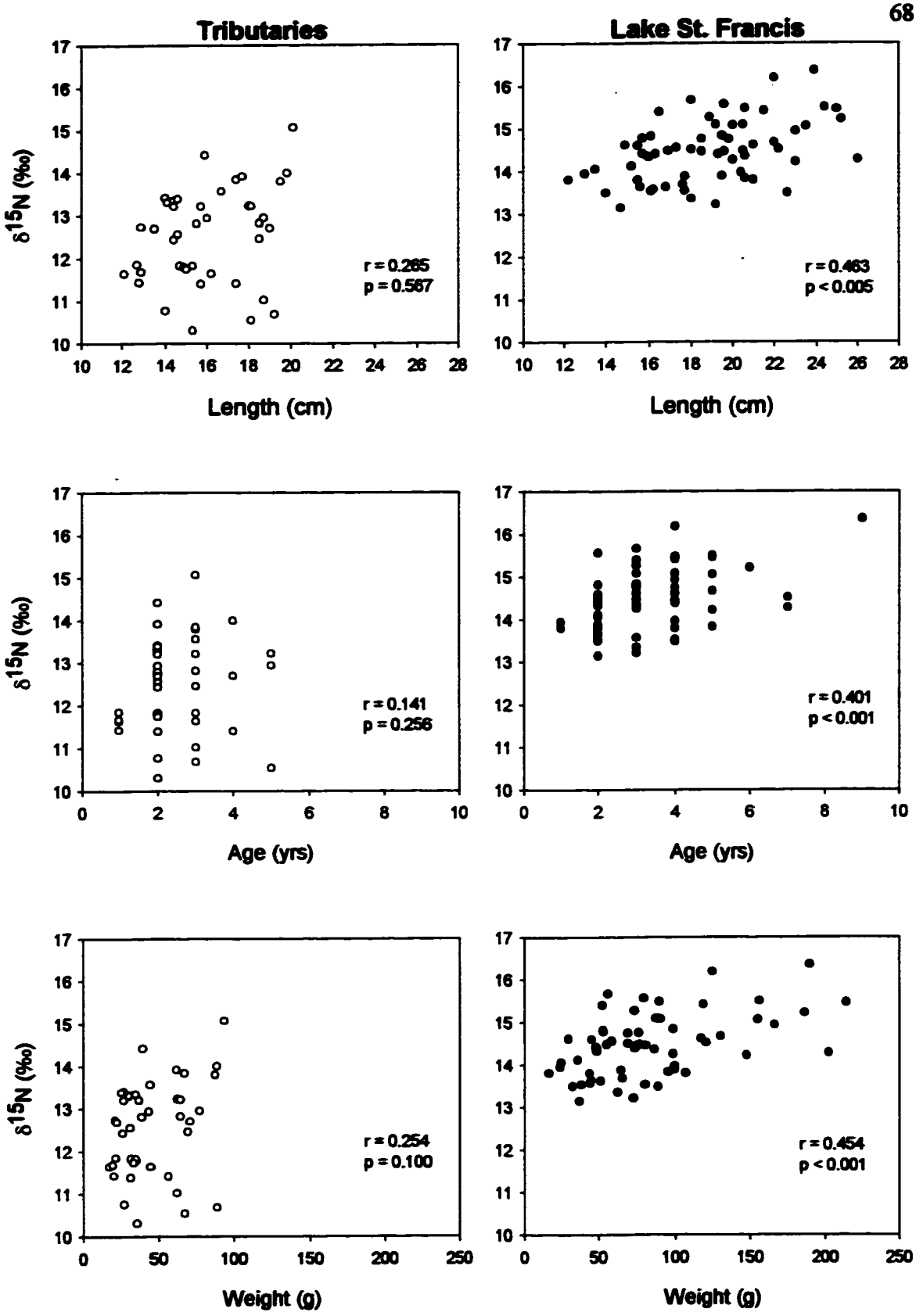

Tributaries
Lake St. Francis
δ15N (‰)
Length (cm)
r = 0.265
p = 0.567
r = 0.463
p < 0.005
Age (yrs)
r = 0.141
p = 0.256
r = 0.401
p < 0.001
Weight (g)
r = 0.254
p = 0.100
r = 0.454
p < 0.001

Figure 3.6. Relationship between mean (± SE) $\delta^{15}N$ (‰) of POM (Lake St. Francis: n=37; tributaries: n=42), zooplankton (Lake St. Francis: n=3; tributaries: n=4), benthic invertebrates (Lake St. Francis: n=3; tributaries: n=2), and yellow perch (Lake St. Francis: n=61; tributaries: n=41) from Lake St. Francis and from tributaries and wetlands. Only zooplankton samples from the 1999 sampling season were included in the calculation of the mean. Fish $\delta^{15}N$ were not corrected for variations in fish size. Error bars not shown if smaller than symbol size.

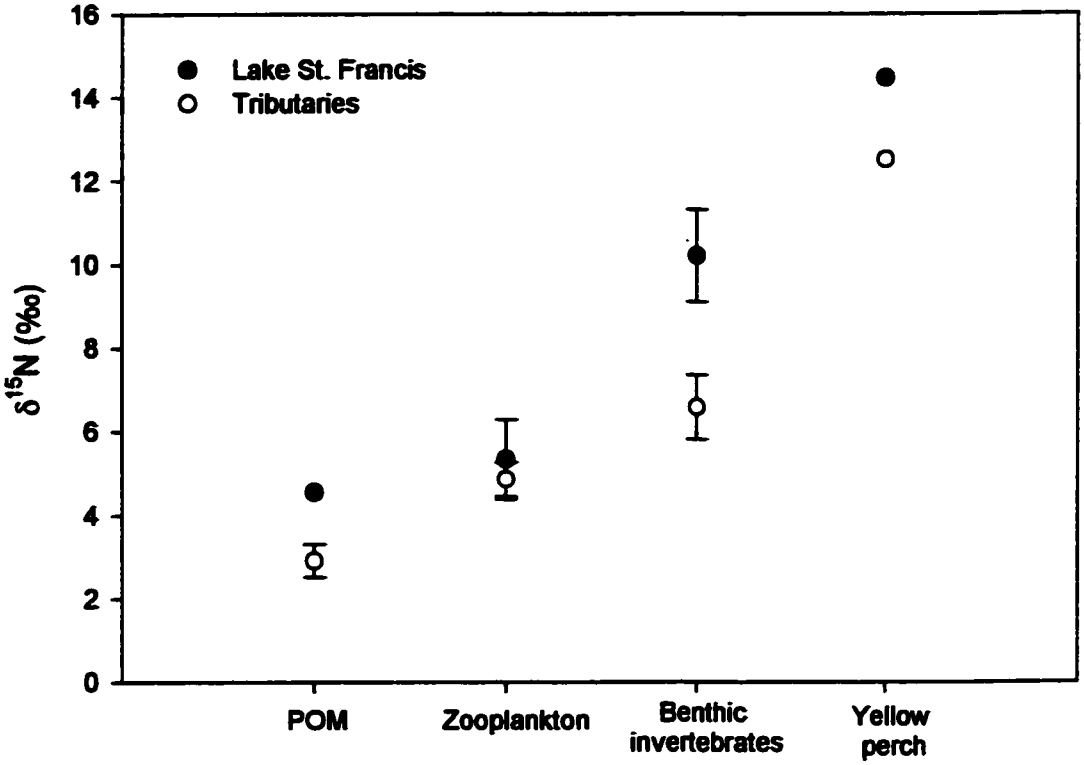

16
14
12
10
8
6
4
2
0
δ15N (‰)
Lake St. Francis
Tributaries
POM
Zooplankton
Benthic invertebrates
Yellow perch

Figure 3.7. Mean (± SE) $\delta^{15}N$ (‰) of POM from various locations in Lake St. Francis and tributaries and wetlands. Error bars not shown if smaller than symbol size. See Table 2.1 for sample sizes. Abbreviations for sampling locations are the same as in Figure 3.1.

