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Mercury in Fish from the Upper St. Lawrence River:
Temporal and Spatial variability and Safe Consumption Rate

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ABSTRACT

Mercury (Hg) levels in fish from the lower Thousand Islands to the Lake St. Francis region of the St. Lawrence River were analyzed over a 20 year period (from 1975 to 1995) by the Ontario Ministry of Natural Resources and the Ontario Ministry of the Environment as part of the Sport Fish Contaminant Monitoring Program. A general linear model was used to extract temporal trends and spatial variability while correcting the data for fish length. The analysis was done on four species of fish: white sucker (*Catostomus commersoni* [Lacepède]) an obligate benthivore, yellow perch (*Perca flavescens* [Mitchill]) an omnivore, and two piscivores, northern pike (*Esox lucius* Linnaeus) and walleye (*Stizostedion vitreum* [Mitchill]).

Over time, Hg concentrations declined in white sucker, yellow perch, walleye and northern pike at all stations. The only exceptions were for northern pike of the Brockville and Lake St. Lawrence sectors. The decrease of Hg concentration was most rapid for lower trophic level fish (white sucker and yellow perch) compared to the higher trophic level fish (northern pike and walleye). This suggests that lower trophic level fish respond faster to changes in their environment. Using recent data (from 1990 to 1995), no one region was found to contain systematically higher Hg concentrations for all fish species. This result is surprising since in 1985, the International Joint Commission designated one of the studied regions, Lake St. Francis, as an Area of Concern due to high levels of Hg in the nearby sediments.

Fish consumption is the major exposure pathway of Hg to humans. Using current Hg levels, I calculated the safe fish consumption rate. These calculations were based on three reference doses stating the maximum daily exposure of Hg per unit mass of individuals. The first one is the Canadian reference dose developed in 1972 by the Joint Food and Agriculture

Organization/ World Health Organization Expert Committee on Food Additives (JECFA; 0.47 $\mu\text{g}/\text{Kg}/\text{day}$), the second was proposed in 1997 by the United States Environmental Protection Agency (U.S. EPA; 0.10 $\mu\text{g}/\text{Kg}/\text{day}$) and the last one was recently proposed by Health Canada as a provisional Tolerable Daily Intake (0.20 $\mu\text{g}/\text{Kg}/\text{day}$) for children and women of child bearing age.

To minimize Hg exposure, the safest eating pattern is to eat smaller, lower trophic level fish because Hg concentration increases with the size and the trophic level of the fish. In the worst case scenario, one meal of fish/month can be eaten using the Canadian reference dose, one meal per two months using the provisional Tolerable Daily Intake developed by Health Canada and less than one meal per 3 months when the U.S. EPA reference dose is used. If put forward, the last two reference doses would require a serious modification of existing fish eating habits.

RÉSUMÉ

Dans le cadre du programme de surveillance du poisson gibier, le Ministère de l'Environnement de l'Ontario ainsi que le Ministère des Ressources Naturelles de l'Ontario ont mesurés les teneurs en mercure (Hg) de poissons provenant du fleuve Saint-Laurent, des Miles-Îles au lac Saint-François, durant les 20 dernières années (de 1975 à 1995). J'ai déterminé les tendances temporelles et les variations spatiales des concentrations de Hg des poissons à l'aide d'un modèle statistique général linéaire. Celui-ci permet de comparer les concentrations de Hg dans le temps (années) et dans l'espace (régions) en les corrigeant pour la longueur du poisson. Quatre espèces de poissons ont été analysées: le meunier noir (*Catostomus commersoni* [Lacepède]) un benthivore obligatoire, la perchaude (*Perca flavescens* [Mitchill]) un omnivore, ainsi que deux piscivores, le grand brochet (*Esox lucius* Linneaus) et le doré jaune (*Stizostedion vitreum* [Mitchill]).

J'ai observé que les concentrations en Hg ont diminué au cours des 20 dernières années chez les meuniers noirs, les perchaudes, dorés jaunes et chez les grands brochets. Deux exceptions à cette diminution généralisée ont été notées, les grands brochets de la région de Brockville et du lac Saint-Laurent. Le rythme de diminution était plus rapide chez les espèces appartenant aux échelons de base de la chaîne trophique (meunier noir et perchaude) comparativement à celles appartenant aux échelons plus élevés (doré jaune et grand brochet). Cette observation suggère que les espèces plus près de la base de la chaîne trophique sont plus sensibles aux changements de leur environnement. Aucune région ne contenait des concentrations plus élevées en Hg pour l'ensemble des espèces de poissons si l'on tient compte des données récentes (de 1990 à 1995). Ce résultat est surprenant car la région du lac Saint-

François a été désignée en 1985 comme étant à risque par la Commission Internationale Mixte due à la présence d'une contamination élevée en Hg dans les sédiments.

L'exposition des humains au Hg se fait principalement par la consommation de poissons. J'ai estimé le rythme de consommation de poisson qui n'expose pas les consommateurs d'une manière nocive au Hg. Ce calcul a été fait à l'aide de trois doses de référence qui dictent l'exposition journalière maximum au Hg par unité de poids corporel. La dose de référence canadienne a été émise en 1972 par le Joint Food and Agriculture Organization/ World Health Organization Expert Committee on Food Additives (JECFA; $0.47 \mu\text{g}/\text{Kg}/\text{jour}$), la deuxième a été proposée en 1997 par le United States Environmental Protection Act (U.S. EPA; $0.10 \mu\text{g}/\text{Kg}/\text{jour}$) et la troisième est une dose de référence provisoire récemment émise par Santé Canada pour les enfants et les femmes en âge de procréer ($0.20 \mu\text{g}/\text{Kg}/\text{jour}$).

Pour minimiser l'exposition au Hg, il est préférable de consommer des repas de poissons ayant une petite taille et appartenant au bas de la chaîne trophique étant donné que les concentrations en Hg augmentent avec la taille et le niveau trophique de ceux-ci. La dose de référence canadienne permet la consommation d'un repas de poisson par mois. Celle de Santé Canada suggère un repas à tout les deux mois alors que la dose de référence proposée par le U.S. EPA suggère un repas à tout les trois mois. Ces faibles rythmes de consommation entraîneraient d'importantes modifications dans le régime alimentaire.

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CHAPTER 1

GENERAL INTRODUCTION

Mercury (Hg) is one of the most toxic and dynamic metals in the environment. It is found naturally in soil, bedrock, atmosphere, fresh water and marine water systems (Nriagu 1979). Such a widespread presence is possible because it occurs in inorganic and organic compounds, in solid, dissolved, liquid and gaseous phase (Matheson 1979). In all of these forms, it is the methylated form of Hg (organic Hg) that is accumulated by living organisms, and therefore the most toxic. It should be noted that many of the chemical forms of Hg could be converted to other forms by chemical or biological reactions (Jonassen and Boyle 1972). Therefore, no form of Hg can be considered environmentally benign.

In the following chapter, I will review the biogeochemistry cycle of Hg in fresh water ecosystems (Figure 1), the way Hg accumulates in fish and how it affects human health. In chapter two, the temporal and spatial variability of Hg concentration in fish caught in the Ontario portion of the St. Lawrence River will be analyzed. In chapter three, current Hg levels in the studied area of the St. Lawrence River will be used to calculate a 'safe' fish consumption rate for humans. The last chapter includes the general conclusions of the thesis.

1.1. MERCURY IN THE ENVIRONMENT

The distribution of inorganic and methylated Hg compounds reflects their affinity for inorganic, organic and biotic matter (Meili 1997). A high proportion of the inorganic

Hg is found in the sediments while only a fraction is found in the water (approximately 5%), for the most part combined with dissolved organic carbon but also found as a dissolved ionic state, while approximately 1% is found in the biota (Meili 1997). In contrast, similar amounts of methyl-Hg are found in the biota, in the water and in the sediments.

The major sources of total Hg for surface waters are from direct wet and dry depositions in the water and from watershed runoffs (Mierle 1990). The remaining import (30%) of exogenous Hg was thought to come from the minerals and the organic matter of the soil (Mierle 1990). The mobilization of Hg from the soil was explained later by its strong affinity to humic substances (a constituent of dissolved organic matter) (Mierle and Ingram 1991; St. Louis et al. 1994). In a polluted Swedish region, Lee and Hultberg (1990) calculated that enough methyl-Hg was deposited directly into the lake and indirectly (deposition into the watershed) to induce high levels of Hg in the entire biota. However, in near-pristine boreal lakes, St. Louis et al. (1994) found that wetlands were the major sources of methyl-Hg compared to precipitation while the converse was true for total Hg.

The sediments are also a potential source of Hg. Inorganic Hg can be liberated from the oxidation of the cinnabar (HgS) found in the sediments (Björnberg et al. 1988). This process occurs mainly in well-oxygenated conditions with low hydrogen sulfide (H_2S) concentration (Björnberg et al. 1988). The resulting Hg^{2+} is made available for methylation by bacteria found in the water column (Furutani and Rudd 1980) or in the sediments (Jensen and Jernelöv 1969) and adds to the Hg burden.

The net production of methyl-Hg in water is given by the methylation of Hg minus its demethylation (Ramsey 1991). Both antagonistic processes are mainly controlled by microorganisms through direct methylation of Hg or indirectly by their products (Meili 1997). Different species and strains of free-living bacteria and fungi ranging from anaerobes to aerobes mediate the methylation reaction (Jensen and Jernelöv 1969). Methylation is usually accomplished with or without the help of enzymes whereby methyl groups are added to inorganic Hg by a common coenzyme (methylated cobalamin or vitamin B₁₂; Choi et al. 1994). In addition, the by-products of microbial decomposition (humic matter, acetate, methyl Sn, and H₂S) were observed to both enhance and inhibit the methylation reaction (Jackson 1989). Also, Sellers et al. (1996) observed the degradation of methyl-Hg by ultra-violet radiation.

Mechanisms also exist to remove Hg from freshwater ecosystems. Amyot et al. (1994) found that ultra-violet radiation was converting Hg²⁺ to elemental Hg (Hg⁰). This form is volatile and is transferred to the atmosphere. Reduction of Hg²⁺ by microorganisms was also observed in natural waters (Mason et al. 1995). These processes reduce the Hg available for methylation and accumulation in the food chain. Volatilization of Hg⁰ to the atmosphere is part of a global cycling process. When oxidized it is soluble in rainwater and returns to earth to remote lakes, rivers and oceans (Vandal et al. 1991). The sediments of the ocean are thought to be the ultimate sink of Hg of the world (Andren and Nriagu 1979).

The existent pool of Hg was increased by the exploitation of the earth surface, the exploitation of the underground, and by anthropogenic emissions (Andren and Nriagu 1979). The exploitation of the earth surface released the existing Hg and the emissions

contributed to increasing the natural pool (Andren and Nriagu 1979). The majority of anthropogenic emissions originate from the combustion of fossil fuel but to a lesser extent from industries utilizing Hg as a fungicide (STLRT 1994). Anthropogenic emissions have been estimated to contribute approximately 40% of the total global Hg emissions into the atmosphere (Nriagu 1989). The evidence showing a temporal increase of atmospheric Hg deposition since the beginning of the industrialization include profiles of Hg concentrations observed in sediment cores from remote unpolluted lakes (for e.g. Louchouart et al. 1993).

1.2. ACCUMULATION AND BIOMAGNIFICATION

Hg can reach high levels in fish even in the presence of water showing low Hg concentration. Bioconcentration factors ($[\text{Hg}]_{\text{fish}}/[\text{Hg}]_{\text{water}}$) were found to be in the order of 1 million for northern pike (Lindqvist et al. 1991) and nearly 500 000 for yellow perch (Watras et al. 1994). The bioconcentration factor was found to vary intra-specifically. Older or bigger fish contain higher Hg concentration compared to younger or smaller fish due to difficulty in elimination of Hg obtained through food and longer exposure time to Hg (MacCrimmon et al. 1983).

Bloom (1992) estimated that 95% of the total Hg present in the flesh of the fish was in the methyl-Hg form. For the majority of fish, the level of organic Hg (methyl-Hg) increases with the size of the fish but the inorganic fraction (Hg^{2+} as a free metal ion) remains constant. Thus, in a fully-grown fish, most of the Hg is in the methyl-Hg form (Holsbeek et al. 1997). However, bottom dwellers were found to accumulate more inorganic Hg (Sadhukhan et al. 1996). In fact, Holsbeek et al. (1997) found that for

bottom feeders, the organic and inorganic Hg concentrations increased at similar rates to the length of the fish.

Although the accumulation of Hg in phytoplankton and zooplankton is through passive absorption (D'Itri 1990), most methyl-Hg found in fish comes from the ingestion of contaminated prey (Lindqvist et al. 1991). According to Spry and Wiener (1991), the ingestion of prey account for more than 90% of the total Hg present in piscivorous fish.

The concentrations of Hg were also observed to biomagnify or increase with increasing trophic level. Watras and Bloom (1992) observed an increase of 0.5 log units per trophic level, from phytoplankton to zooplankton to fish. Biomagnification was also determined by comparing the Hg levels between fish communities, which were characterized by the presence/absence of certain prey groups (Cabana et al. 1994). The trophic status of a species can change between regions. For example, a yellow perch from the upstream portion of a river can be piscivorous while fish from the same species can be omnivorous in the downstream portion of the same river. By measuring a 'continuous trophic level' using stable isotope, it was discovered that Hg concentrations increased with the relative trophic levels (Vander Zanden and Rasmussen 1996). For example, an omnivorous fish consuming a higher proportion of fish compared to an omnivore consuming mostly benthos would be more concentrated in Hg. A continuous trophic level can be calculated by comparing ratios of a lighter and heavier stable isotope because organisms assimilate a larger proportion of the heavier stable isotope as they consume prey of higher trophic level.

The above properties of Hg (bioaccumulation and biomagnification) are the fundamental processes that explain the temporal and spatial variations of Hg levels in fish discussed in chapter two.

1.3. HUMAN HEALTH

In humans, methyl-Hg affects the central nervous system (Mottet et al. 1997). There is an ongoing discussion regarding the effects of methyl-Hg on prenatal life and infants, where safe levels of Hg exposure are lower than in adults (WHO 1990). There is also a concern regarding the toxic effects of methyl-Hg on the reproduction, behavior and survival of fish-consuming birds and marine mammals (e.g. Meyer et al. 1995). The toxicity of this compound is caused by its passive transport through cell membranes and its long half-life in biological tissues. Such problems become critical in carnivores.

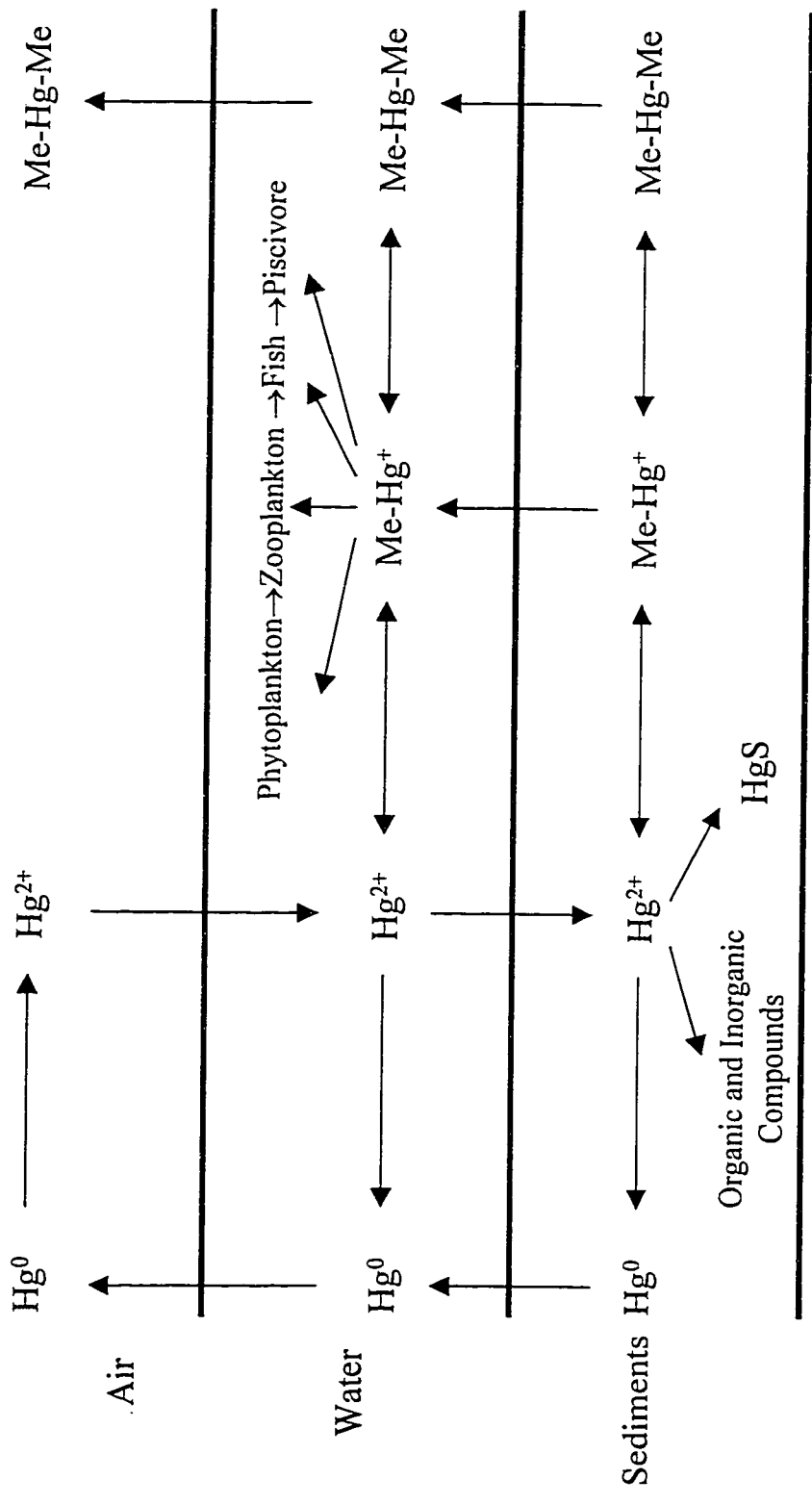
The half-life of methyl-Hg is among the longest known for metals. It takes approximately 60 days for Hg^{2+} and from 45 to 105 days for methyl-Hg to degrade by half its initial amount in human blood (WHO 1976). The reported biological half-life of total Hg for fish is even longer, 640, 780, and 1200 days for flounder, pike and eel respectively (Jarvenpaa et al. 1970). After having one fish meal, Hg in blood of humans peaks after 5 to 14 hours but because of the low excretion rate, the decline is very slow (52 days half-life; Kertshaw et al. 1980).

The consumption of fish is the primary, non-occupational source of exposure to methyl-Hg in humans (WHO 1990). There have been situations where severe acute exposures to methyl-Hg have caused fatalities. A good example is the Minimata case in Japan where a large epidemic of methyl-Hg poisoning resulted from the consumption of

fish from an area contaminated with methyl-Hg released from a chemical plant (Takeuchi et al. 1962). The most severe case of intoxication occurred in Iraq after the consumption of bread made with contaminated grain (Bakir et al. 1973). High methyl-Hg intoxication was associated with sensory disturbances, constriction of the visual field and hearing and speaking impairments (Tsubaki et al. 1977).

As discussed above, the focus of the third chapter of this thesis is the calculation of the 'safe' fish ingestion rate using current Hg levels of fish from the St. Lawrence River. The maximum consumption rates were calculated with maximum tolerable daily intake of Hg put forward by different health organizations based on Hg toxicity.

Figure 1. Biogeochemical cycle of mercury (Hg) in freshwater systems (modified from Winfrey and Rudd 1990).



CHAPTER 2

TEMPORAL TRENDS AND SPATIAL VARIABILITY IN FISH

2.1. INTRODUCTION

The Cornwall, Ontario/Massena, New York region of the St. Lawrence River was designated as an area of concern (AOC 42) by the International Joint Commission in 1985 (IJC 1985). The designation resulted from the fact that the area showed high Hg concentration in the sediment and a high level of fish habitat deterioration. The contamination problem is thought to have originated from industry emissions located on both shores of the river (STLRT 1994). Mercury contamination in that area has caused restrictions on fish and wildlife consumption (STLRT 1994).

Previous studies reported a decline in Hg concentration through time in fish from Lake Ontario (Borgmann and Whittle 1991, 1992), from the Quebec portion of the St. Lawrence River (Ion et al. 1997) and in lampreys from the estuary section of the St. Lawrence River (Hodson et al. 1994). However, the longer and/or higher trophic level fish still exceeded the commercial restriction guideline of 0.5 $\mu\text{g/g}$ wet weight (WHO 1990). Spatial differences due to point sources could also affect this apparent amelioration of the St. Lawrence River ecosystem.

The Ontario Ministry of the Environment and the Ontario Ministry of Natural Resources has been monitoring the contaminant levels in the sport fish of the St. Lawrence River since 1975 (OMOE 1997). The same analytical procedure was used to measure Hg concentration in the dorsal muscle of fish samples over that 20 year period. Thus, this data set offers a unique opportunity to evaluate the temporal trend and present

spatial trends in Hg concentration in the fish from the Ontario portion of the St. Lawrence River.

The objectives of this study are to assess the temporal trend of Hg concentration in fish from 1975 to 1995 and the spatial variability in different fish species caught in four regions of the St. Lawrence River from the Thousand Islands region to Lake St. Francis. Furthermore, an evaluation of the current levels of Hg contamination and a comparison between levels observed elsewhere in the St. Lawrence River and in lakes of Ontario are discussed. Lastly, the contaminant monitoring implications will be discussed based on the results of this study.

I expect that Hg concentrations will decrease with time (year of sampling) and that the rate of decrease will differ between fish species. The rate of decrease should be slower for higher trophic level species like piscivores compared to non-piscivores. Finally, it is expected that fish from the area of concern (Lake St. Francis) should contain more Hg compared to the other regions of the St. Lawrence River.

Four species of fish were used to test these predictions: white sucker (*Catostomus commersoni* [Lacepède]) an obligate benthivore, yellow perch (*Perca flavescens* [Mitchill]) an omnivore, and two piscivores, the northern pike (*Esox lucius* Linnaeus) and the walleye (*Stizostedion vitreum* [Mitchill]). These species were chosen because they represent distinct trophic levels, they are the most frequently used species in studies dealing with fish contaminants, and they are of commercial importance. In this region of the St-Lawrence river, the yellow perch, northern pike and walleye are the three most popular angling fish while the white sucker is captured for the production of forage food.

2.2. STUDY AREA AND METHODS

2.2.1. Study area

The data for this study originate from fish sampling done in the St. Lawrence River from the Thousand Islands region to Lake St. Francis. The river was divided in four distinct regions (Fig. 2): The Thousand Islands (region 1), situated immediately downstream of Lake Ontario (from 44°15'N 76°04'W to 44°16'N 76°00'); The Brockville region (region 2), a straight stretch of the St. Lawrence River (from 44°23'N 75°52'W to 44°43'N 75°19'W); Lake St. Lawrence (region 3), (from 44°50'N 75°11'W to 44°50'N 75°04'W) a 136 km² reservoir for the Moses-Saunders power dam that was completed in 1958 and Lake St-Francis (Region 4), a 233 km² enlargement of the St. Lawrence River (from 44°55'N 74°45'W to 45°05'N 74°23'W). Lake St. Francis is a shallow productive section of the St. Lawrence and was designated as an area of concern in 1985 by the IJC. Several industries residing on the river's shores in that region discharged Hg to the river, notably, ICI Forest Product (until 1995) and Courtaulds Fibers Canada (until 1992).

2.2.2. Fish collection

Fish were collected from the St. Lawrence River during a province-wide survey of contaminant levels in sport fish through a joint effort of the Ontario Ministry of Environment and the Ontario Ministry of Natural Resources from 1975 to 1995. The fish were collected throughout the open-water season but mostly during the later summer months and beginning of autumn. The four regions were sampled sporadically during the first ten years but approximately every alternate year from 1985 until now. The actual fish net sites were dispersed within each general region and varied between years of

sampling when the fish yield was low. Generally, more than ten fish of representative size were sampled in each region (Appendix A). Total length, weight, and sex were recorded for each captured fish.

2.2.3. Mercury analysis

A boneless, skinless fillet of dorsal muscle tissue was removed from captured fish by OMNR employees, packaged and frozen for shipment to the Ontario Ministry of the Environment Central Laboratory in Toronto where the Hg analysis was done. The tissue samples were homogenized mechanically and placed in glass vials. They were later digested by adding 5 ml of concentrated sulfuric:nitric (4:1) acids to approximately 0.250 g of tissue placed in a 50 ml Folin-Wu digestion tube. The tubes were then put in an aluminum hot block for overnight heating. The following day, samples were diluted to 25 ml with deionized and distilled water, mixed and analyzed.

The analytical method used to measure Hg concentration was cold vapor atomic absorption using an automated continuous-flow system. The initial detector used in 1975 was a LDC model 1265 mercury monitor manufactured by Pharmacia. Later instruments were variations of that model.

2.2.4. Quality Control

The specific types of quality control varied slightly over the 20 year period but always included replicates, spikes, reagent blanks, control samples and other typical items deemed appropriate at the time. The laboratory also participated in numerous round robin and inter-lab comparisons. Probably the best evidence of long-term data integrity

over the 20 year time frame comes from a round-robin program organized by Environment Canada at the Fisheries Research Board in Winnipeg, Manitoba. For the first five years, four samples were submitted quarterly to a variety of private and government (including all federal laboratories) laboratories and for 1980 onward, the samples were submitted semi-annually. The data obtained from those round-robins indicate that there was no time-related false drift.

2.2.5. Detection Limit

Since 1975 the lab has used an effective detection limit of $0.01 \mu\text{g}\cdot\text{g}^{-1}$ total Hg in fish tissue. The method of determining and defining detection limit has varied over the years but its value remained identical. Half the detection limit was arbitrarily given as the value for samples that had Hg levels below the detection limit.

2.2.6. Statistical analysis

At least 10 fish for each species for a particular year and location were used in the statistical analyses to insure the results were representative (Appendix A). The yearly sample size, the median Hg concentration, and total length of each species of fish caught in the four different regions from 1975 to 1995 are reported in Appendix A. The sample size, the median Hg concentration, and total length of each species of fish caught from 1991 to 1995 combined are reported in Appendix B.

A general linear model was used to calculate the temporal trends of Hg concentration for each species of fish and region. The dependent variable was set as the Hg concentration log-transformed and the independent variables set as the total length of

the fish log-transformed and the sampling year. The log-transformation was applied to normalize the distribution of the data. Comparisons in rates of decrease between fish species within a region were done by adding fish species as the third independent variable in the same general linear model. Both continuous variables were log-transformed to collapse the differences in fish length variability among sampling years. Pairwise comparisons between years were done using the Bonferroni correction.

This model enabled us to extract the variability in Hg levels that was due to the bioaccumulation property of Hg (Hg concentration increases with the size of the fish) and verifying if the remaining variability could be explained by the year of sampling while including our entire data set. To correct for fish length, other studies have normalized the Hg levels for a particular length (Parks et al. 1991; Wren et al. 1991) or included in their analysis a small range of fish length (Ion et al. 1997).