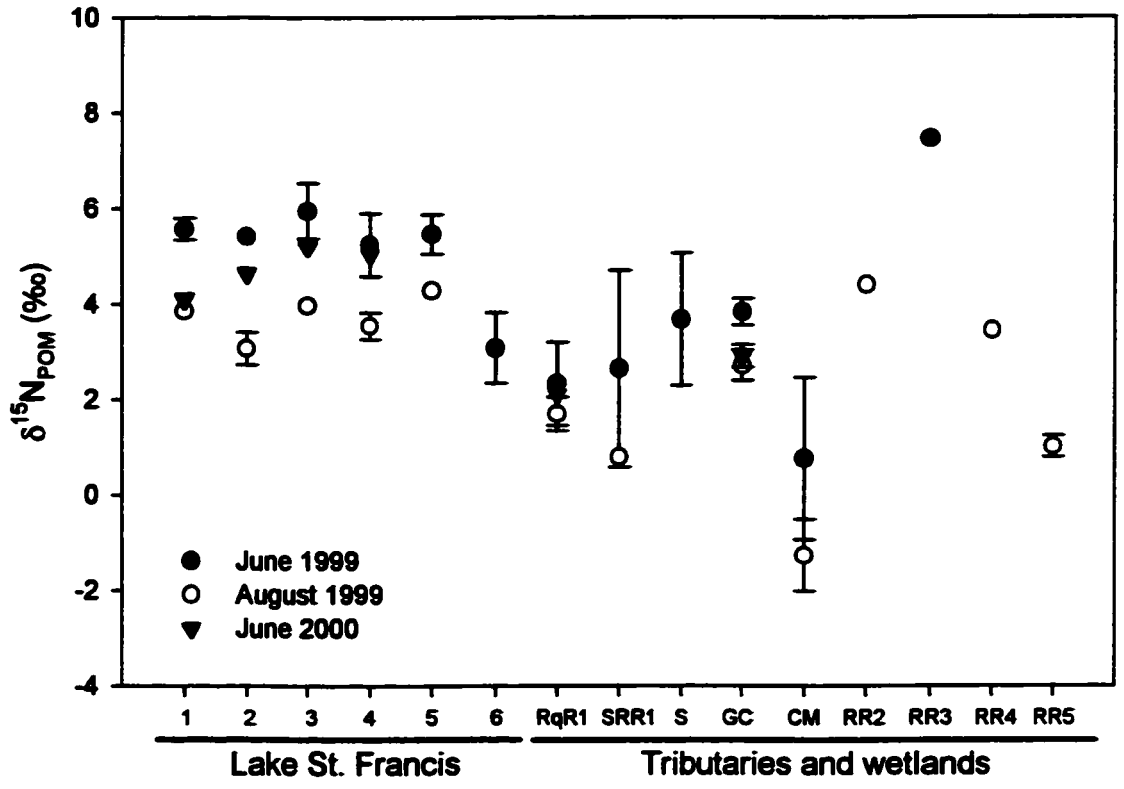
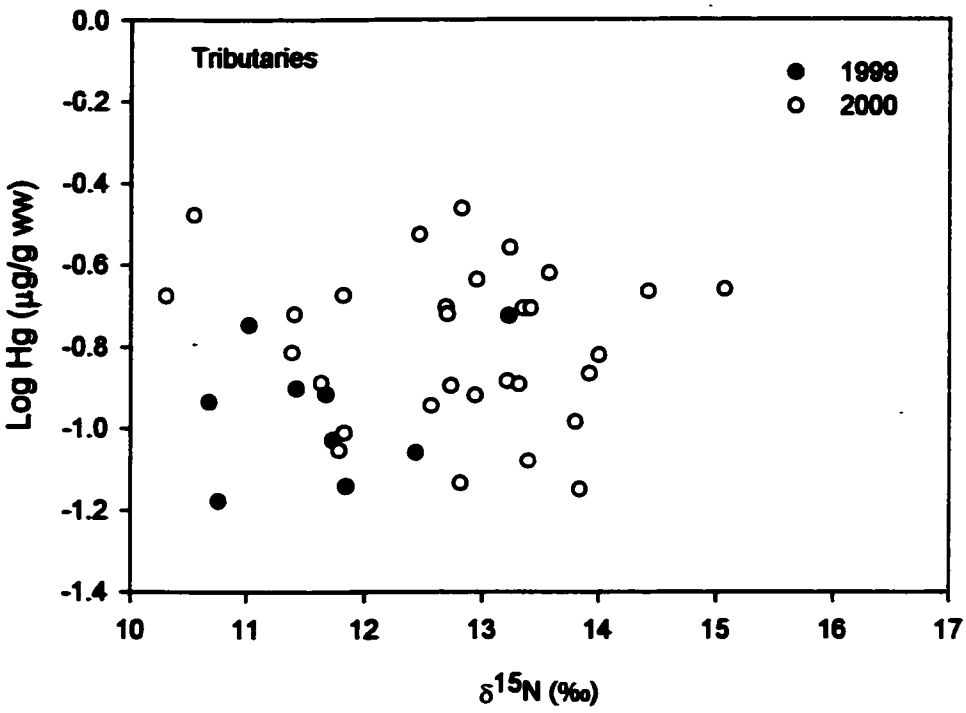

10
8
6
4
2
0
-2
-4
δ15NPOM (‰)
June 1999
August 1999
June 2000
1
2
3
4
5
6
RqR1
SRR1
S
GC
CM
RR2
RR3
RR4
RR5
Lake St. Francis
Tributaries and wetlands

Figure 3.8. Relationship between log Hg (μg/g ww) and $\delta^{15}N$ (‰) in yellow perch from tributaries (1999 (n=11) and 2000 (n=30)) and Lake St. Francis (1999 (n=30) and 2000 (n=31)). The regression line is for the relationship between log Hg and $\delta^{15}N$ of yellow perch from Lake St. Francis caught in the year 2000 only. Error bars not shown for mercury concentrations.

No significant relationship was found for fish from tributaries (r^2=0.01, RMS=0.04, p=0.56) or for those from Lake St. Francis that were caught in the year 1999 (r^2=0.02, RMS=0.02, p=0.50). The model II reduced major axis regression analysis for the fish from Lake St. Francis caught in the year 2000 resulted in the following model:

$$\log Hg = -5.81(0.79) + 0.35(0.05)\delta^{15}N,\ r^2=0.32,\ RMS=0.05,\ p<0.005$$


Tributaries
1999
2000
Log Hg (µg/g ww)
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
10
11
12
13
14
15
16
17
δ15N (‰)

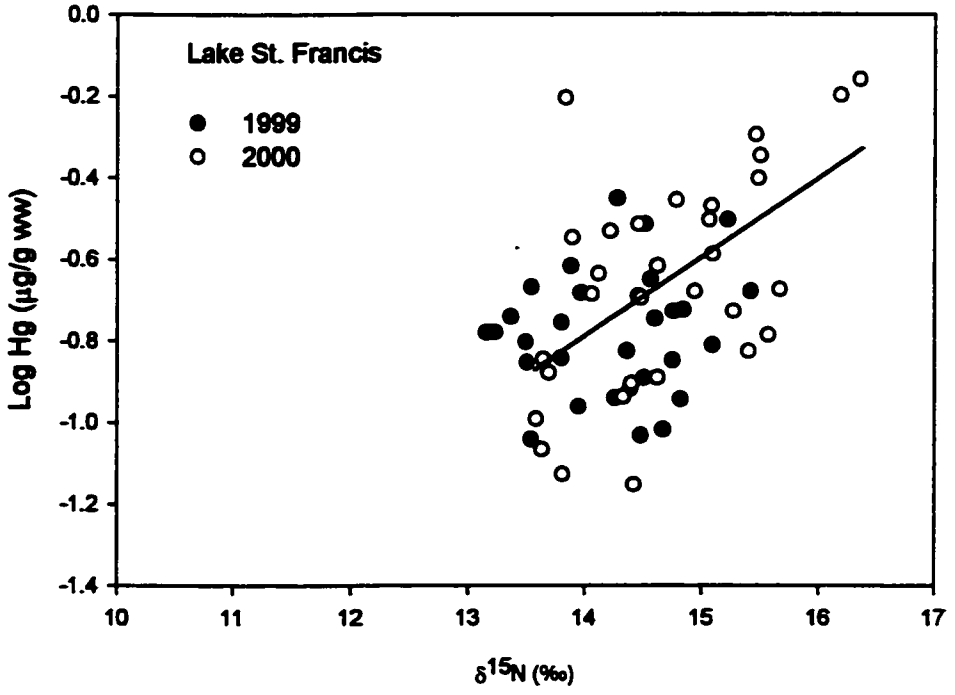

Lake St. Francis
1999
2000
Log Hg (µg/g ww)
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
10
11
12
13
14
15
16
17
δ15N (‰)

Figure 3.9. Regressions of log Hg (μg/g ww) and total length (cm) of yellow perch from Lake St. Francis and nearby tributaries combined in 1999 (n=41, solid line) and 2000 (n=61, dashed line). Error bars not shown for mercury concentrations.