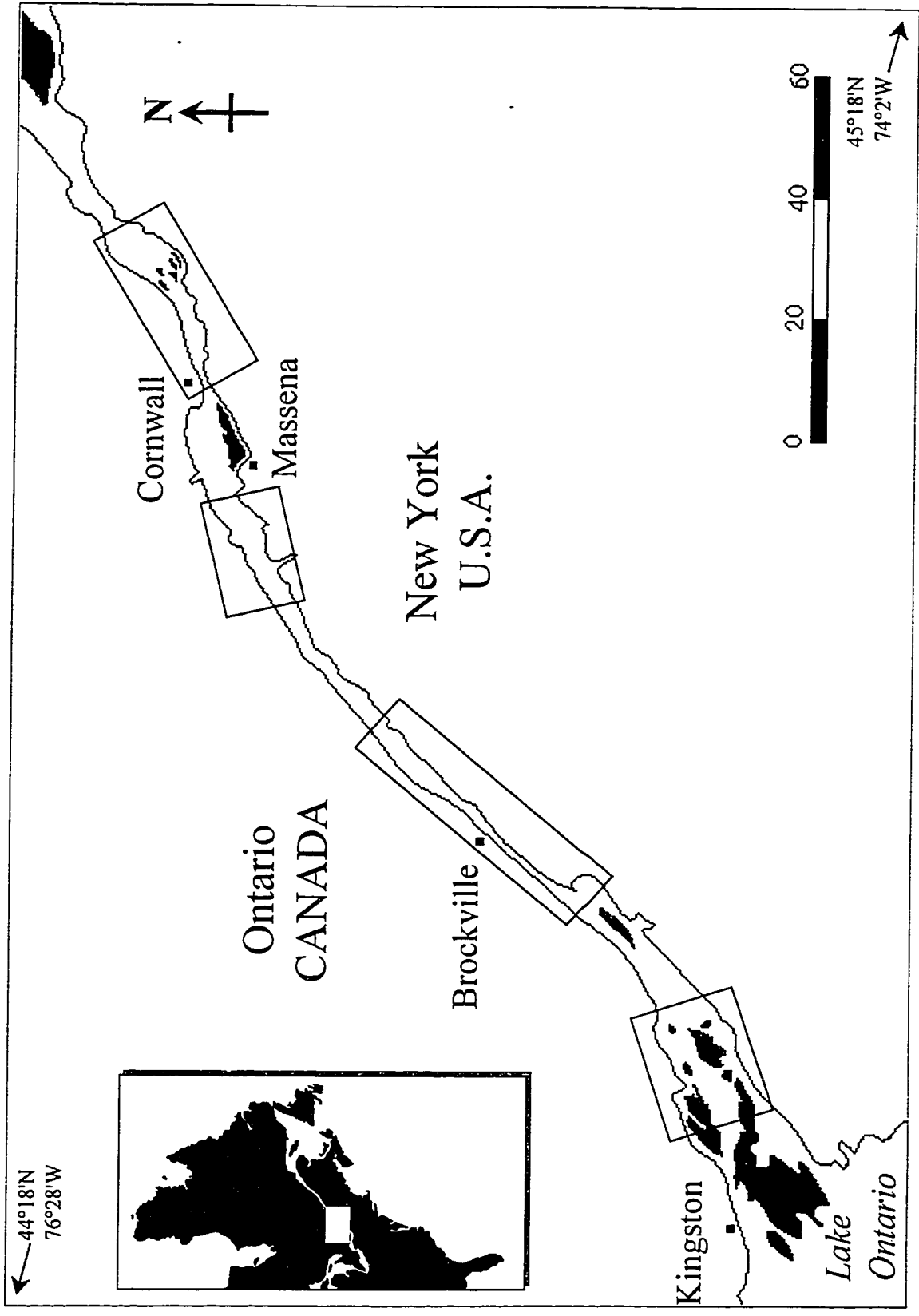
Hg concentrations were compared between regions for each species of fish using ANCOVAs. Combined data from 1991 to 1995 were used for this analysis to ensure representative current Hg concentrations. Before combining the five years of data, I used a general linear model to verify the absence of a year effect because the sampling was not done during the same years in each region. The comparisons of the intercepts of the regressions of Hg concentration (log-transformed) *versus* fish length (log-transformed) enabled us to compare Hg levels between the four regions while correcting the data for fish length. Differences in the slopes provide the rate of Hg accumulation in the fish relative to its length but should be interpreted with caution given the high variability in Hg levels and consequently, the low power of the test. The pair wise comparisons between regions were done using the Bonferroni correction. The power of the pairwise

comparisons and the sample size required to detect a possible difference with a power of 80% were calculated using the equation in Zar (1996) for general linear models.

It should be noted that a 'coarse-graining' approach could also have been used to verify if Hg concentration declined through time. For example, the first and last ten years could have been combined and compared. Such an approach would increase the sample size and insure that the data represent the real levels because one should keep in mind that 20 or more data points only were used to verify for temporal variability for each region. However, a year-to-year comparison provided a finer temporal resolution which was of interest to me.

The null hypothesis was rejected when $p < 0.05$. All analyses were performed using SYSTAT[®] version 7.01 software package for Windows[®] (Wilkinson 1997).

Figure 2. Map of the Ontario portion of the St. Lawrence River showing the regions of sampling from 1975 to 1995. The first region (represented by the box) downstream of Lake Ontario is the Thousand Islands sector, the second the Brockville sector, the third Lake St. Lawrence and the fourth Lake St. Francis.



2.3. RESULTS

2.3.1. Temporal trends

The results for each term of the general linear model are in appendix C. Hg concentrations varied significantly with sampling years between 1975 and 1995 (Table 1). There was a general decrease of Hg concentration with time in white sucker, yellow perch, walleye and northern pike caught in the Thousand Islands (Fig. 3) and Brockville (Fig. 4) regions, Lake St. Lawrence (Fig. 5) and Lake St. Francis (Fig. 6). Mercury levels have remained stable for northern pike caught in the Brockville and in Lake St. Lawrence regions.

2.3.1.1. Thousand Islands region

Northern pike was the only fish caught in the Thousand Islands region over the 20 years period. Pair wise comparisons between sampling years revealed that levels in 1976 were significantly higher compared to 1985 and later years ($p < 0.0005$, Fig. 3). The concentrations remained stable between 1985 and 1995 (Fig. 3).

2.3.1.2. Brockville region

The Hg levels in white sucker and yellow perch were significantly higher in 1975 compared to levels from 1983 and later years. The Hg levels in white sucker were higher in 1985, 1986 and 1988 compared to 1994 Hg levels (Fig. 4A). Yellow perch in 1985, 1986, and 1990 were also more contaminated as compared to 1992 and the concentrations further decreased between 1992 and 1994 (Fig. 4A). However, Hg concentrations in northern pike did not decrease from 1975 to 1995 even if there was an overall significant

year effect. The only variability came from higher concentrations in 1992 than in 1986 and 1994 (Fig. 4B).

2.3.1.3. Lake St. Lawrence

The Hg concentrations in white sucker caught in Lake St. Lawrence were significantly higher in 1975 and 1977 compared to later years of sampling ($p < 0.004$) and the levels remained stable from 1985 to 1993 ($p \geq 0.907$, Fig. 5A). For yellow perch, Hg levels decreased significantly from year to year starting in 1977 up to 1993 (Fig. 5A). No pairwise differences in the variability of Hg concentration were detected between the years of sampling for northern pike caught in Lake St. Lawrence ($p \geq 0.25$, Fig. 5B).

2.3.1.4. Lake St. Francis

Hg concentration in white suckers was significantly higher in 1976, 1977, 1978, 1981 and 1982 compared to later years but remained stable between 1988 and 1994 (Fig. 6A). The Hg levels generally decreased in yellow perch from year to year from 1977 to 1990 but have remained stable from 1990 to 1994 (Fig. 6B). Hg concentration in northern pike was higher in 1977 compared to 1984 and 1990 while Hg concentrations from 1981, 1988, and 1989 were higher compared to 1992 and 1994 (Fig. 6B). For walleye, 1976 data showed higher concentrations compared to 1982 and later years, 1977 and 1978 data were also higher compared to later years but levels remained stable between 1989 and 1994 (Fig. 6B).

2.3.1.5. Differences in rates of decrease between fish species

The rate of Hg decrease differed significantly between the four species of fish (n=1154, F-ratio=12.01, p<0.0005). Hg concentrations decreased faster through the years in white sucker and progressively slower in yellow perch, walleye and slowest in northern pike caught in Lake St. Francis (p<0.0005 for each pair wise comparisons).

Figure 3. Relationships between average total Hg concentration \pm 1 standard deviation, in $\mu\text{g/g}$ ww, and total length of northern pike caught in the Thousand Islands region of the St. Lawrence River from 1976 to 1995. For this and Fig. 3-5, inset shows the relationship between Hg concentration corrected for the total length of the fish (residuals of the regression of Hg concentration *versus* total length of the fish pooled over the years of sampling) and the year of sampling. Data gathered by the Ontario Ministry of the Environment and the Ontario Ministry of Natural Resources for the Sport Fish Contaminant Program (unpublished data).

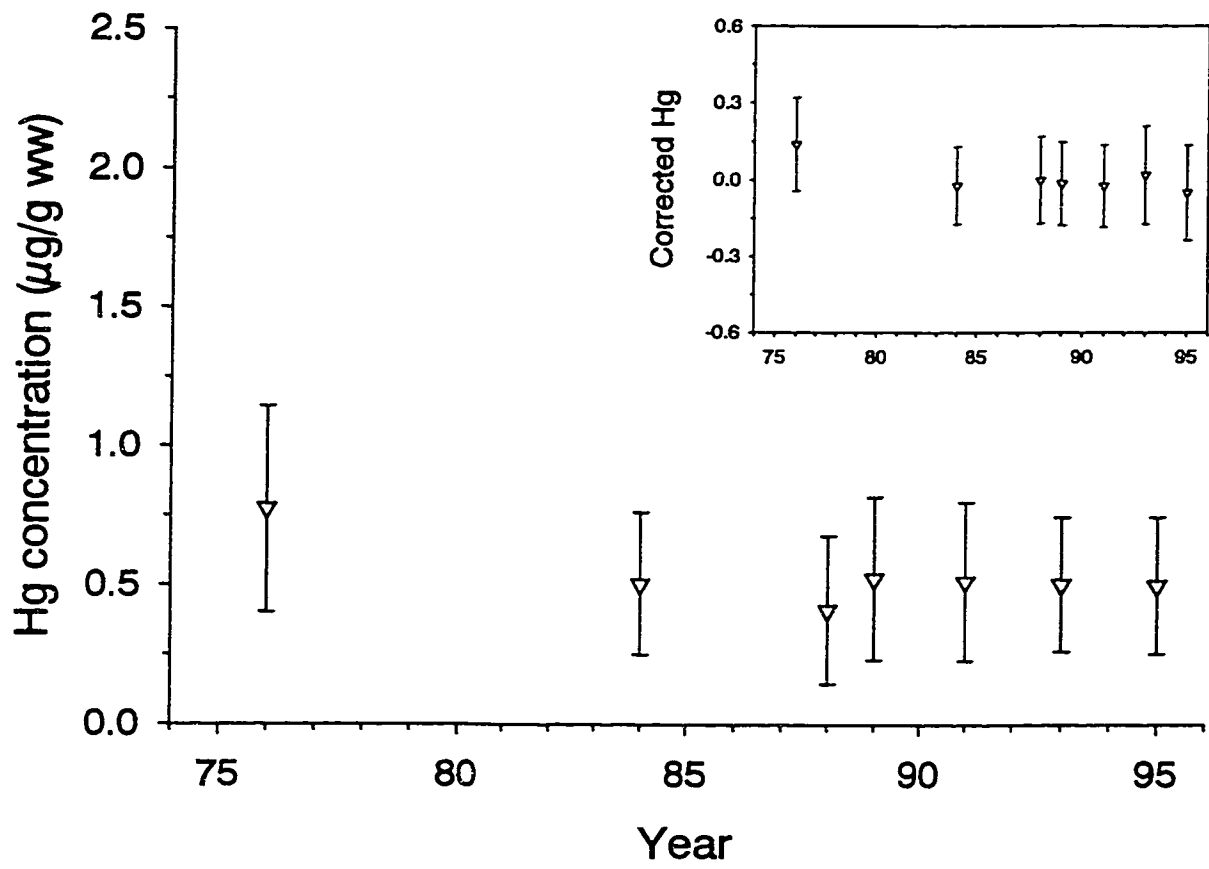


Figure 4. Relationships between average total Hg concentration ± 1 standard deviation, in $\mu\text{g/g}$ ww, and total length of A) white sucker (●) and yellow perch (○) and B) northern pike (▽) caught in the Brockville region of the St. Lawrence River from 1975 to 1995. Data gathered by the Ontario Ministry of the Environment and the Ontario Ministry of Natural Resources for the Sport Fish Contaminant Program (unpublished data).

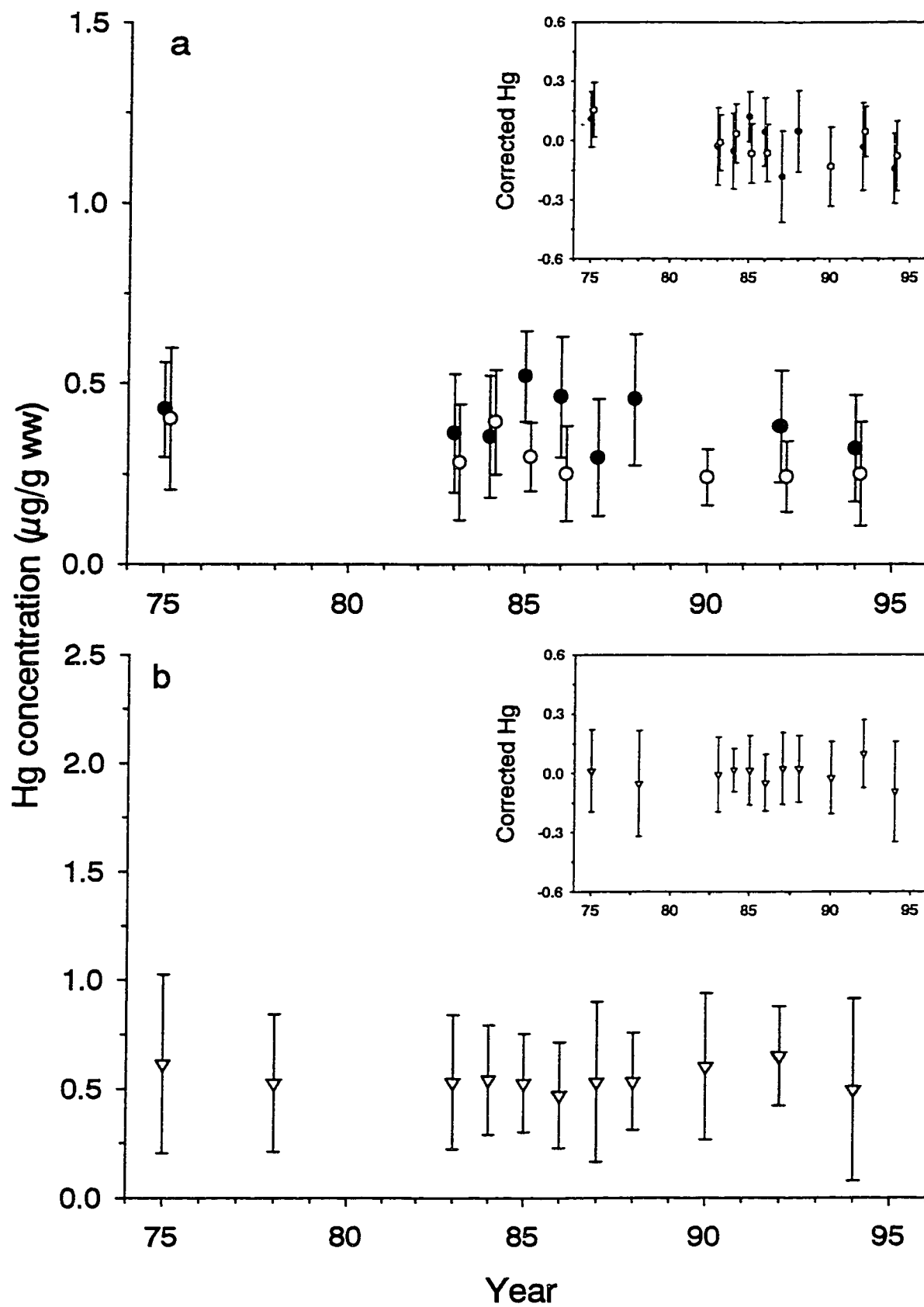


Figure 5. Relationships between average total Hg concentration \pm 1 standard deviation, in $\mu\text{g/g}$ ww, and total length of A) white sucker (●) and yellow perch (○) and B) northern pike (∇) caught in Lake St. Lawrence in the St. Lawrence River from 1975 to 1995. Data gathered by the Ontario Ministry of the Environment and the Ontario Ministry of Natural Resources for the Sport Fish Contaminant Program (unpublished data).