The regression analyses resulted in the following models:

1999 $\log Hg = -1.336(0.064) + 0.029(0.004)length$, $r^2=0.32$, RMS=0.020, $p<0.005$

2000 $\log Hg = -1.635(0.088) + 0.052(0.005)length$, $r^2=0.39$, RMS=0.039, $p<0.005$

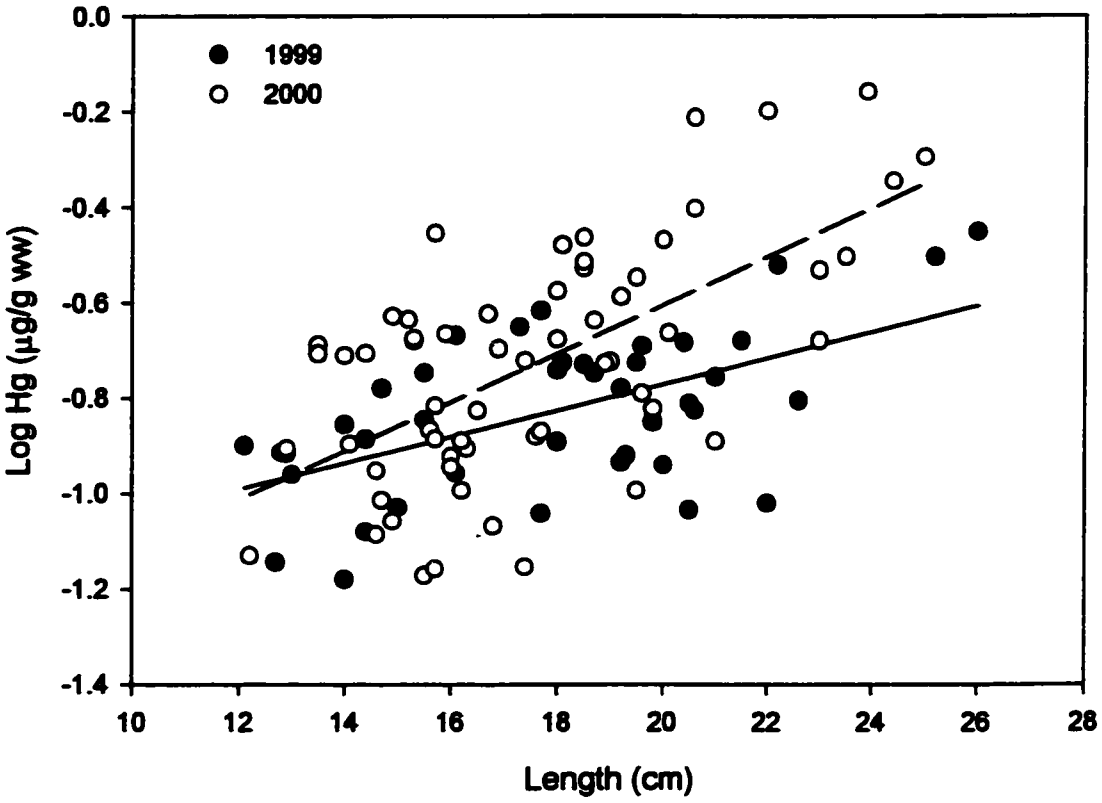

0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
Log Hg (µg/g ww)
1999
2000
10
12
14
16
18
20
22
24
26
28
Length (cm)

Figure 3.10. Regressions of log Hg (μg/g ww) and age (yrs) of yellow perch from Lake St. Francis and nearby tributaries combined in 1999 (n=41, solid line) and 2000 (n=61, dashed line). Error bars not shown for mercury concentrations.

The regression analyses resulted in the following models:

1999 $\log Hg = -1.01(0.05) + 0.06(0.02)age$, $r^2=0.30$, RMS=0.02, $p<0.005$

2000 $\log Hg = -1.10(0.06) + 0.12(0.02)age$, $r^2=0.46$, RMS=0.03, $p<0.005$

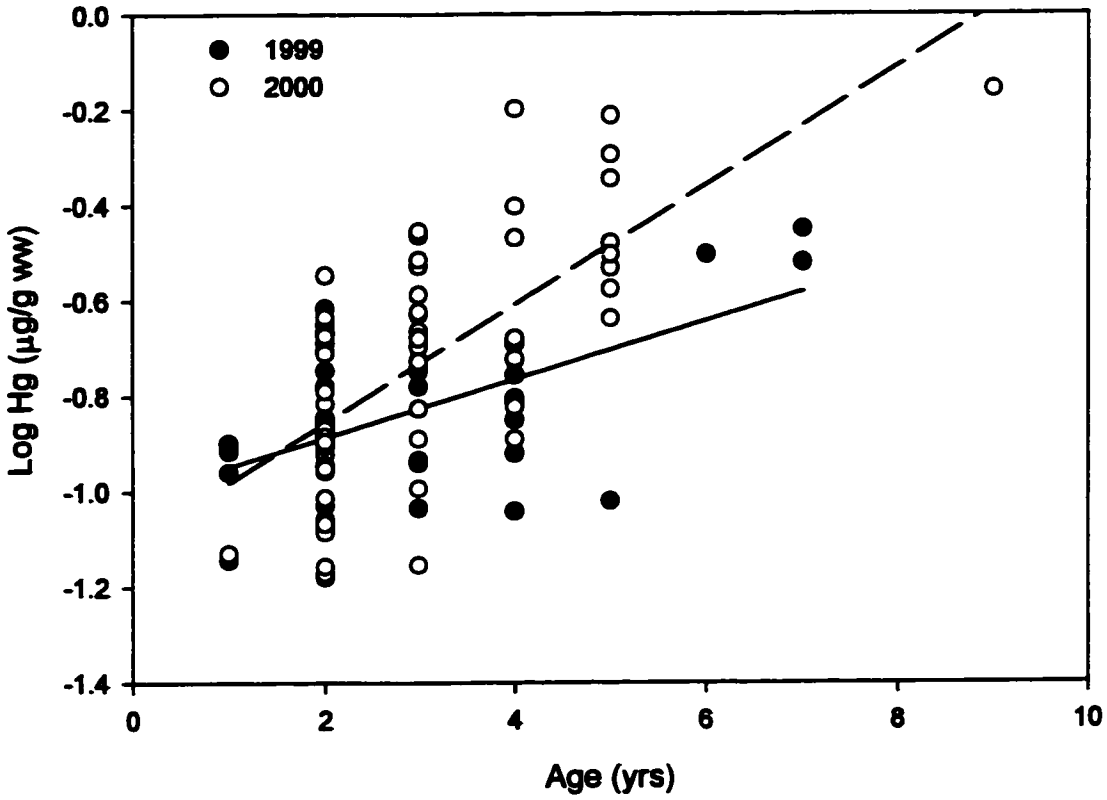

0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
Log Hg (µg/g ww)
1999
2000
0
2
4
6
8
10
Age (yrs)

Figure 3.11. Regression of log Hg (μg/g ww) and weight (g) of yellow perch from Lake St. Francis and nearby tributaries combined (n=102). Error bars not shown for mercury concentrations.

The regression analysis resulted in the following model:

logHg = -0.97(0.03) + 0.003(0.0004)weight, r^2=0.32, RMS=0.04, $p<0.005$

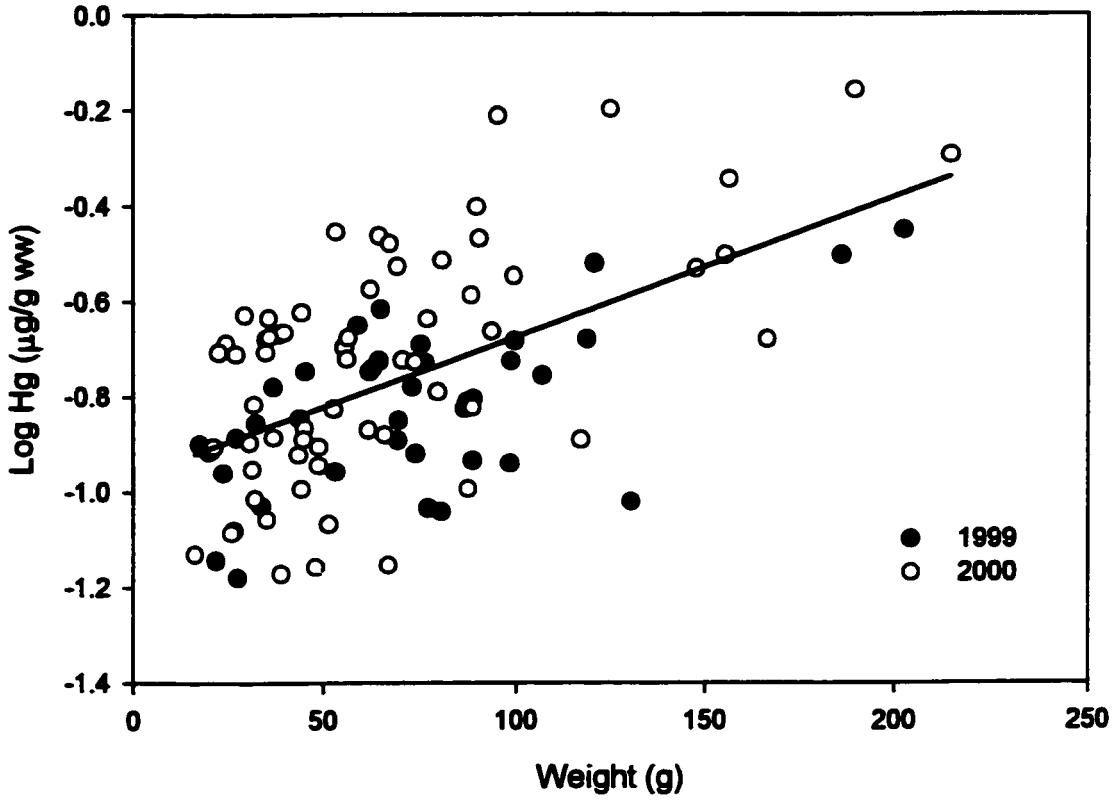
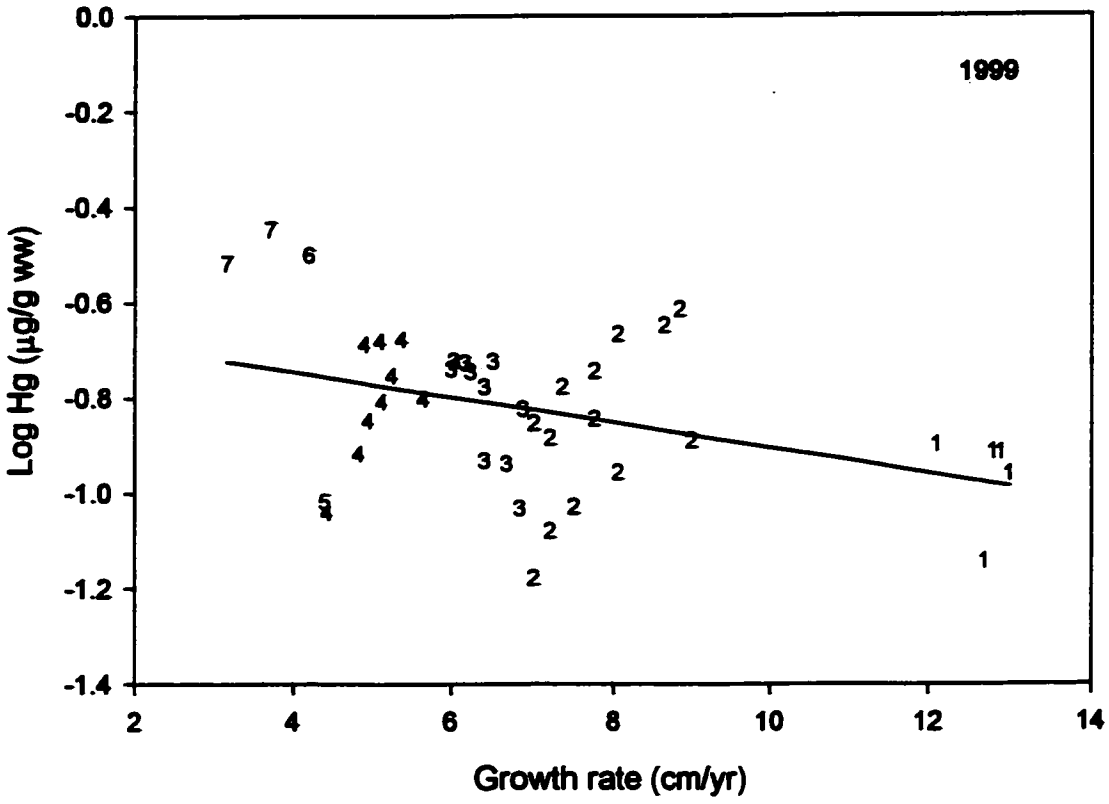

0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
Log Hg (µg/g ww)
0
50
100
150
200
250
Weight (g)
1999
2000

Figure 3.12. Relationship between log Hg (μg/g ww) and growth rate (cm/yr) of yellow perch of different ages (1-9) from Lake St. Francis and nearby tributaries combined in 1999 (n=41) and 2000 (n=61). Symbols represent the age of the fish. Error bars not shown for mercury concentrations.

The regression analyses resulted in the following models:

1999 logHg = -0.64(0.07) - 0.06(0.01)growth rate, r^2=0.16, RMS=0.02, p=0.009

2000 logHg = -0.20(0.10) - 0.08(0.02)growth rate, r^2=0.33, RMS=0.04, p<0.005


1999
Log Hg (µg/g ww)
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
2
4
6
8
10
12
14
Growth rate (cm/yr)

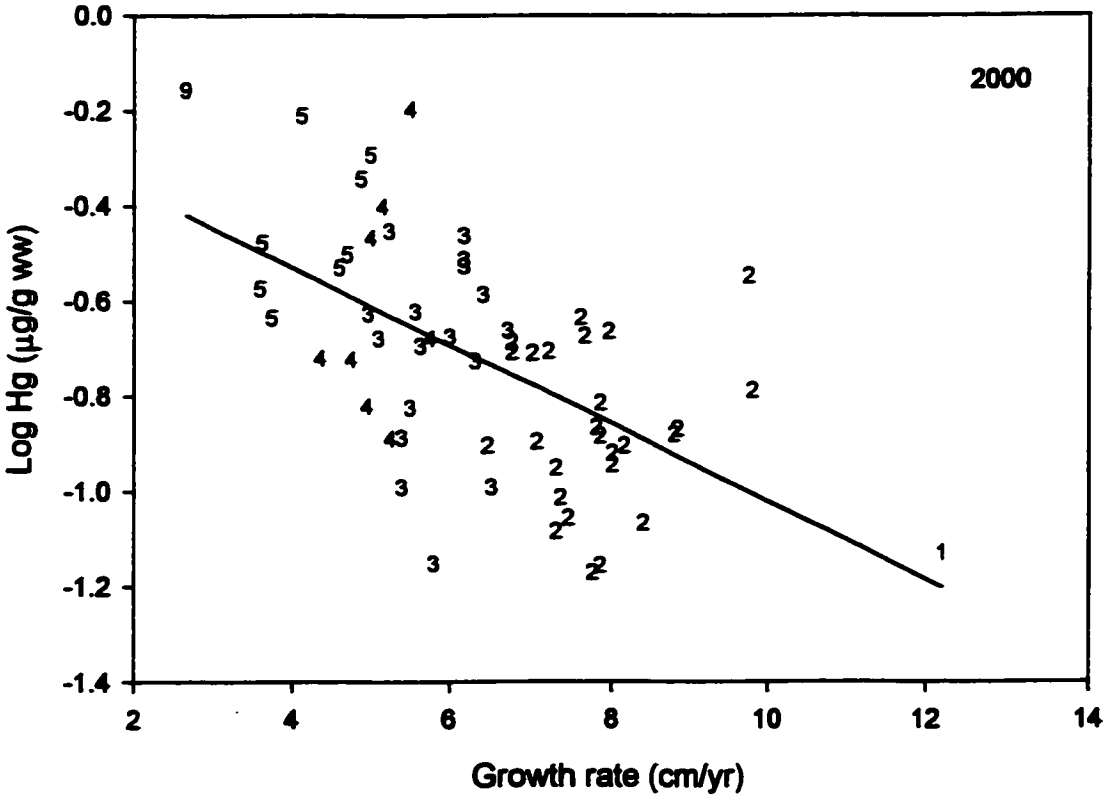
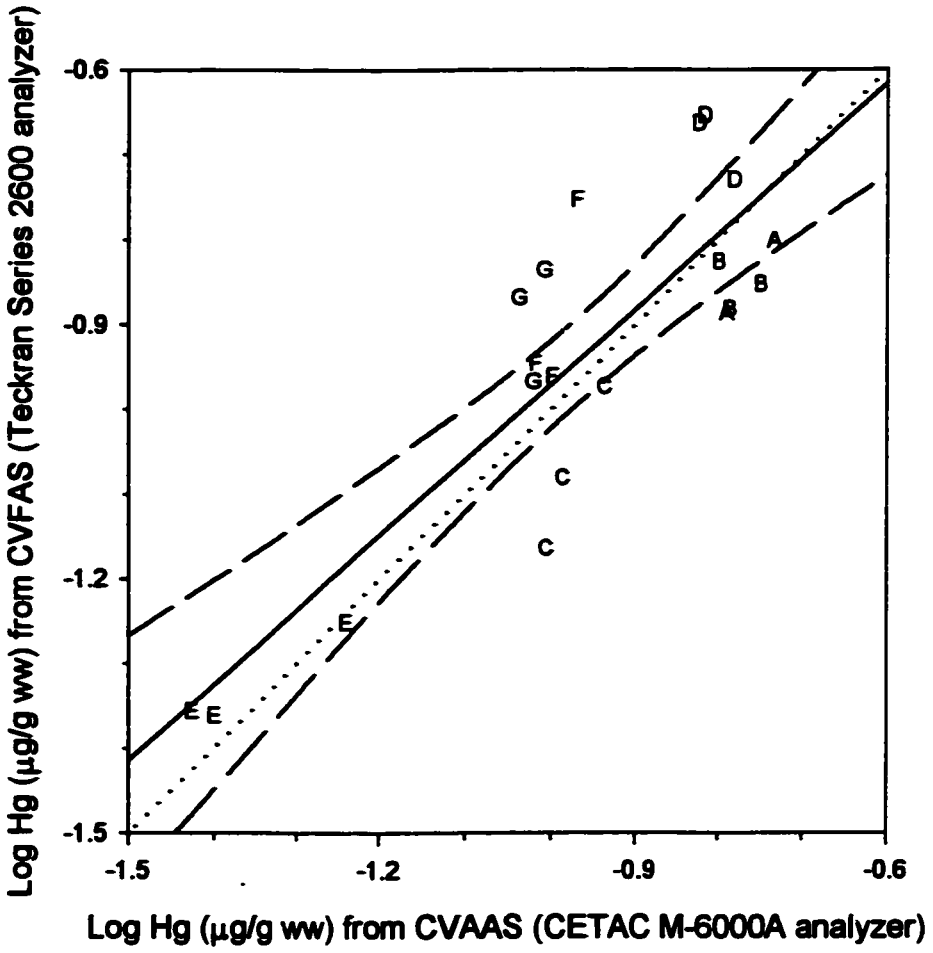