Figure 6. Relationships between average total Hg concentration \pm 1 standard deviation, in $\mu\text{g/g}$ ww, and total length of A) white sucker (●) and yellow perch (○) and B) northern pike (▽) caught in Lake St. Francis in the St. Lawrence River from 1975 to 1995. Data gathered by the Ontario Ministry of the Environment and the Ontario Ministry of Natural Resources for the Sport Fish Contaminant Program (unpublished data). Error bars represent standard deviations.

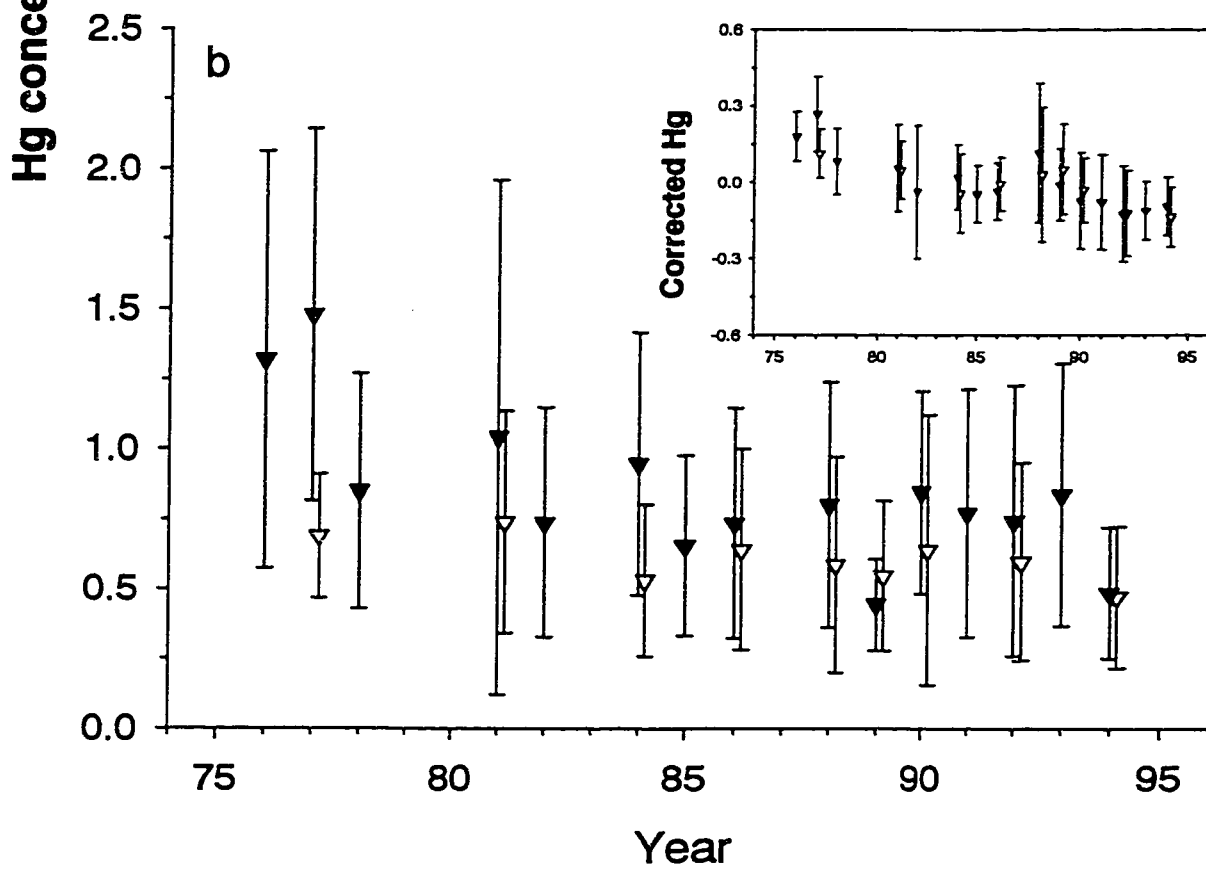
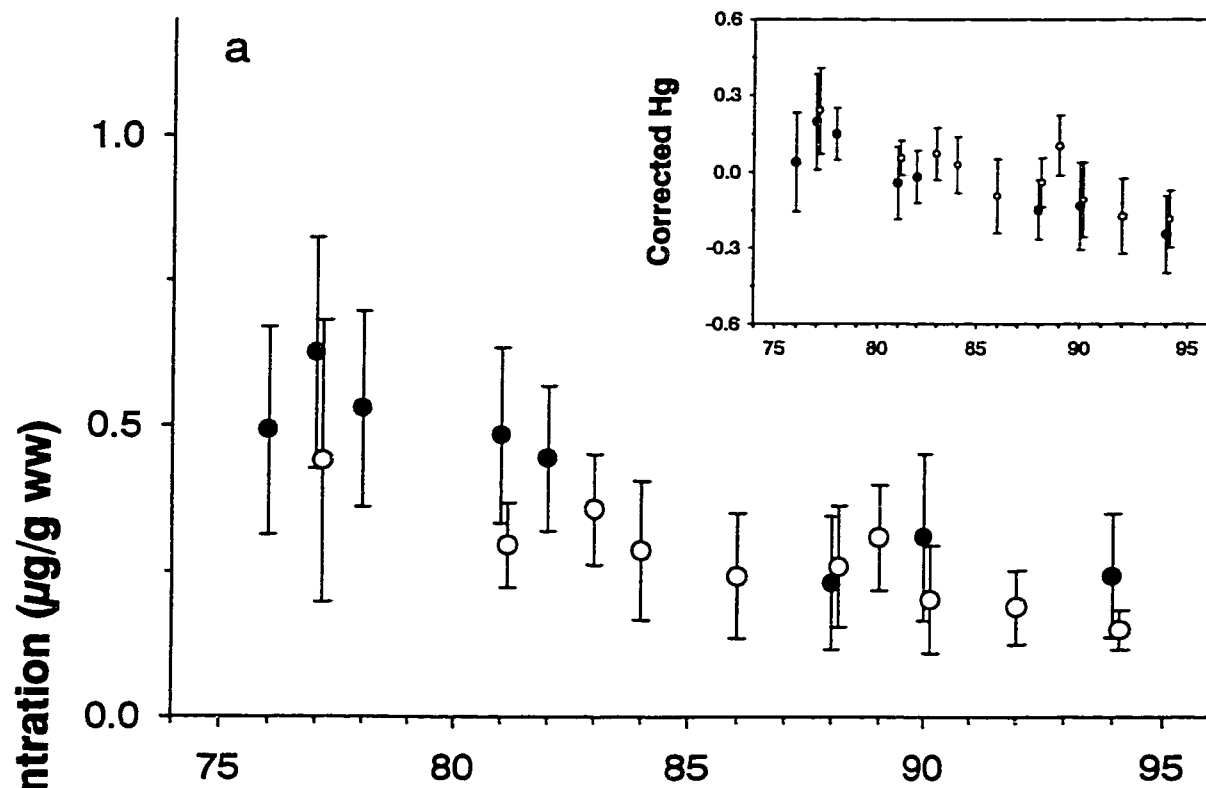


Table 1. Significant year of sampling effect on Hg concentrations in white sucker, yellow perch, walleye and northern pike caught in four regions of the Ontario portion of the St. Lawrence River from 1975 to 1995. Results of the general linear model testing for year effect are indicated.

Region	Species	N	F	p	EMS ¹
Thousand Islands	Northern pike	139	3.45	0.003	0.027
Brockville	White sucker	324	7.43	<0.005	0.035
	Yellow perch	328	11.1	<0.005	0.022
	Northern pike	365	2.13	0.021	0.032
Lake St.Lawrence	White sucker	114	17.5	<0.005	0.036
	Yellow perch	179	15.9	<0.005	0.021
	Northern pike	134	2.33	0.036	0.024
Lake St. Francis	White sucker	237	34.2	<0.005	0.025
	Yellow perch	309	33.4	<0.005	0.016
	Walleye	349	9.76	<0.005	0.029
	Northern pike	258	9.41	<0.005	0.024

¹ Error Mean Square

2.3.2. Spatial variability

The results for each term of the general linear model are in appendix D. All of the intercept values associated with the regressions are negative and the total length of each species of fish explained from 11 to 80% of the variability in Hg concentrations (Table 2). In general, the length explained a higher proportion of the variability for walleye and a decreasingly lower proportion of the variability for northern pike, yellow perch and white sucker. The results of the ANCOVAs are presented in Table 2.

The power of the tests varied from less than 1% to more than 99%. In general, the power was relatively high and the sample size needed to discern a difference between the regions was lower than what was used to perform the test. There was therefore a low probability that a type II error (concluding that there is no significant difference when in fact, there is a difference) was made.

2.3.2.1. *White sucker*

The rate of Hg accumulation with length in white sucker from Lake St. Lawrence was significantly slower compared to those caught in the other three regions. This result is due to the apparent lack of relationship between Hg concentration and length of white sucker caught in Lake St. Lawrence. The lower sample size (N=13) and the significantly smaller size of fish ($p < 0.0005$) analyzed for that particular region are probably responsible for that lack of relationship. For the remaining three regions, rates of Hg accumulation with size were homogeneous but the height of these relations varied significantly one with another. The highest levels were found in the Brockville region, lower levels were observed in Lake St. Francis and lower levels again were found in the

Thousand Islands region (Fig. 7A). On average, Hg levels in white sucker from Lake St. Lawrence were the lowest ($0.13 \pm 0.05 \mu\text{g/g}$) which is most likely a reflection of the smaller size of fish analyzed compared to elsewhere. Therefore, I am not able to conclude from this result that the contamination level is actually the lowest in white sucker from Lake St. Lawrence.

2.3.2.2. *Yellow perch*

The rate of Hg accumulation in yellow perch caught in the Brockville region was significantly greater compared to the other three regions (Fig. 7B). Also, the middle of the relationship of Hg concentration versus length seemed to be slightly higher with respect to those found for the other three regions suggesting that Hg concentration corrected for length would be higher in Brockville compared to elsewhere (Fig. 7B). For the Thousand Islands region, Lake St. Lawrence and Lake St. Francis, concentrations and Hg rates of accumulation were homogeneous. The power associated with the pair wise tests was high (>79%) except for the comparison of the Thousand Islands region with Lake St. Francis (1.1%). This particular comparison would have required a sample size of 674 to discern a difference.

2.3.2.3. *Walleye*

The rate of Hg accumulation with length for walleye caught in Lake St. Francis was faster compared to walleye caught in Lake St. Lawrence or in the Thousand Islands region (Fig. 7C). The mean length-corrected Hg concentration seemed to be higher compared to elsewhere suggesting that the mean concentration in the Brockville region would be higher (Fig. 7C). The rates and the concentrations were similar for walleye

from Lake St. Lawrence and the Thousand Islands region. The power associated with this test was very low (0.3%) and more fish (37 in total) would have been needed from both region to discern a difference with a confidence of 80.

2.3.2.4. *Northern pike*

The rate of accumulation of Hg in northern pike was constant throughout the four regions but the levels were lower in the Lake St. Lawrence region compared to the other three regions where the levels were similar (Fig. 7D). The power was low for the comparisons between the Thousand Islands and Brockville regions (0.9%) and more than nine times the actual sample size would have been needed to discern a difference with 80% confidence. The power of the remaining pair wise tests were high (>60%).

2.3.2.5. *Inter-species comparisons*

On average, northern pike are more contaminated by Hg than other fish species except for walleye when caught in Lake St. Francis ($0.75 \pm 0.45 \mu\text{g/g}$) (Appendix B). For the other regions, walleye are the second most contaminated species followed by either yellow perch or white sucker. Yellow perch and white sucker are equally contaminated in the Thousand Islands region but yellow perch are less contaminated in the Brockville region and in Lake St. Francis but more contaminated in Lake St. Lawrence (Appendix B).

No region was found to be systematically more contaminated. However, the analysis is limited because it is only for two species, northern pike and yellow perch, for which data for the four regions of the St. Lawrence River were available. The concentrations of Hg were found to be higher in yellow perch caught in the Brockville

region compared to other regions and for northern pike, the levels in that same region were not significantly different from the Thousand Islands and Lake St. Francis.

Figure 7. Relationships between average total Hg concentration \pm 1 standard deviation, in $\mu\text{g/g}$ ww, and total length of A) white sucker, B) yellow perch, C) walleye and D) northern pike. The fish were caught from 1991 to 1995 in four regions of the Ontario portion of the St. Lawrence River, Thousand Islands (∇), Brockville (\blacktriangledown), Lake St. Lawrence (\circ), and Lake St. Francis (\bullet). Data gathered by the Ontario Ministry of the Environment and the Ontario Ministry of Natural Resources for the Sport Fish Contaminant Program (unpublished data).