2000
Log Hg (µg/g ww)
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
2
4
6
8
10
12
14
Growth rate (cm/yr)

Figure 3.13. Regression of log Hg (μg/g ww) estimated by cold vapor atomic fluorescence spectrometry (Tekran Series 2600 analyzer) versus log Hg (μg/g ww) estimated by cold vapor atomic absorbance spectrometry (CETAC M-6000A analyzer). Sample size: n=20. The 95% confidence intervals on the regression are shown. The dotted line represents a concentration ratio of 1:1. Letters represent individual fish.

The model II major axis regression analysis resulted in the following model:

$\text{Log Hg}_{\text{Tekran Series 2600}} = 0.069(0.126) + 1.045(0.127) \log \text{Hg}_{\text{CETAC M-6000A}}$, $r^2=0.73$, RMS=0.01, $p<0.005$.


Log Hg (µg/g ww) from CVFAS (Teckran Series 2600 analyzer)
-0.6
-0.9
-1.2
-1.5
-1.5
-1.2
-0.9
-0.6
Log Hg (µg/g ww) from CVAAS (CETAC M-6000A analyzer)

4. DISCUSSION

4.1. Carbon isotopes as tracers of energy sources

There was a significant difference in the isotopic composition of DIC between tributaries and wetlands. This difference was detected using a non-parametric test, conservative in nature, thus supporting the contention that carbon available for photosynthesis was different between tributaries and wetlands. Differences in $\delta^{13}C$ among these systems potentially allows $\delta^{13}C$ to be used to trace carbon sources into the food webs, and different fish that may migrate among systems.

In Lake St. Francis, June values were slightly more depleted in ^{13}C than August values, with respective mean carbon signatures of -1.50‰ and -0.59‰ (Figure 3.1). These values are almost identical to those previously reported by Yang et al. (1996) for the St. Lawrence River near Cornwall (-1.5‰ and -0.4‰ for spring and fall, respectively). They are also in the range of $\delta^{13}C$ values reported by Barth et al. (1998) (-1.8‰ to 0.3‰), and Barth and Veizer (1999) (-1.7‰ to 2.2‰) for Lake St. Francis DIC.

The $\delta^{13}C_{DIC}$ signals in the six sites from Lake St. Francis were very similar to each other, probably reflecting the homogeneity of water originating from Lake Ontario, as previously observed by Yang et al. (1996). The enrichment of carbon signatures has been attributed to the long residence time of Lake Ontario water, thus allowing carbon isotopes in the water to equilibrate with those in the atmosphere (~-7.5 ‰) (Yang et al. 1996). The enrichment of $\delta^{13}C_{DIC}$ in Lake St. Francis from late spring to early summer (Figure 3.1) has also been noted by these authors, and is most probably a result of the preferential uptake of

the lighter ^{12}C isotope during photosynthesis in the Great Lakes during the summer months (Park and Epstein, 1960; Yang et al., 1996).

The $\delta^{13}C_{DIC}$ signals for tributaries and wetlands were also similar to those found in the literature. Carbon signatures of DIC in the Raquette River (means of -10.67‰ and -10.53‰ respectively for June and August, 1999; Figure 3.1.) were very similar to the spring value of -11.1‰ reported in Yang et al. (1996). Mean $\delta^{13}C_{DIC}$ values for Cooper Marsh (-7.15‰ and -10.09‰ respectively for June and August 1999) were in the range of values reported by Barth et al. (1998) from August 1995 to April 1996 (-5.6‰ to -11.3‰).

The $\delta^{13}C$ signals of Lake St. Francis POM measured in this study (from –23.3‰ to -29.18‰) were similar to those reported by Barth et al. (1998) (from -26.3‰ to -30.0‰). As for Cooper Marsh, the $\delta^{13}C_{POM}$ values estimated in this study (-30.54‰ to -34.0‰) were slightly more depleted than those estimated by Barth et al. (1998) (-25.7‰ to -31.4‰). For Cooper Marsh, the wider range in $\delta^{13}C_{POM}$ values from the study by Barth et al. (1998) is likely a result of samples having been collected at different times of the year (August, October, December and April) while only late spring to summer sampling was done here.

The difference in signatures of carbon available for photosynthesis between Lake St. Francis and its tributaries and wetlands was maintained in the primary producers and consumers of these two systems (Figure 3.4). The positive correlations between the carbon signatures of DIC and those of POM and of POM and zooplankton support using $\delta^{13}C$ values to trace energy flow through the tributaries, the wetlands and Lake St. Francis. The lack of significant correlation between $\delta^{13}C$ values of POM and those of benthic invertebrates could likely be due to the low sample size (n=5). POM and zooplankton $\delta^{13}C$ values were

consistently lighter in tributaries than in Lake St. Francis by about 4‰. This trend was not observed in yellow perch from the two systems. However, the difference in $\delta^{13}C$ of benthic invertebrates was much more apparent, and was similar to the range of values reflected in yellow perch from these two systems. This linkage is likely due to benthic invertebrates being important prey items of yellow perch.

Acidification resulted in a depletion of less than 2‰ in $\delta^{13}C$ and $\delta^{15}N$ values of *Gammarus fasciatus* (Table 3.2). In a study conducted by Bunn et al. (1995), acidification did not significantly affect the carbon signatures of seagrass and shrimp tissue samples, however, it decreased the $\delta^{15}N$ of seagrass by approximately 1.8‰, and increased the nitrogen signal of shrimp tissue by approximately 3‰. Since carbon and nitrogen isotopes were affected by acidification, and since the general pattern between tributaries and Lake St. Francis was not changed by the treatment, only non-acidified values were used for comparisons.

In this study, the accuracy of the classification of yellow perch into one group or another was based on the discriminant analysis preformed on the training set. This analysis was conducted on 34 fish caught in the Grass and Raisin Rivers or in Lake St. Francis. The very similar carbon signals of yellow perch to those of benthic invertebrates provides evidence that the classification is a reasonable one.

For analytical purposes, fish were categorized as feeding entirely in tributaries and wetlands or in Lake St. Francis. However, it is probable that fish with $\delta^{13}C$ values near -20.07‰ (the 'cut off' line of the discriminant function) may incorporate carbon from both systems. Nearly 40% of the fish that were caught in, or near, the mouth of tributaries had

carbon signatures representative of fish feeding in Lake St. Francis. This demonstrates the usefulness of carbon isotopes as a tracer of energy source, since fish can incorporate energy from more than one system, and since the location where a fish is caught may not necessarily correspond with where it is feeding.