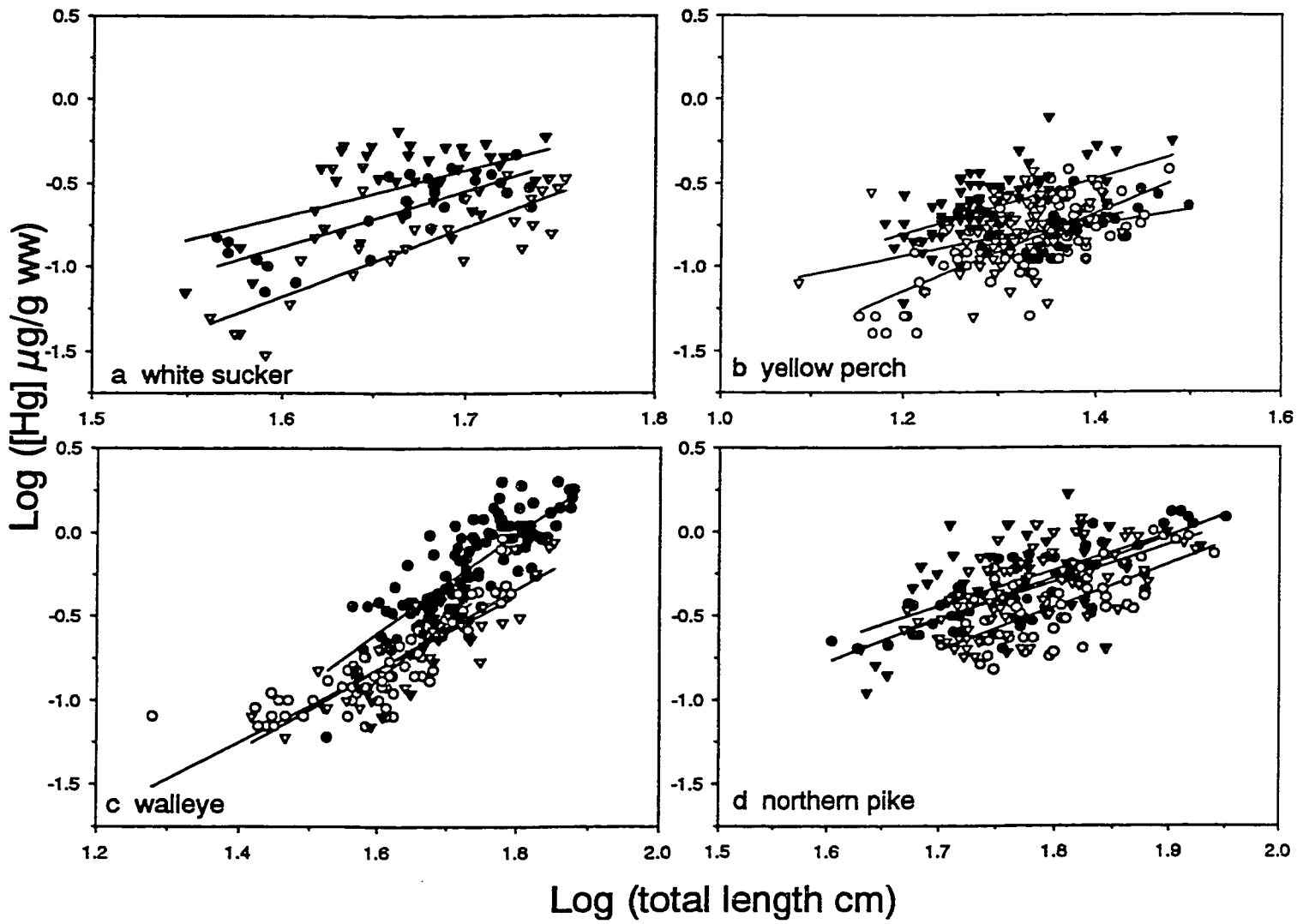


Table 2. Intercept ($a \pm 1$ standard error) and slope ($b \pm 1$ standard error) of the regression equations $\log(\text{Hg}) = a + b \log(\text{total length})$ for northern pike, walleye, yellow perch and white sucker caught in four different regions along the Ontario portion of the St. Lawrence River during autumn 1991 to 1995. Significantly different slopes or intercepts within a fish species between regions are represented by different superscript letters (when $p < 0.05$ of a Bonferroni pair wise comparisons test).

Species	Region	$-a \pm \text{s.e. (t, p)}$	$b \pm \text{s.e. (t, p)}$	N	r^2	RMS ¹
White sucker	Thousand Islands	$7.94^a \pm 0.95 (8.34, <0.005)$	$4.23^a \pm 0.57 (7.43, <0.005)$	25	0.71	0.029
	Brockville	$5.20^b \pm 1.17 (4.45, <0.005)$	$2.81^a \pm 0.70 (4.00, <0.005)$	44	0.28	0.041
	Lake St. Lawrence	$2.76 \pm 1.35 (2.05, <0.065)$	$1.15 \pm 0.84 (1.37, 0.197)$	13	0.15	0.029
	Lake St. Francis	$6.30^c \pm 0.85 (7.46, <0.005)$	$3.39^a \pm 0.51 (6.68, <0.005)$	28	0.63	0.019
Yellow perch	Thousand Islands	$2.30^a \pm 0.57 (4.06, <0.005)$	$1.14^a \pm 0.43 (2.65, 0.010)$	61	0.11	0.033
	Brockville	$2.79^b \pm 0.35 (7.93, <0.005)$	$1.65^b \pm 0.27 (6.08, <0.005)$	92	0.29	0.024
	Lake St. Lawrence	$3.97^a \pm 0.36 (11.1, <0.005)$	$2.35^a \pm 0.27 (8.73, <0.005)$	66	0.54	0.028
	Lake St. Francis	$1.96^a \pm 0.48 (4.10, <0.005)$	$0.87^a \pm 0.35 (2.47, 0.017)$	51	0.11	0.017
Walleye	Thousand Islands	$4.63^a \pm 0.44 (10.6, <0.005)$	$2.38^a \pm 0.26 (9.13, <0.005)$	23	0.80	0.024
	Lake St. Lawrence	$4.30^a \pm 0.28 (15.7, <0.005)$	$2.18^a \pm 0.17 (12.8, <0.005)$	69	0.71	0.023
	Lake St. Francis	$5.32^b \pm 0.33 (15.7, <0.005)$	$2.95^b \pm 0.19 (15.7, <0.005)$	112	0.69	0.025
Northern pike	Thousand Islands	$4.31^a \pm 0.60 (7.25, <0.005)$	$2.23^a \pm 0.33 (6.67, <0.005)$	72	0.39	0.031
	Brockville	$3.82^a \pm 0.75 (5.13, <0.005)$	$1.99^a \pm 0.42 (4.71, <0.005)$	46	0.33	0.053
	Lake St. Lawrence	$5.06^b \pm 0.68 (7.45, <0.005)$	$2.56^a \pm 0.38 (6.83, <0.005)$	54	0.47	0.024
	Lake St. Francis	$4.78^a \pm 0.43 (11.0, <0.005)$	$2.50^a \pm 0.24 (10.3, <0.005)$	55	0.67	0.018

¹Residual Mean Square

2.4. DISCUSSION

2.4.1. Temporal trend

A general linear model was used for year-to year comparisons by including the complete data set and correcting it for differences in length. This correction is necessary for inter-year and inter-region comparisons because Hg concentration increases with fish size (Wren et al. 1991; Sorensen et al. 1990; McMurthy et al. 1989). Length is the best predictor of Hg concentration in fish due to its strong association with exposure duration (Huckabee et al. 1979). A decrease in Hg concentration over time could therefore be obtained if fish captured were smaller with time. The length-corrected Hg concentration can be shown visually by plotting the residuals of the Hg-length regression, pooled over the years of sampling (inset of Fig. 2-5).

I found that the Hg-length relationships (or the rate of Hg accumulation with length) varied with the years of sampling for each fish species. As expected, the rate of Hg accumulation increased with the mean length of fish. However, there was no relationship between the average fish length and the year of sampling indicating that the variability in the Hg-length relationship did not explain the decline in Hg. Also, the heterogeneity in the Hg-length relationship was not systematically the same for all sampling years. Progressively lower Hg bioavailability to fish translates in a slope of Hg-length with time, progressively reaching zero. No correlation was found between the individual regression coefficient and the year of sampling ($p > 0.25$ $r^2 = 0.11$ for each fish species).

A general decrease in Hg concentration was observed for white sucker, yellow perch, walleye and northern pike caught throughout the Ontario portion of the St.

Lawrence River. The only exceptions were for northern pike caught in the Brockville sector and Lake St. Lawrence. For northern pike and walleye, the decrease in Hg was observed when the first years of sampling were compared with later years while for white sucker and more apparently for yellow perch, the decrease was more gradual (from year to year).

The Hg concentrations decreased most rapidly through time in white sucker and progressively less rapidly in yellow perch and walleye. It was the slowest for northern pike caught in Lake St. Francis. These results seem to indicate that the lowest trophic level fish (white sucker) responded more rapidly to changes in the environment compared to the highest trophic level fish (walleye or pike).

The absence of a decrease in Hg over time for northern pike, caught in the Brockville sector, could be caused by the fact that these fish had a lower level of contamination in the mid-70's (0.51 $\mu\text{g/g}$ in 1975). The Thousand Islands (0.84 $\mu\text{g/g}$ in 1976) and Lake St. Francis sectors (0.67 $\mu\text{g/g}$ in 1977) showed a significant Hg decrease in subsequent years but the contamination level in the mid-70's was higher than in the Brockville sector. When the Hg concentration in the earlier years of sampling are low, the slope has a tendency to be near zero when Hg is examined through time. The power of these tests is also always low decreasing the ability of the test to detect significant differences in Hg concentration between the years of sampling.

Larger variability in the Hg levels could also explain the lack of significant difference between the years of sampling in northern pike from Brockville. The Brockville sector is the largest of the four regions and may contain larger spatial variability in the Hg concentrations found in fish. However, the residual mean squares in

the statistical model of each region was similar indicating that the unexplained variability in Hg concentrations from the Brockville region is similar to the other regions (Table 1).

For northern pike caught in Lake St. Lawrence, the lack of decrease in Hg over sampling years could simply reflect the later start of the monitoring program in that sector (1981) compared to mid 1970's for the other sectors. Possibly, by 1981 the levels had already returned to 'background levels'.

A decrease in Hg concentration has been observed by other researchers. Hg in rainbow smelt (*Osmerus mordax*), slimy sculpin (*Cottus cognatus*) and lake trout (*Salvelinus namaycush*) caught in Lake Ontario decreased by half between 1977 and 1988 (Borgmann and Whittle 1991, 1992). Similarly, Hg concentrations in yellow perch caught in the eastern section of Lake St. Francis from 1975-76 to 1988 dropped by 25% (Laliberté 1993). Ion et al. (1997) also observed a decrease by a factor of two for Hg concentration in yellow perch from Lake St. Francis between 1975 and 1991-1992. Finally, Hg concentrations in the American eel (*Anguilla rostrata*) captured in the estuary of the St. Lawrence River has significantly decreased between 1982 and 1990 (Hodson et al. 1994).

Researchers have speculated the decrease in Hg concentration was due to lower Hg input by the industries in the Cornwall/Ontario, Massena/New York area (Laliberté 1993). However, the reduction in Hg emissions in that area of the St. Lawrence River cannot account for the decrease in the upstream area. Hg emitted into the atmosphere by the industries from Cornwall/Messena could travel approximately 100 km, both upstream and downstream in its reduced and volatile form (Hg^0) before oxidizing and becoming less volatile (Hg^{2+} ; Vandal et al. 1991). With our present understanding, it is unlikely

that the interruption of these emissions (completely stopped in 1996) could be responsible for the generalized decrease of Hg for the Great Lakes-St. Lawrence River basin, which covers more than twice this distance. However, a generalized decrease in the Hg air emissions of the surrounding industries may explain in part the decrease in Hg concentration found in fish along the St. Lawrence River.

The Hg decrease in the fish may also reflect other remedial programs in the Great Lakes-St. Lawrence River that affected the biogeochemical cycle of Hg. One of the most important changes in the chemical properties has been the decline of phosphorus loading to Lake Ontario from 14 600 t/yr in 1969 and 89 000 t/yr in 1982 (Stevens and Neilson 1987) to levels which range between 6700 and 8000 t/year in 1987 (Lean et al. 1987). This resulted in lower phosphorus concentrations (from approximately 30 to 10 $\mu\text{g P/L}$). Declines in phosphorus in Lake Ontario were reflected in declines in phosphorus in the St. Lawrence River (STLRT 1997). The decrease in phosphorus may have reduced primary productivity and the rate of bacterial decomposition of organic matter. This decomposition may result in less methyl-Hg production.

2.4.2. Spatial variability

My ability to monitor the spatial variation of contamination was limited because complete data were available for only two species, northern pike and yellow perch, within the Ontario portion of the St. Lawrence River. Yellow perch showed similar levels across the St. Lawrence River and the only spatial difference for northern pike came from lower levels when pike was caught in Lake St. Lawrence. When comparing three regions, white sucker from the Brockville sector were found to be more contaminated

compared to the Thousand Islands and Lake St. Francis and in the three regions where walleye was caught, the most contaminated specimens were found in Lake St. Francis.

It is puzzling that white sucker and yellow perch seem to be more contaminated in the Brockville region relative to the other regions. Furthermore, why would northern pike be less contaminated in Lake St. Lawrence relative to other regions? No specific point sources of Hg are known in these regions. The physico-chemical properties of the four regions are very similar indicating that naturally occurring Hg is probably not a factor. The characteristics of the fish populations from these regions could be different from elsewhere in the St. Lawrence River. For example, faster growth rate is thought to 'dilute' the accumulation of Hg so relatively older populations of a particular mean length would be more contaminated compared to a younger population of that same length (Birgit 1987; Berninger and Pennanen 1995). A comparison of age data would be necessary to clarify this point.

Lake St. Francis is the only region of the Ontario portion of the St. Lawrence River where Hg was emitted by industries. It was designated an Area of Concern (AOC) by the International Joint Commission due to high Hg concentrations in the sediments of Lake St. Francis and due to fish habitat deterioration (STLRT 1994). From the fish sampled in Lake St. Francis from 1991 to 1995, only walleye was found to contain higher Hg concentration ($0.75 \pm 0.45 \mu\text{g/g}$) compared to elsewhere ($0.30 \pm 0.24 \mu\text{g/g}$ for the Thousand Islands region and $0.20 \pm 0.17 \mu\text{g/g}$ for Lake St. Lawrence).

The levels reported in this study for yellow perch are comparable to those found in the Quebec portion of the St. Lawrence River. Ion et al. (1997) found levels ranging from 0.05 - $0.44 \mu\text{g/g}$ ww (from the eastern portion of Lake St. Francis up to Lake St.

Pierre). The data presented here ranged from 0.09 to 0.47 $\mu\text{g/g}$ ww for the western portion of Lake St. Francis. Also, the levels for the St. Lawrence River seem similar to those of Ontario lakes, Canada. Province-wide data combined from 1978 to 1984 reveal geometric means of 0.50 and 0.45 $\mu\text{g/g}$ ww for walleye and northern pike respectively (Richardson and Currie 1993) compared to 0.37 and 0.42 $\mu\text{g/g}$ ww for the Ontario portion of the St. Lawrence River.

2.4.3. Monitoring implications

I found that the relationship between Hg concentration and the length of the fish varied randomly with the year of sampling. However, there was a positive correlation between the slope of the relationship and mean length of the fish sampled. This implies that in order to compare the levels of Hg without sampling bias, it would be important to analyze Hg concentration in fish of representative spectrum lengths. Also, it would be important that the mean length be similar for each pair wise comparison.

Only length was used as a correction for bioaccumulation. In general, length covaries with weight and the age of the fish. However, having age data would be beneficial to factor out additional variation in the Hg concentration for inter-region or inter-year comparisons.

CHAPTER 3

SAFE FISH CONSUMPTION RATE: A SIMPLE PROBABILISTIC APPROACH

3.1. INTRODUCTION

Contaminant levels in the environment are now of great concern to scientists and to the general public. In a survey on risk perception and fish consumption in the St. Lawrence River, the majority of the riverside residents said they feared eating fish and approximately half of them stated that Hg contamination was their main concern (Larue et al. 1998).

There is concern about Hg exposure because anthropogenic, in addition to naturally occurring Hg, can be methylated by sediment microbiota and bioaccumulated up the aquatic food chain, in which humans are one of the top predators (Fitzgerald 1993). Methyl Hg exposure in the food chain has even led to catastrophic episodes of intoxication. In Minamata (Japan) a large epidemic of methyl Hg poisoning resulted from the consumption of fish from an area where there was methyl Hg released from a chemical plant (Takeuchi et al. 1962). However, the largest tragedy happened in Iraq when uninformed people consumed bread made with methyl-Hg contaminated grains (Bakir et al. 1973).

To maintain methyl-Hg exposure at safe levels, fish consumption advisories were developed. These advisories were calculated using Reference Dose (RfD) or Tolerable Daily Intake (TDI) which are the maximum amount of Hg that can be consumed per day before being at risk due to Hg exposure. The current RfD used by the Canadian

government ($0.47 \mu\text{g}$ of Hg/kg of body weight/day) was established by the Joint Food and Agriculture Organization/World Health Organization Expert Committee on Food Additives (JECFA) in 1972 (WHO 1989). While this RfD was recommended for the general population, a concern was raised by the JECFA for pregnant women and nursing mothers that were thought to be more sensitive groups.

Recently, two new studies and the re-evaluation of the Iraq data by the U.S. Environmental Protection Agency (U.S. EPA) (IRIS 1995) brought additional information on methyl-Hg toxicity which prompted the calculations of new RfDs and TDI. First, there was a large-scale investigation on prenatal exposures to Hg through maternal ingestion of fish, known as the Seychelles project. The goal of the project was to examine the relationship between fetal neurodevelopmental effects and low-level methyl-Hg exposure from dietary fish consumption in mother-infant pairs until the infant's age reached 66 months. After the infant reached an age of 29 months, the results showed no definite adverse neurodevelopmental effects in maternal hair with Hg levels up to $12 \mu\text{g/g}$ (Myers et al. 1995). Secondly, Grandjean et al. (1997) conducted a neurobehavioral examination on a cohort of 7-year old children born to mothers with mean hair Hg levels of $4.27 \mu\text{g/g}$. They found Hg-related neuropsychological dysfunctions in language, attention and memory after adjustments for covariates and the exclusion of children whose mother's hair were above $10 \mu\text{g/g}$.

Based on the above hair Hg NOAELs (No-Observable-Adverse-Effect-Level) and LOAELs (Lowest-Observable-Adverse-Effect-Level), Health Canada approximated a benchmark dose of $10 \mu\text{g/g}$ for estimating a provisional TDI of methyl-Hg for women of child bearing age and infants while waiting for the completion of the Seychelles project

(HC 1998). By converting hair total Hg levels to blood methyl-Hg levels (dividing the levels by 250), converting the blood methyl-Hg levels to dietary methyl-Hg intake levels (IRIS 1995) and by applying a 5-fold uncertainty factor, a provisional TDI was proposed ($0.20 \mu\text{g}/\text{Kg bw}/\text{day}$; HC 1998).

On the American side of the St. Lawrence River, the U.S. EPA developed a new RfD for methyl-Hg ($0.10 \mu\text{g}$ of Hg/kg-day), one-fifth compared to the one set by WHO (Egeland and Middaugh 1997). Such a conservative approach would reduce considerably the safe ingestion rate of fish and therefore raises a debate on the risk arising from exposure to methyl-Hg versus the benefits of eating fish (Egeland and Middaugh 1997, Weathley and Paradis 1996). Amongst the benefits, fish and shellfish are excellent food sources that are high in protein and low in saturated fat. They also provide beneficial polyunsaturated fatty acids (Kinsella 1987) and antioxidants such as selenium (Siu and Berman 1989) and vitamin E (Bauernfeind 1980). Such nutritional advantages make it important to provide safe consumption rates to prevent complete avoidance of fish while protecting the population from methyl-Hg exposure.

The goal of this study is to provide a simple method to compute safe consumption rates (in meals/month) of fish for the riverside residents of the St. Lawrence River. The calculations were made using both the Canadian and the proposed U.S. EPA RfDs (0.47 and $0.10 \mu\text{g}/\text{Kg bw}/\text{day}$ respectively) and the new provisional TDI developed by Health Canada for women of child bearing age and children ($0.20 \mu\text{g}/\text{Kg bw}/\text{day}$). The safe ingestion rates will be done separately for different fish species caught in four regions of the St. Lawrence River: the Thousand Islands, the Brockville region, Lake St. Lawrence and Lake St. Francis. Four species of fish were used for the analysis: white sucker

(*Catostomus commersoni* [Lacepède]) an obligate benthivore, yellow perch (*Perca flavescens* [Mitchill]) an omnivore, and two piscivores, the northern pike (*Esox lucius* Linnaeus) and the walleye (*Stizostedion vitreum* [Mitchill]).

The procedure used to calculate safe consumption rates is unique since I used a probabilistic approach as opposed to a deterministic approach, currently used by the federal governments. Probabilistic methods have the advantage of providing a distribution of safe consumption rates estimated for the total population (Richardson 1996) while the average case is currently in use in Canada for regulatory purposes (HC 1994) or the worst case scenario chosen by the U. S. (U.S. EPA 1991). For example, the entire data set of Hg concentration found in fish was included in the model as opposed to the average or top value. From the resulting distribution of safe consumption rate, it is then possible to choose the proportion of the population to protect (the average individual or up to any percentile of the population) or calculate the economic implications of protecting such groups of the population.

3.2. STUDY AREA AND METHODS

3.2.1. Study area

The present study has been carried out in the St. Lawrence River starting from the mouth of Lake Ontario in the Thousand Islands region to the Cornwall/Ontario, Massena/New York region in Lake St. Francis. This stretch of the St. Lawrence was separated in four regions where separate risk analysis was carried out (Figure 2). The first region contains the Thousand Islands (from 46°15'N 76°04'W to 44°16'N 76°00'), the second region is simply a stretch of the St. Lawrence River passing by Brockville/Ontario (from 44°23'N 75°52'W to 44°43'N 75°19'W). The third region is Lake St. Lawrence (from 44°50'N 75°11'W to 44°50'N 75°04'W) which is the reservoir of the Moses-Saunders power dam created in 1958 and Lake St. Francis (from 44°55'N 74°45'W to 45°05'N 74°23'W) is the last region. This productive section of the St. Lawrence was designated as an area of concern in 1980. The concerns were raised in part by the presence of a chlor-alkali plant (ICI Forest Product) on its shore discharging Hg in their effluent and in the atmosphere until recently and of Courtland Fibers (closed in 1993) that discharged Hg until 1987 (STLRT 1994).

3.2.2. Environmental contamination

The fish used in the analysis were caught by Ontario Ministry of Natural Resources and analyzed for their Hg concentration by the Ontario Ministry of the Environment. A sample of the epaxial muscle was used for the study using Cold Vapor Atomic Absorption (Document No.: HGBIO-E33057A, 1993). Data gathered included the sampling seasons of 1990 to 1995. The Hg concentrations of fish included in the

analysis, were longer than 15cm reflecting the minimal length of fish that are more likely to be eaten.

The means and standard deviations of Hg concentrations of the fish caught in the St. Lawrence River used in the calculations of safe consumption rates are present in Table 3. Analyses of variance reveal that Hg levels in northern pike are significantly lower in Lake St. Lawrence compared to the other three regions (see chapter 2). Walleye contain significantly higher Hg levels in Lake St. Francis compared to the other regions. The Hg levels are significantly higher in Yellow perch caught in Brockville region compared to the other three regions. Lake St. Lawrence contains the lowest Hg levels in white sucker compared to the higher levels in the Brockville region and highest levels in Lake St. Francis.

3.2.4. Exposure Assessment

Probabilistic calculation was used to evaluate the number of meals per month that can be eaten before being at risk of Hg exposure. ExcelTM version 7.0 (Microsoft Corp., 1992) and Crystal BallTM version 4.0a (Decisioneering Inc., 1993) were used to perform Monte Carlo ingestion rate calculations. The sample size for correlation and Latin Hyper Cube number was set as 500, the maximum number of iterations as 1000 and the initial seed value was set as 109. Probability density functions (PDFs) used to represent the input variables for the risk assessment modeling are presented in Table 4. All Hg concentration in fish was assumed to be methyl Hg.

PDFs were described as the log-normal distribution by a mean and standard deviation. The distribution of Hg concentration for each fish species was tested for log-

normality using Crystal Ball while it was tested by Richardson (1997) for the body weight data.

Individual ingestion rates were calculated for white sucker, yellow perch, walleye and northern pike separately. These series of ingestion rates were calculated for the four regions of the St. Lawrence River. The general equations for assessment of chronic exposure for ingestion were applied (U.S. EPA 1989):

$$\text{Ingestion intake } (\mu\text{g/kg}\cdot\text{day}) = \frac{\text{IC} \cdot \text{IR}}{\text{BW}} \quad (1)$$

Where: IC = Fish Hg concentration ($\mu\text{g/g}$ wet weight)
 IR = Ingestion rate of fish (g/day)
 BW = Body weight (kg)

By equalizing the ingestion intake of Hg to the RfD and TDI of Hg, the safe ingestion rate can be calculated. This analysis was done with the WHO RfD commonly used in Canada, the proposed RfD developed by the U.S. EPA and the new provisional TDI estimated by Health Canada for children and women of child bearing age:

$$\text{Ingestion intake } (\mu\text{g/kg}\cdot\text{day}) = \text{RfD (WHO, } 0,47 \mu\text{g/kg}\cdot\text{day)} \quad (2)$$

$$\text{Ingestion intake } (\mu\text{g/kg}\cdot\text{day}) = \text{RfD (USEPA, } 0,10 \mu\text{g/kg}\cdot\text{day)} \quad (3)$$

$$\text{Ingestion intake } (\mu\text{g/kg}\cdot\text{day}) = \text{RfD (HC, } 0,20 \mu\text{g/kg}\cdot\text{day)} \quad (4)$$

$$\text{IR} = \frac{\text{RfD (WHO, } 0,47 \mu\text{g/kg}\cdot\text{day)} \cdot \text{BW}}{\text{IC}} \quad (5)$$

$$\text{IR} = \frac{\text{RfD (USEPA, } 0,10 \mu\text{g/kg}\cdot\text{day)} \cdot \text{BW}}{\text{IC}} \quad (6)$$

$$\text{IR} = \frac{\text{TDI (HC, } 0,20 \mu\text{g/kg}\cdot\text{day)} \cdot \text{BW}}{\text{IC}} \quad (7)$$

Considering that a regular fish meal is approximately 227g (8 ounces), a calculation can be made to get an average number of meals per month that can be safely consumed for each species of fish caught in the four regions of the St. Lawrence River:

$$\text{Number of meals/month} = (\text{IR (g/day)} \cdot 30.5 \text{ days}) / 227 \text{ g}$$

Table 3. Means and standard deviations of Hg concentrations in the fish caught in the St. Lawrence River.

Region	Species	[Hg] $\mu\text{g/g ww}$		
		Mean	s.d.	N
Thousand Isl.	White sucker	0.16	0.10	25
	Yellow perch	0.17	0.07	61
	Walleye	0.30	0.24	23
	Northern pike	0.51	0.26	73
Brockville	White sucker	0.35	0.15	44
	Yellow perch	0.24	0.11	92
	Northern pike	0.58	0.33	46
Lake St. Lawrence	White sucker	0.13	0.05	13
	Yellow perch	0.16	0.08	66
	Walleye	0.20	0.17	69
	Northern pike	0.42	0.21	54
Lake St. Francis	White sucker	0.24	0.11	28
	Yellow perch	0.17	0.06	51
	Walleye	0.75	0.45	112
	Northern pike	0.53	0.31	55

Table 4. Values of the input for the Probabilistic Risk Assessment Model to calculate the safe consumption rate of fish caught in the St. Lawrence River.

Parameters ^a	Unit	Distribution ^b	Value
Canadian RfD (WHO 1989)	µg/kg·day		0.47
New U.S. EPA RfD (U.S. EPA 1997)	µg/kg·day		0.10
Provisional TDI (HC 1998)	µg/kg·day		
[Hg] fish	µg/g ww	LN	
Body weight	kg	LN	70.0±14.5

^aRfD=Reference Dose and TDI=Tolerable Daily Intake

^bLN=Log-normal distribution

3.3. RESULTS AND DISCUSSION

The safe ingestion rates (meal/month) for different fish species caught in four regions of the St. Lawrence River are presented in Table 5. The mean and 5th percentile of the PDFs were reported to enable comparison with similar studies since they are the results usually presented. These consumption rates apply to female and male adults only, since the average weight of this group (70 kg) was incorporated in the model. The body weight for adults was taken from the 1981 Canada Fitness Survey based on 16,000 individuals of 20 years of age and older (EHD 1993) and is the value used by Health Canada (1994) and U.S. EPA (1991) for regulatory purposes. Since the RfD and TDI are based on a maximum amount of ingested contaminants per Kg of body weight, the allowable meals of fish per month for children would be lower considering their lower weight even if the pTDI of HC in theory can be applied to that population group (see equation 7).