To summarize this section, significant differences in carbon signatures of DIC were detected between the waters of tributaries and wetlands and Lake St. Francis. These differences were also observed in organisms from the two systems: from POM to consumer organisms such as zooplankton, benthic invertebrates, and fish (Figure 3.4). Stable isotopes of carbon, as tracers of energy source, can be used to differentiate yellow perch feeding in Lake St. Francis from those eating in tributaries and wetlands.

4.2. Nitrogen isotopes as estimates of trophic position

$\delta^{15}N$ is expected to increase if fish move up trophic levels as they grow. This trend is observed in yellow perch from Lake St. Francis, as $\delta^{15}N$ is positively correlated with length, age and weight (Figure 3.5). In tributaries, no relationship was found between nitrogen isotope ratios and either age, weight or total length of yellow perch (Figure 3.5). This relationship between $\delta^{15}N$ and fish attributes (i.e., length, age, weight) was shown to be species specific in a study by Kidd et al. (1995b). These researchers found that length and weight were positively correlated with $\delta^{15}N$ for northern pike, white sucker and yellow perch. Length and age were correlated to $\delta^{15}N$ for lake whitefish (*Coregonus clupeaformis*), while only age was correlated to the $\delta^{15}N$ of lake cisco (*Coregonus artedii*). On the other hand, lake trout, burbot (*Lota lota*) and walleye $\delta^{15}N$ were not correlated with either age, weight or

length measurements.

In the present study, there was no relationship between tributary fish $\delta^{15}N$ values and length, weight, or age. This could be due to the restricted range in size variables in tributary fish, compared to Lake St. Francis fish. Alternatively, it could imply that fish feeding in tributaries do not increase trophic levels as they grow, or that nitrogen composition and/or measures of fish size are not indicators of trophic position in this system. The strong correlation between nitrogen and carbon isotopes in fish from tributaries seems to support the latter explanation that, in this system, nitrogen isotopes are more indicators of energy source than estimates of trophic position.

There was little overlap between nitrogen signatures of fish from tributaries and those from Lake St. Francis. Statistical analyses confirmed that, after correcting for size, there were baseline differences in nitrogen composition of yellow perch between these two systems, and fish from tributaries and wetlands had lighter nitrogen signatures than Lake St. Francis fish. The $\delta^{15}N$ values of other organisms (POM, zooplankton and benthic invertebrates) also showed this trend. The very enriched signal of the leech (12.39‰, Table 3.4) indicated that this organism was feeding on an enriched food source compared to the other invertebrates, and had the $\delta^{15}N$ value of a top predator. It was not determined whether the leech was one feeding on detritus or on blood.

For yellow perch, the strong correlation of $\delta^{15}N$ with carbon isotopes in tributaries, as well as the narrow range of overlapping nitrogen signals between systems could signify that, as fish feed closer to Lake St. Francis, their isotopic signatures become more and more similar to those of Lake St. Francis. This could be tested fairly easily by sampling organisms at

regular distance intervals from far upstream in a tributary, down to where it flows into Lake St. Francis. If $\delta^{15}N$ is an indicator of source, then one would expect carbon and nitrogen isotopes to be more negative in organisms from the farthest locations from Lake St. Francis. The $\delta^{15}N$ values should become progressively more positive as distance to Lake St. Francis decreases, until the $\delta^{15}N$ signatures are equal to those of Lake St. Francis organisms.

A possible explanation for the lighter $\delta^{15}N$ signal in tributaries could include greater nitrogen run-off from agricultural land. The use of fertilizers (depleted in $\delta^{15}N$) in agricultural lands around the Cornwall area may ultimately affect the nitrogen signal of tributaries, as well as species composition (i.e., nitrogen fixers vs non-fixers).

Other researchers have observed baseline differences in $\delta^{15}N$ among systems (Estep and Vigg, 1985; Kling et al., 1992; Kidd et al., 1995b; Cabana and Rasmussen, 1996; Vander Zanden et al., 1997; Vander Zanden and Rasmussen, 1999). In order to make among-system comparisons when basal $\delta^{15}N$ values differ, a correction for this baseline difference (involving the adjustment of $\delta^{15}N$ relative to long-lived primary consumers such as unionid mussels) has been proposed by Cabana and Rasmussen (1996). The validity of this correction method has been tested and confirmed by Vander Zanden et al. (1997). Unfortunately, neither unionid mussels nor other long-lived primary consumers were found in this study. Benthic invertebrates were collected at only three sampling sites, and primary consumers from every sampling location were needed in order to standardize the $\delta^{15}N$ signals adequately. One might attempt to use primary producers to standardize $\delta^{15}N$ values between systems, however, this would not be a good choice, as large temporal and spatial variability can be observed in the $\delta^{15}N$ of POM and zooplankton samples (which may include plant material).

Knowledge of basal differences in $\delta^{15}N$ existing between Lake St. Francis and surrounding tributaries should help with the experimental design of future studies. After correcting for baseline differences in $\delta^{15}N$, nitrogen isotopes might then become better estimates of trophic positioning in fish from tributaries. Comparisons of fish $\delta^{15}N$ values between tributaries and Lake St. Francis might then become possible.

4.3. Mercury accumulation with $\delta^{15}N$

A comparison of mercury accumulation between tributaries and wetlands and Lake St. Francis was not possible using $\delta^{15}N$ as an estimate of trophic position. Baseline differences in $\delta^{15}N$ existed between the two systems, and this variable seemed to be an indicator of trophic position in fish from Lake St. Francis only. This observation was reinforced even further by the lack of relationship between $\delta^{15}N$ and log Hg in yellow perch from tributaries. As for Lake St. Francis fish, which had positively correlated $\delta^{15}N$ and size variables, a significant positive relationship between $\delta^{15}N$ and log Hg was observed (Figure 3.8).

In Lake St. Francis, mercury accumulated differently with $\delta^{15}N$ between sampling years. For fish caught during the 2000 sampling season, the relationship between log Hg and $\delta^{15}N$ had a slope of 0.35, indicating that from one trophic position to the next (i.e., for every increase of 3.4‰, Minigawa and Wada, 1984) mercury levels increase by a factor of 15.5 times. The slope of 0.35 was similar to those reported in several other studies of various food webs. In a study conducted by Jarman et al. (1996) in a marine food web from the Gulf of the Farallones, the slope of the relationship between log Hg and $\delta^{15}N$ was 0.32. The slope observed here was slightly higher than the slope of 0.15 obtained by Kidd et al. (1995b) for

the relationship between log Hg and $\delta^{15}N$ in yellow perch from northwestern Ontario lakes. However, a slope of 0.35 is in the range of slopes (0.17 to 0.48) of relationships encompassing a variety of fish species from these lakes (Kidd et al., 1995b). A slope of 0.2 was obtained for the accumulation of log Hg with $\delta^{15}N$ in marine organisms from the North West Territories (Atwell et al., 1998). Also, a slope of 0.205 was obtained by Yoshinaga et al. (1992) for the relationship between log Hg and $\delta^{15}N$ values in a food web in Papua, New Guinea.

The lack of significant relationship between log Hg and $\delta^{15}N$ in fish caught in 1999 could be due to the small range in $\delta^{15}N$, not spanning the estimated 3.4‰ between one trophic level and the next (e.g., DeNiro and Epstein, 1981; Minigawa and Wada, 1984; Peterson and Fry, 1987). Only a few fish with more enriched $\delta^{15}N$ were influencing the relationship in the year 2000. Future studies encompassing a greater range of nitrogen signatures, possibly by including other fish species, could provide a better estimate of the relationship between mercury and nitrogen isotopes in fish from Lake St. Francis.

4.4. Mercury accumulation with size variables

As the relationships of log Hg and $\delta^{15}N$ could not be compared between systems, the accumulation of mercury with size variables served as a substitute. Since yellow perch from this study had a very small range in $\delta^{15}N$ to begin with, length, age or weight are probably equivalent, or better, estimates of the trophic level of these fish, as seen in numerous studies (Driscoll et al., 1995; Ion et al., 1997; Lalonde, 1998). In fact, when both $\delta^{15}N$ and either of the three size variables were simultaneously put in a regression analysis, the term $\delta^{15}N$ always

became non-significant. This is probably due to size variables and $\delta^{15}N$ being correlated. All of the variability in mercury concentrations explained by $\delta^{15}N$ was explained by variations in fish size. The term $\delta^{15}N$ dropping out of the model indicates that size variables are better predictors of mercury concentrations in yellow perch than nitrogen isotopes, and $\delta^{15}N$ is not a consistent indicator of trophic position.