3.3.1. Safe fish consumption patterns

To reduce methyl-Hg exposure, the safest fish consumption pattern would be to eat smaller, lower trophic-level fish. In the worst case scenario, the piscivores like northern pike and walleye should be eaten no more than 3.4, 0.7 and 1.4 times/month (using the WHO, U.S. EPA and HC's pTDI respectively) compared to more than twice these values for omnivorous or benthivorous fish like yellow perch and white sucker. These trends follow the bioaccumulation and biomagnification properties of methyl-Hg (see for e.g. Watras and Bloom 1992).

Table 5. Safe Ingestion rates (meal/month) of different species of fish found in four regions of the St. Lawrence River. The rates of ingestion were calculated probabilistically using the Canadian Reference Dose (0.47 $\mu\text{g}/\text{kg}\cdot\text{day}$), the new U.S. EPA Reference Dose (0.10 $\mu\text{g}/\text{kg}\cdot\text{day}$) and the new provisional Tolerable Daily Intake developed by Health Canada for women of child bearing age and children (0.20 $\mu\text{g}/\text{kg}\cdot\text{day}$). A fish meal represents 227 g (eight ounces) and a month 30.5 days.

Region	Species	Canadian RfD		U.S. EPA RfD		HC pTDI	
		Mean	5%	Mean	5%	Mean	5%
Thousand Isl.	White sucker	31.9	11.6	6.80	2.46	13.6	4.91
	Yellow perch	27.9	13.3	5.93	2.84	11.9	5.67
	Walleye	18.4	5.71	3.91	1.21	7.82	2.43
	Northern pike	9.51	3.97	2.02	0.85	4.05	1.69
Brockville	White sucker	13.5	6.32	2.88	1.34	5.76	2.69
	Yellow perch	19.9	8.97	4.24	1.91	8.47	3.82
	Northern pike	8.60	3.35	1.83	0.71	3.66	1.42
Lake St. Lawrence	White sucker	35.7	17.7	7.60	3.77	15.2	7.54
	Yellow perch	30.0	12.9	6.38	2.74	12.8	5.48
	Walleye	28.6	7.96	6.09	1.69	12.2	3.39
	Northern pike	11.5	4.96	2.44	1.06	4.88	2.11
Lake St. Francis	White sucker	19.8	9.06	4.20	1.93	8.43	3.85
	Yellow perch	27.1	14.1	5.77	3.00	11.5	5.99
	Walleye	6.65	2.55	1.41	0.54	2.83	1.08
	Northern pike	9.45	3.63	2.01	0.77	4.02	1.54

However, it should be noted that even when more than two meals per weeks are allowed for Hg exposure purposes, the Canadian Food Guide recommends not more than 8 meals of fish per month for a balanced diet (OMOE 1997).

The four regions of the St. Lawrence River under scrutiny reflect different safe consumption rates depending on the fish species. For example, more meals/month of walleye can be eaten when caught in the Thousand Islands region compared to the other three regions. Moreover, more white sucker can be eaten from Lake St. Lawrence compared to elsewhere and less yellow perch can be eaten from the Brockville region of the St. Lawrence River compared to elsewhere. No region contained systematically higher Hg contaminated fish species, therefore no region was found to allow a higher consumption rate consistently for all fish species (see Chapter 2).

3.3.2. Limitations and advantages of the model

The choice of a fix meal size of 227g (8oz) to calculate the safe number of meals/month to consume is arbitrary. This is approximately the same meal size used by others to compute risk assessment analysis (MEF and MSS 1995; OMOE 1997). However, it does not necessarily represent the amount consumed by anglers nor does it reflect individual variability. The only accurate measurement of food intake by individuals is by direct weighing of consumed food that makes the method expensive and intrusive for the individuals (Marr 1971; Sanjur 1982). Using the fixed meal size to compute safe consumption rates is valid as long as anglers keep in mind that a meal represents 227 g.

It is also important to keep in mind that treating the meal size deterministically versus probabilistically reduces the variability in the model. Using a distribution of meal size instead of a fixed amount would have elongated the tails of the resulting PDF.

Taking the probabilistic approach would have therefore resulted in a smallest allowable fish ingestion rate making it more conservative compared to the deterministic approach.

The entire Hg concentration data set for each fish species was used to quantify the Hg exposure to humans. Therefore, the Hg levels are dependent on the fish sampled and do not necessarily reflect the size of fish consumed by the anglers. It has been hypothesized that anglers target the larger fish (Hoover et al. 1997). However, the probabilistic approach allows the choice of protecting 95% of the population, the safe consumption rate at this level of protection represents a small individual consuming the highly contaminated fish (longer fish) translating into a conservative approach.

Methyl-Hg exposure was assumed to come solely from fish consumption. Studies estimating the relative importance of Hg exposure pathways (through soil ingestion, breathing air, drinking water) concluded that fish consumption was by far the most significant source of exposure (FAO/WHO 1972; WHO 1976; Clarkson 1990).

However, the consumption of fish should be less than those reported if an individual is in contact with Hg through their occupation.

3.3.3. Comparing safe consumption rates to published Canadian rates

By comparing published fish consumption rates for different groups of the population to the calculated safe fish ingestion rates from the St. Lawrence River, it can be speculated that the riverside populations of fish eaters are at risk. It was calculated that the general

Canadian population consumed 10.43 g of fish/day or 1.4 meal/month (Conacher et al. 1989; HWC 1977). Considering the RfD of the WHO, it can be assumed that the average adult Canadian can consume fish from Thousand Islands to Lake St. Francis. However, the pTDI for women of child bearing age indicates that the average Canadian fish consumption rate is close to or sometimes exceeds the calculated safe consumption rate (Table 5). Moreover, the anglers and First Nation People are known to consume considerably more of this country food. Cox and Johnson (1990) estimated an average daily intake of freshwater fish of 19.69 g/day (2.6 meal/month) for anglers and Nobmann et al. (1992) estimated that First Nation People from Alaska consumed an average of 109 g fish/day (14.6 meal/month). The allowable fish consumption rates using the Canadian RfD, indicates that the anglers are not overexposed to Hg while using the pTDI of Health Canada indicates that women of child bearing age are at risk when walleye and northern pike are consumed. The published consumption rates for First Nation People exceed systematically the safe consumption rates calculated for every fish species with all three RfDs when 95% of the population is protected. The anglers and the First Nation People could be at serious risk.

3.3.4. Implications of the RfDs and pTDI

The number of meals/month that can be safely consumed vary dramatically with the RfD or TDI used in the analysis. For example, to protect 95% of the population, approximately 13, 3 and 6 meals of perch per month can be consumed when the WHO, U.S. EPA and HC's pTDI are applied respectively. Incorporating the new RfD of U.S. EPA of 0.10 $\mu\text{g}/\text{kg}\cdot\text{day}$ would greatly reduce the allowable ingestion rates. Less than a

meal/month of northern pike would be considered safe and up to 3.5 meal/month for white sucker. The average Canadian fish eater would be considered to be at risk when consuming the higher trophic level fish caught anywhere in the St. Lawrence River.

Adopting this new RfD would ask for a slight lowering of the consumption rate of the average Canadian, to reduce by half the fish intake by anglers and women of child bearing age but a complete change in the eating patterns would be required for the First Nation People. Previous fish consumption advisories were associated with worsened social and economic situations (Egeland and Middaugh 1997; Wheatley and Paradis 1996; Shilnyk 1985). Therefore, the benefits of eating fish versus the negative effects of Hg exposure should be considered before implementing this new RfD.

Confusion over fish consumption is reflected in the recent province-wide pamphlet published by a group of three ministries from Québec promoting the beneficial nutritional values of fish while reducing the recommended quantity of fish from 8 to 4 meals per month (MAPA et al. 1998).

Clearly, more information on Hg toxicology is needed to narrow down the range of possible RfDs. Particular attention should also be raised at low level exposure of methyl-Hg since the national consumption rate of fish is close (especially for women of child bearing age) to the maximum allowable exposure to Hg.

CHAPTER 4

CONCLUDING REMARKS

Anthropogenic emissions have increased the naturally occurring Hg found in the environment. Living organisms accumulate Hg by direct exposure to their environment but mostly through the ingestion of food that already contains Hg. Therefore, Hg concentration increases in the food chain so that higher trophic level organisms like piscivore fish and humans contain the highest concentrations. After a certain level of exposure, Hg alters the good functioning of the nervous system and has caused fatalities in extreme conditions.

Since fish consumption is the main route of exposure of Hg to humans, it is important that contaminant levels in fish are monitored. The OME and OMNR fulfilled this mandate by creating the Ontario Sport Fish Contaminant Monitoring Program in 1975. The resulting data set is unique of its kind in its consistency to analyze the Hg concentrations from 1975 to 1995. Such uniformity is critical because it is possible to observe an artificial decrease in Hg levels through time caused by different analytical methods and not by a real decrease in the environment. I am therefore confident in the values of Hg concentrations that I used to detect the temporal trends and spatial variability in fish and to calculate the safe consumption rate of fish from the St. Lawrence River.

A general decrease in Hg concentration was observed for white sucker, yellow perch, walleye and northern pike caught throughout the Ontario portion of the St. Lawrence River. The only exceptions were for northern pike caught in the Brockville sector and Lake St. Lawrence. For northern pike and walleye, the decrease in Hg was observed when the first years of sampling

were compared with later years while for white sucker and more apparently for yellow perch, the decrease was more gradual (from year to year).

The decrease in Hg concentration that I found is concordant with the results of other researchers. Hg in Rainbow smelt, slimy sculpin and lake trout caught in Lake Ontario decreased by half between 1977 and 1988. Similarly, Hg concentrations in yellow perch caught in the eastern section of Lake St. Francis from 1970's to 1990's dropped by 25%. Finally, Hg concentrations in the American eel captured in the estuary of the St. Lawrence River has significantly decreased between 1982 and 1990.

Up to now, researchers have explained the Hg decrease by a lower antropogenic input of Hg in the Cornwall/Ontario, Massena/New York area. However, the reduction in Hg emissions in that area of the St. Lawrence River cannot account for the decrease observed more than 100 km upstream and downstream of that area. I speculate that the Hg decrease in the fish could reflect changes in physical/chemical properties of the St. Lawrence River that could have affected the biogeochemical cycle of Hg. For example, phosphorus levels have decreased considerably since 1969. This could have reduced primary productivity and the rate of bacterial decomposition of organic matter, which could result in less methyl-Hg production.

I found differences in Hg contamination between regions when one of the fish species was considered but no region was found to contain higher contamination for all fish species. This result was surprising since one of my sampling location, Lake St. Francis, was designated an Area of Concern by the International Joint Commission in 1985 due to high Hg concentrations in the sediments.

To reduce methyl-Hg exposure, the safest fish consumption pattern would be to eat smaller, lower trophic-level fish. In the worst case scenario, the piscivores like northern pike and walleye should be eaten no more than 3.4, 0.7 and 1.4 meals/month (using the WHO, U.S. EPA

and HC's pTDI respectively) compared to more than twice these values for omnivorous or benthivorous fish like yellow perch and white sucker. These trends follow the bioaccumulation and biomagnification properties of methyl-Hg.

When the published fish consumption rates for different groups of the population are compared to the calculated safe fish ingestion rates from the St. Lawrence River, it is clear that women of child bearing age and First Nation People could be at risk. The problems originate from different sources for the two groups: women of child bearing age because they are allowed to consume less fish (with the new pTDI) and First Nation People because they consume more fish and exceed the safe consumption rates consistently for every fish species.

The new, more conservative RfDs for Hg would greatly reduce the safe ingestion rate of fish. If put forward, these new reference doses could seriously affect the eating habits of the riverside residents possibly pushing them to consume foods of lower nutritional value or modify their traditional lifestyle. It would also create confusion and possible complete omission of fish from their diets. Clearly, more information on Hg toxicology is needed to narrow down the range of possible RfDs. Particular attention should also be raised at low level methyl-Hg exposure since the national consumption rate of fish is close (especially for women of child bearing age) to the maximum allowable exposure to Hg.

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APPENDIX A

Sample size and the median and range of Hg concentration and total length of northern pike, walleye, yellow perch and white sucker caught in four regions of the Ontario portion of the St. Lawrence River. Data provided by the Ontario Ministry of the Environment and Ontario Ministry of Natural Resources for the Sport Fish Contaminant Monitoring Program (unpublished data).