Mercury accumulated positively with fish length, age and weight (Figures 3.9, 3.10, 3.11). Lalonde (1998) found a positive relationship between mercury concentrations and fish length for several species of the St. Lawrence River, from Thousand Islands to Lake St. Francis. For a section of the St. Lawrence River from Lake St. Francis to Lake St. Pierre, Ion et al. (1997) observed a significant positive relationship between mercury concentrations and age of yellow perch, but not with weight or length. In another study, Driscoll et al. (1995) found that all three variables (age, length and weight) were positively related to mercury levels in yellow perch from Adirondack lakes.

Mercury levels in fish reported here were somewhat higher than those presented in other studies conducted in Lake St. Francis. Overall, yellow perch from this study had mercury concentrations averaging 0.20 ± 0.12 μg/g ww, and ranged from 0.07 to 0.70 μg/g ww (Table 3.4). Only four fish (less than 5% of fish caught) had mercury levels that exceeded the 0.5 μg/g ww Canadian consumption guideline (Health and Welfare Canada, 1990). Lalonde (1998) reported levels ranging from 0.09 to 0.32 μg/g ww from 1991 to 1995, while values ranging from 0.06 to 0.24 μg/g ww were detected by Ion et al. (1997) in Lake St. Francis yellow perch. This last study only had a sample size of ten fish from Lake St. Francis. The range in mercury concentration increases from 0.05 to 0.44 μg/g ww when yellow perch

from Lake St. Francis to Lake St. Pierre are combined. Sample size then increases to 50 yellow perch (Ion et al., 1997).

The range in fish lengths were also different among these studies. Yellow perch sampled here ranged from 12.1 to 26.0 cm (Table 3.4), and included fish that are much smaller than those in the studies of Lalonde (1998) (size range: 18.1 to 31.5 cm) and Ion et al. (1997) (size range: 21.5 to 25.8 cm). The average age of all yellow perch from this study was 3.0 ± 0.1 years (range: 1-9 years). Yellow perch in the study conducted by Ion et al. (1997) were 4.7 ± 0.1 years old (range: 4-8 years). Lalonde (1998) did not have age measurements for the fish in her study.

I predicted that the intercept of the relationship between mercury accumulation and size (or estimate of trophic level) of fish from tributaries would be greater than the one for fish from Lake St. Francis (i.e., for a given size or trophic level, tributary fish would be more contaminated in mercury than Lake St. Francis fish). However, the slopes and the intercepts of the relationships between the two systems were not significantly different. For a given length or trophic position, there was no difference in log Hg between fish from Lake St. Francis and fish from tributaries and wetlands.

This lack of difference may be due to other variables obscuring the relationship. Perhaps feeding behaviours of some fish differ within systems, and therefore the prediction would hold for some fish but not others. There were also significant differences in the accumulation of mercury between years. However, after accounting for variation caused by differences in sampling year, there was still no difference in log Hg of yellow perch between the two systems. This indicates that the effects of year were not obscuring the relationship

between tributaries and Lake St. Francis. Lalonde (1998) also found that the relationship between mercury levels and length varied with the year of sampling for fish caught in the St. Lawrence River. The difference in mercury accumulation between years could not be due to an effect of mercury analyzers. At most, the average mercury concentrations for a given fish deviated from the 1:1 ratio line by 0.12 log units (Figure 3.13). The differences in slopes of the log Hg versus length or age relationships were larger, differing on average by approximately 0.2 log units (Figures 3.8 and 3.9).

The potential effect of other variables such as sex and growth rate were investigated. No difference in mercury accumulation between sexes was observed. Differences in growth rates (Figure 3.12) show that mercury concentrations are higher in organisms that grow more slowly (Lindqvist et al., 1991; Driscoll et al., 1995). Younger fish tend to grow faster. Mercury is diluted into the tissues of fast growing fish, as uptake of mercury is slower than the rate of tissue formation. However, in this study, statistical analyses show that fish from both systems grow at the same rate. Therefore, this variable could not be obscuring a potential relationship between tributary fish and Lake St. Francis fish.

The assumption that methylation rates are greater in tributaries, and the resulting prediction that higher mercury levels would be observed in tributary fish compared to Lake St. Francis fish, must be rejected. Methylation rates in tributaries and wetlands versus Lake St. Francis can not be measured using present technology, although methylmercury and total mercury levels are higher in tributaries and wetlands (Lean and Holmes, 2000; Holmes, unpublished). The amount of bioavailable mercury seems to be similar in both systems. Results from this study seem to show that yellow perch accumulate the same amount of

mercury regardless of where they are feeding.

4.5. Mercury accumulation with other variables

Length, age or weight explained approximately 30 to 40% of the variability in log Hg of yellow perch. However, a large portion of the variability in mercury remains unexplained. The variation in the log Hg versus length relationship (approximately 0.8 log units, Figure 3.9) is consistent with the scatter observed in Lalonde (1998) for the relationship between log Hg and log length of yellow perch. The cause of the large variation in mercury levels within age classes doesn't seem to be related to the growth rate of individual fish, as fish from a given age class had very similar growth rates (Figure 3.12). One explanation for the variability in mercury is that fish are feeding on prey with highly variable mercury levels. Previous studies investigating mercury levels in littoral sediments and macroinvertebrates from Lake St. Francis have found that levels of mercury do vary within Lake St. Francis. Contaminated sediments and invertebrates were often associated to areas affected by local sources of mercury, as well as with higher proportions of organic matter and of silt and clay (Filion and Morin, 2000). This heterogeneity in the mercury levels of prey could possibly be a cause for the high autocorrelation (i.e., the violation of the assumption of independence of residuals) of the General Linear Models in Lake St. Francis fish.

4.6. Future studies

Future studies investigating the cause of the large variation in mercury concentrations for a given length, age, or weight of fish could give us a better idea of the factors regulating

mercury accumulation in fish from Lake St. Francis and its surrounding tributaries and wetlands. In addition, a study could be conducted to correct for the between-system variation in nitrogen isotopes at the base of the food web. Sampling primary consumers along a distance gradient from inside tributaries and wetlands to Lake St. Francis could allow for this correction between systems. Then, a comparison of fish from tributaries and wetlands and Lake St. Francis using $\delta^{15}N$ could be feasible.

Incorporating other species of fish in future studies from Lake St. Francis would increase the range in $\delta^{15}N$ and provide a better estimate of the relationship between trophic position and mercury accumulation in fish from this system. Mercury measurements in prey items such as benthic invertebrates could provide further information on the bioaccumulation of mercury in the food webs of the Lake St. Francis area. Finally, direct measures of mercury methylation would be needed in order to test the assumption that rates of methylation are higher in tributaries and wetlands than in Lake St. Francis.

5. CONCLUSIONS

Stable isotopes of carbon can be used as tracers of energy sources for organisms in Lake St. Francis and its surrounding tributaries and coastal wetlands. The carbon signatures of DIC and of organisms such as POM, zooplankton, benthic invertebrates and yellow perch that derive energy from Lake St. Francis were enriched compared to those assimilating carbon from tributaries.

Although restricted in range, nitrogen isotopes seemed to be estimates of trophic position in Lake St. Francis. However, in tributaries, the lack of correlation between size variables and nitrogen signatures, as well as the strong correlation between $\delta^{15}N$ and $\delta^{13}C$ seem to indicate that nitrogen isotopes are indicators of source, rather than trophic level in this system. This difference in function, as well as the observation of baseline differences in $\delta^{15}N$ between both systems, prevented the use of $\delta^{15}N$ to compare mercury accumulation in fish from the two systems. In Lake St. Francis, log Hg in yellow perch increased with $\delta^{15}N$ for the 2000 sampling season, but the relationship was not significant for the 1999 sampling season, possibly because of the narrow range in $\delta^{15}N$ for that year.

Log Hg accumulated positively with length, age and weight of yellow perch, but differences in the accumulation of mercury with length and age were observed between sampling seasons. Contrary to my original prediction, for a given size or estimate of trophic level, mercury concentrations in yellow perch feeding in Lake St. Francis were equal to those measured in fish deriving energy from tributaries and wetlands. Direct measures of mercury methylation would be needed to test the assumption that methylmercury production is greater

in tributaries and wetlands than in Lake St. Francis.

Large variability in mercury concentrations was observed, indicating that variables other than size are affecting mercury levels in yellow perch. One possible explanation for this variability could be the heterogeneity of mercury levels in the prey of yellow perch, the variability of which have been previously established in Lake St. Francis.

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APPENDIX A

Sampling location, date of collection, total length (cm), weight (g), age (yrs), and sex of individual yellow perch. Fish in bold were used in a discriminant function analysis to classify fish into tributaries or Lake St. Francis based on their carbon signatures.

Fish	Sampling location	Date	Total length (cm)	Weight (cm)	Age (yrs)	Sex
1	Cooper Marsh canal	08/28/99	12.7	22.23	1	F
2	Cooper Marsh canal	08/28/99	12.8	20.78	1	M
3	Cooper Marsh canal	08/28/99	12.1	17.76	1	F
4	Cooper Marsh canal	08/28/99	14.0	27.87	2	F
5	Cooper Marsh canal	08/28/99	19.2	72.89	3	F
6	Cooper Marsh canal	08/28/99	12.9	20.20	1	F
7	Cooper Marsh canal	08/28/99	19.2	88.63	3	F
8	Cooper Marsh canal entrance	08/28/99	13.0	24.06	1	M
9	Cooper Marsh canal entrance	08/28/99	20.4	99.57	4	M
10	Cooper Marsh canal entrance	08/28/99	14.7	37.19	2	M
11	Cooper Marsh canal entrance	08/28/99	15.5	44.00	2	M
12	Cooper Marsh canal entrance	08/28/99	17.7	80.37	4	M
13	Cooper Marsh canal entrance	08/28/99	21.0	106.95	4	M
14	Lake St. Francis 8	08/28/99	14.0	32.63	2	F

Fish	Sampling location	Date	Total length (cm)	Weight (cm)	Age (yrs)	Sex
15	Lake St. Francis 7	09/17/99	16.1	38.69	2	F
16	Raquette River 2	09/28/99	20.5	76.98	3	F
17	Raquette River 2	09/28/99	22.0	130.48	5	F
18	Raquette River 2	09/28/99	22.6	88.78	4	F
19	Raquette River 2	09/28/99	19.3	73.79	4	F
20	Raquette River 2	09/28/99	26.0	202.46	7	M
21	St. Regis River 2	09/28/99	19.8	69.31	4	F
22	St. Regis River 2	09/28/99	20.5	87.15	4	M
23	St. Regis River 2	09/28/99	22.2	120.61	7	M
24	St. Regis River 2	09/28/99	20.6	86.33	3	F
25	St. Regis River 2	09/28/99	25.2	186.29	6	F
26	St. Regis River 2	09/28/99	19.6	75.06	4	F
27	Grass River 1	09/28/99	15.0	34.10	2	F
28	Grass River 1	09/28/99	18.1	64.28	3	F
29	Grass River 1	09/28/99	14.4	27.52	2	M
30	Grass River 1	09/28/99	14.4	26.97	2	F
31	Grass River 1	09/28/99	18.7	61.90	3	F
32	Lake St. Francis 14	09/28/99	18.5	76.17	3	F
33	Lake St. Francis 14	09/28/99	17.7	64.73	2	F
34	Lake St. Francis 14	09/28/99	20.0	98.48	3	M
35	Lake St. Francis 14	09/28/99	16.1	53.08	2	F
36	Lake St. Francis 14	09/28/99	17.3	58.80	2	M
37	Lake St. Francis 14	09/28/99	15.5	45.41	2	F
38	Lake St. Francis 14	09/28/99	18.0	69.24	2	F
39	Lake St. Francis 14	09/28/99	18.0	62.55	3	M

Fish	Sampling location	Date	Total length (cm)	Weight (cm)	Age (yrs)	Sex
40	Lake St. Francis 14	09/28/99	19.5	98.68	3	F
41	Lake St. Francis 14	09/28/99	21.5	118.74	4	F
42	Cooper Marsh canal	08/09/00	15.6	45.25	2	F
43	Cooper Marsh canal	08/09/00	17.4	66.70	3	F
44	Cooper Marsh canal	08/09/00	24.4	156.29	5	F
45	Cooper Marsh canal	08/09/00	12.2	16.52	1	F
46	Cooper Marsh canal	08/09/00	15.5	39.19	2	F
47	Cooper Marsh canal	08/09/00	19.5	87.39	3	F
48	Cooper Marsh canal	08/09/00	17.7	61.54	2	F
49	Cooper Marsh canal	08/09/00	16.0	43.65	2	F
50	Cooper Marsh canal entrance	07/19/00	17.6	65.80	2	F
51	Cooper Marsh canal entrance	08/09/00	16.2	44.40	3	M
52	Raisin River 2	08/22/00	20.1	93.56	3	F
53	Raquette River 2	09/20/00	16.8	51.48	2	F
54	Raquette River 2	09/20/00	19.8	88.51	4	F
55	Raquette River 2	09/20/00	19.6	79.44	2	F
56	Raquette River 2	09/20/00	13.5	24.86	2	F
57	Raquette River 2	09/20/00	13.5	22.97	2	F
58	Raquette River 2	09/20/00	19.5	99.37	2	M
59	Raquette River 2	09/20/00	15.3	35.38	3	M
60	Raquette River 2	09/20/00	15.9	39.96	2	M
61	Raquette River 2	09/20/00	14.9	29.73	3	F
62	Raquette River 2	09/20/00	17.4	56.04	4	F
63	Raquette River 2	09/20/00	12.9	21.62	2	M

Fish	Sampling location	Date	Total length (cm)	Weight (cm)	Age (yrs)	Sex
64	St. Regis River 2	09/20/00	14.9	35.55	2	F
65	St. Regis River 2	09/20/00	16.2	44.97	3	F
66	St. Regis River 2	09/20/00	15.7	32.08	2	M
67	St. Regis River 2	09/20/00	14.6	26.26	2	M
68	St. Regis River 2	09/20/00	15.2	36.02	2	F
69	St. Regis River 2	09/20/00	14.7	32.34	2	F
70	St. Regis River 2	09/20/00	18.5	69.05	3	F
71	St. Regis River 2	09/20/00	18.0	56.34	3	F
72	St. Regis River 2	09/20/00	18.5	64.15	3	F
73	St. Regis River 2	09/20/00	19.0	70.41	4	F
74	Grass River 2	09/20/00	16.7	44.43	3	F
75	Grass River 2	09/20/00	18.1	67.01	5	F
76	Grass River 2	09/20/00	15.7	37.31	2	M
77	Grass River 2	09/20/00	14.4	35.28	2	F
78	Grass River 2	09/20/00	18.0	62.03	5	M
79	Grass River 2	09/20/00	14.0	27.41	2	M
80	Grass River 2	09/20/00	14.1	31.04	2	M
81	Grass River 2	09/20/00	15.3	36.18	2	M
82	Grass River 2	09/20/00	14.6	31.69	2	F
83	Grass River 2	09/20/00	18.7	76.78	5	F
84	Lake St. Francis 14	07/25/00	16.0	48.80	2	F
85	Lake St. Francis 14	07/25/00	15.7	48.01	2	F
86	Lake St. Francis 14	07/25/00	21.0	117.10	4	F
87	Lake St. Francis 14	07/25/00	16.5	52.56	3	F
88	Lake St. Francis 14	07/25/00	16.9	55.46	3	F

Fish	Sampling location	Date	Total length (cm)	Weight (cm)	Age (yrs)	Sex
89	Lake St. Francis 14	07/25/00	16.3	48.85	2	M
90	Lake St. Francis 12	09/23/00	20.6	89.63	4	F
91	Lake St. Francis 11	09/23/00	18.9	73.60	3	F
92	Lake St. Francis 11	09/23/00	23.9	189.69	9	M
93	Lake St. Francis 13	09/23/00	22.0	124.80	4	F
94	Lake St. Francis 13	09/23/00	20.6	95.11	5	F
95	Lake St. Francis 13	09/23/00	20.0	90.30	4	F
96	Lake St. Francis 13	09/23/00	25.0	214.30	5	F
97	Lake St. Francis 9	09/23/00	15.7	53.23	3	F
98	Lake St. Francis 9	09/23/00	18.5	80.52	3	F
99	Lake St. Francis 9	09/23/00	19.2	88.25	3	F
100	Lake St. Francis 10	09/23/00	23.0	147.71	5	F
101	Lake St. Francis 10	09/23/00	23.5	155.25	5	F
102	Lake St. Francis 10	09/23/00	23.0	166.49	4	F

APPENDIX B

Results of the principal component analysis for variables length (cm), weight (g), and age (yrs) of yellow perch (n=102). The correlation matrix was used since variables are not on the same scale.

	Factor		
	1	2	3
Latent Roots (Eigenvalues)	2.733	0.216	0.051
Component loadings			
Length	0.971	0.175	-0.161
Weight	0.969	0.191	0.157
Age	0.923	-0.386	0.005
Variance explained by components			
	2.733	0.216	0.051
Percent of total variance explained	91.11	7.20	1.69