Region	Species	Year	N	[Hg] ($\mu\text{g/g ww}$)		Total length (cm)			
				Median	Range	Median	Range		
Thousand Isl.	Northern pike	76	14	0.84	0.43-1.60	61.7	47.0-75.6		
		84	20	0.47	0.16-1.10	61.8	44.6-76.5		
		88	14	0.40	0.13-0.84	51.8	42.3-71.1		
		89	19	0.51	0.13-1.00	59.1	44.1-83.0		
		91	29	0.39	0.18-1.20	56.9	48.0-84.6		
		93	23	0.50	0.18-1.10	57.5	46.7-76.0		
		95	19	0.42	0.20-0.93	61.6	50.2-83.8		
		Brockville	White sucker	75	28	0.43	0.16-0.66	43.0	37.8-60.0
				83	58	0.35	0.09-0.67	44.6	37.7-52.5
				84	40	0.32	0.13-0.69	45.0	39.0-52.1
85	20			0.54	0.31-0.70	46.2	42.1-54.7		
86	58			0.47	0.10-0.91	47.3	35.1-59.2		
87	16			0.26	0.07-0.53	45.3	35.5-54.0		
88	60			0.51	0.09-0.87	45.7	39.5-54.9		
92	19			0.39	0.08-0.65	44.9	37.8-52.5		
94	25			0.33	0.07-0.60	47.0	35.4-55.4		
Yellow perch	75			27	0.36	0.19-1.11	21.1	17.6-29.5	
	83		49	0.22	0.10-0.76	22.0	14.2-29.5		
	84		72	0.39	0.12-0.71	24.2	21.1-30.1		
	85		18	0.29	0.17-0.51	23.5	22.4-31.0		
	86		51	0.22	0.07-0.78	20.8	16.5-28.5		
	90		19	0.25	0.10-0.39	23.7	16.0-28.0		
	92		64	0.23	0.06-0.56	18.6	15.0-30.1		
	94		28	0.19	0.13-0.77	21.0	18.7-26.6		
Northern pike	75		24	0.51	0.17-2.00	59.0	37.0-87.0		
	78	23	0.47	0.20-1.50	64.0	38.0-77.5			
	83	44	0.50	0.09-1.20	58.1	40.0-76.2			
	84	60	0.47	0.24-1.30	59.1	39.3-82.2			
	85	19	0.58	0.21-0.99	55.1	47.9-80.9			
	86	50	0.38	0.13-1.40	57.4	40.1-81.8			
	87	20	0.44	0.15-1.70	54.8	40.6-87.5			
	88	59	0.50	0.19-1.30	56.5	45.8-78.5			
	90	20	0.56	0.17-1.20	60.3	47.5-79.0			
	92	26	0.63	0.22-1.10	59.7	47.5-79.0			
94	19	0.37	0.11-1.68	57.5	42.7-72.4				

Lake St. Lawrence	White sucker	75	28	0.43	0.16-0.66	43.0	37.8-60.0	
		77	15	0.44	0.11-0.87	43.4	33.8-64.0	
		85	20	0.07	0.03-0.32	36.2	29.0-43.0	
		87	20	0.12	0.02-0.57	38.1	29.0-44.0	
		89	20	0.11	0.05-0.30	38.0	26.6-43.8	
	Yellow perch	93	13	0.14	0.06-0.26	41.7	27.2-46.5	
		77	25	0.20	0.10-0.72	19.3	13.6-25.5	
		81	19	0.27	0.08-0.67	23.3	16.5-26.8	
		85	20	0.21	0.10-0.47	20.8	15.2-27.5	
		87	20	0.15	0.05-0.30	20.2	15.1-26.1	
		88	10	0.16	0.14-0.24	23.3	18.3-27.4	
		89	20	0.20	0.14-0.46	19.4	15.3-28.7	
		91	20	0.16	0.05-0.38	21.4	16.3-25.2	
		93	26	0.12	0.04-0.38	18.6	14.2-30.0	
		95	20	0.18	0.09-0.33	23.9	20.3-27.0	
	Walleye	81	20	0.18	0.09-0.34	42.6	31.5-53.8	
		85	20	0.18	0.11-0.71	42.4	38.5-63.0	
		86	29	0.49	0.17-0.97	53.6	41.5-60.0	
		87	20	0.14	0.08-0.45	44.9	33.4-59.6	
		88	11	0.51	0.14-1.40	58.3	33.4-74.6	
89		21	0.17	0.12-1.40	43.6	32.5-64.5		
91		23	0.14	0.08-0.92	42.0	31.0-62.0		
93		25	0.12	0.07-0.48	38.2	26.8-61.0		
95		20	0.17	0.09-0.44	43.3	26.5-58.9		
Northern pike		81	21	0.22	0.11-1.30	54.2	32.0-84.5	
	85	28	0.27	0.10-1.10	63.3	47.5-85.5		
	87	11	0.33	0.09-0.65	64.7	51.5-77.6		
	89	20	0.27	0.13-1.00	59.5	40.5-86.0		
	91	20	0.40	0.21-0.88	64.3	50.4-80.5		
	93	14	0.33	0.15-0.93	62.8	54.7-87.1		
	95	20	0.39	0.16-1.00	63.3	54.6-78.5		
Lake St. Francis	White sucker	76	14	0.50	0.20-0.79	47.8	41.0-57.0	
		77	59	0.65	0.21-1.10	46.0	31.0-56.0	
		78	31	0.51	0.24-0.98	44.4	38.1-60.0	
		81	25	0.49	0.22-0.79	53.8	44.1-64.5	
		82	20	0.45	0.24-0.74	49.8	43.6-57.5	
		88	20	0.20	0.09-0.49	44.2	25.8-54.0	
		90	41	0.34	0.09-0.78	45.9	35.2-54.5	
		94	28	0.26	0.07-0.47	47.9	36.8-54.3	
		Yellow perch	77	31	0.39	0.17-1.30	21.5	16.0-29.0
			81	20	0.27	0.22-0.46	22.5	21.3-27.0
	83		28	0.35	0.18-0.62	25.3	22.4-27.5	
	84		61	0.25	0.11-0.72	23.7	14.2-29.3	
	86		20	0.21	0.10-0.49	25.5	18.6-28.3	
	88		20	0.25	0.12-0.55	24.2	14.7-29.2	
	89		38	0.29	0.15-0.54	22.0	18.3-26.0	
	90		40	0.18	0.08-0.54	21.5	18.1-29.0	
	92		31	0.18	0.09-0.32	23.6	18.2-31.5	
	94		20	0.15	0.11-0.21	21.4	18.1-25.5	
	Walleye	76	19	1.00	0.60-3.40	54.0	44.0-75.0	
		77	17	1.20	0.69-2.80	52.0	47.0-60.5	
78		46	0.85	0.30-2.10	49.0	37.9-65.1		
81		21	0.56	0.30-3.40	50.0	31.5-73.8		
82		20	0.65	0.39-2.10	52.6	37.6-72.6		
84		10	0.82	0.58-2.10	55.7	51.7-67.2		
85	20	0.63	0.24-1.30	50.6	38.5-70.0			

	86	20	0.58	0.24-1.90	50.1	38.2-76.5
	88	20	0.71	0.27-1.80	45.6	38.0-57.9
	89	17	0.42	0.24-0.93	41.8	31.0-55.0
	90	28	0.92	0.33-1.50	59.2	42.8-69.9
	91	55	0.77	0.06-1.90	54.0	33.5-75.2
	92	26	0.52	0.20-2.00	54.6	40.2-75.0
	93	20	0.70	0.34-2.00	59.8	44.6-75.7
	94	11	0.38	0.27-1.10	44.9	36.5-63.5
Northern pike	77	40	0.67	0.26-1.20	54.0	37.0-71.0
	81	21	0.71	0.25-1.50	59.2	33.0-77.2
	84	48	0.46	0.18-1.20	52.2	31.4-80.2
	86	17	0.52	0.28-1.60	59.0	38.0-80.7
	88	20	0.47	0.22-1.60	48.8	41.6-59.4
	89	38	0.49	0.16-1.40	49.0	32.5-70.0
	90	20	0.55	0.32-2.60	59.2	42.0-92.0
	92	25	0.51	0.20-1.30	60.4	47.6-89.2
	94	30	0.39	0.20-1.20	58.2	40.2-82.5

APPENDIX B

Sample size and the median and range of Hg concentration and total length of northern pike, walleye, yellow perch and white sucker caught in four regions of the Ontario portion of the St. Lawrence River from 1991 to 1995. Data provided by the Ontario Ministry of the Environment and Ontario Ministry of Natural Resources for the Sport Fish Contaminant Monitoring Program (unpublished data).

Species	Region	N	[Hg] ($\mu\text{g/g ww}$)		Total length (cm)	
			Median	Range	Median	Range
White sucker	Thousand Isl.	25	0.13	0.03-0.36	47.0	36.5-65.5
	Brockville	44	0.34	0.07-0.65	46.7	35.4-55.4
	Lake St.Lawrence	13	0.14	0.06-0.26	41.7	27.2-46.5
	Lake St. Francis	28	0.26	0.07-0.47	47.9	36.8-54.3
Yellow perch	Thousand Isl.	61	0.16	0.05-0.37	20.8	12.2-26.7
	Brockville	92	0.22	0.06-0.77	19.2	15.0-30.1
	Lake St.Lawrence	66	0.15	0.04-0.38	22.1	14.2-30.0
	Lake St. Francis	51	0.17	0.09-0.32	22.7	18.1-31.5
Walleye	Thousand Isl.	23	0.26	0.06-0.87	47.9	26.2-71.0
	Lake St.Lawrence	69	0.14	0.07-0.92	41.0	19.0-62.0
	Lake St. Francis	112	0.63	0.06-2.00	54.0	33.5-75.7
Northern pike	Thousand Isl.	73	0.42	0.18-1.20	57.8	19.2-84.6
	Brockville	46	0.54	0.11-1.68	59.3	27.5-79.0
	Lake St.Lawrence	54	0.38	0.15-1.00	63.8	50.4-87.1
	Lake St. Francis	55	0.40	0.20-1.30	59.0	40.2-89.2

APPENDIX C

Results of the analysis of variance (DF=degrees of freedom) for each term included in the general linear model verifying for temporal variability. The data is reported for each fish species caught in four regions of the Ontario portion of the St. Lawrence River from 1975 to 1995.

Region	Species	Term	N	DF	F-ratio	P
Thousand Islands	Northern pike	Length	139	1	129	<0.005
		Year	139	6	0.52	0.79
		Length*year	139	6	0.54	0.78
Brockville	White sucker	Length	324	1	60.5	<0.005
		Year	324	8	1.44	0.179
		Length*year	324	8	1.31	0.239
	Yellow perch	Length	328	1	76.4	<0.005
		Year	328	7	3.23	0.003
		Length*year	328	7	3.47	0.001
	Northern pike	Length	365	1	201	<0.005
		Year	365	10	3.73	<0.005
		Length*year	365	10	3.69	<0.005
Lake St.Lawrence	White sucker	Length	114	1	76.6	<0.005
		Year	114	5	5.44	<0.005
		Length*year	114	5	5.14	<0.005
	Yellow perch	Length	180	1	74.3	<0.005
		Year	180	8	2.59	0.011
		Length*year	180	8	2.83	0.024
	Northern pike	Length	134	1	141	<0.005
		Year	134	6	2.54	0.024
		Length*year	134	6	2.37	0.034

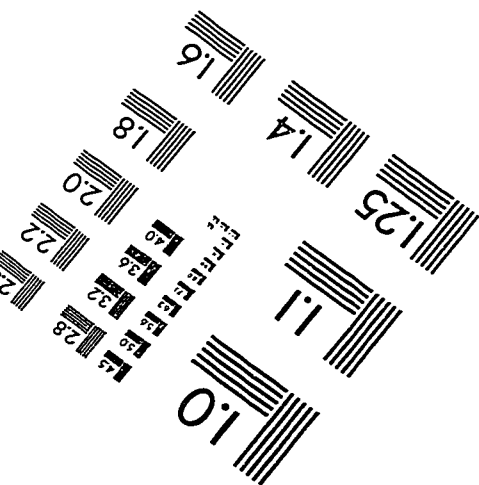
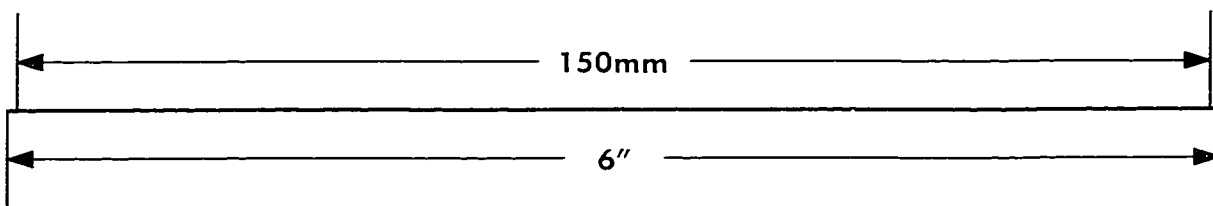
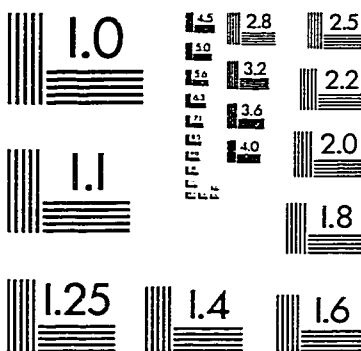
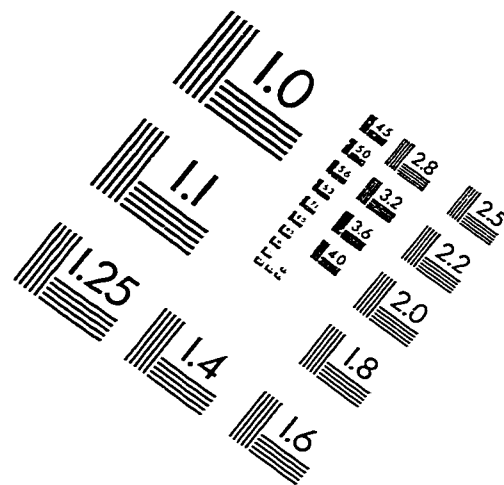
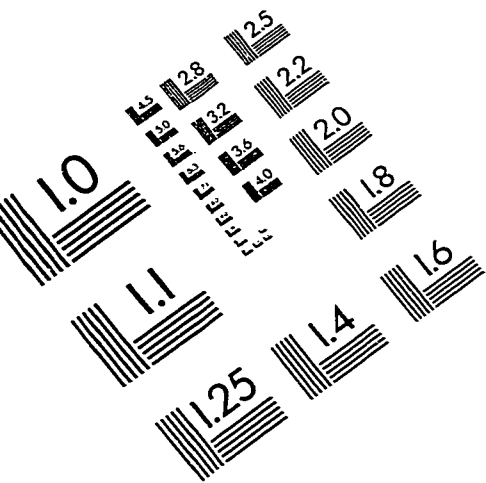
Lake St. Francis	White sucker	Length	237	1	67.0	<0.005
		Year	237	7	6.30	<0.005
		Length*year	237	7	5.62	<0.005
	Yellow perch	Length	309	1	81.7	<0.005
		Year	309	9	1.40	0.188
		Length*year	309	9	1.62	0.107
	Walleye	Length	349	1	193	<0.005
		Year	349	14	5.79	<0.005
		Length*year	349	14	5.62	<0.005
Northern pike	Length	258	1	154	<0.005	
	Year	258	8	1.89	0.063	
	Length*year	258	8	1.64	0.114	

APPENDIX D

Results of the analysis of variance (DF=degrees of freedom) for each term included in the general linear model verifying for spatial variability. The data is reported for each fish species caught in four regions of the Ontario portion of the St. Lawrence River during 1990 to 1995.

Species	Term	N	DF	F-ratio	P
White sucker	Length	110	1	70.5	<0.005
	Region	110	3	3.31	0.023
	Length*region	110	3	3.01	0.034
Yellow perch	Length	270	1	76.2	<0.005
	Region	270	3	4.49	0.004
	Length*region	270	3	4.11	0.007
Walleye	Length	204	1	424	<0.005
	Region	204	2	2.85	0.060
	Length*region	204	2	4.71	0.010
Northern pike	Length	227	1	175	<0.005
	Region	227	3	0.75	0.521
	Length*region	227	3	0.58	0.628

IMAGE EVALUATION TEST TARGET (QA-3)



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