MERCURY MASS BALANCE AND UPTAKE BY FISH

IN ACID LAKE ECOSYSTEMS

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MERCURY IN ACID LAKE ECOSYSTEMS

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ABSTRACT

The phenomenon of increasing the mercury body burdens of fish, on a lake to lake basis with decreasing pH, is found to exist. Although the interactions between fish, the ecosystem, water chemistry and other variables are extremely complex, a simple conceptual solution is established to explain why mercury uptake by fish increases with decreasing pH.

A study on mercury in an acid lake watershed ecosystem (near Espanola, Ontario) was done as a precursor exercise. Mercury concentrations of various ecosystem compartments are within the ranges of values found by other workers for other systems. All values found are considered background or below background. For this type of lake-watershed system, the main mercury repository is the watershed soils and overburden materials. The main mercury fluxes are from the atmosphere to the soils and from the soils, via streams and groundwater, to the lake. The net result is that the watershed is being depleted in mercury at the rate of about 30 μ g m⁻² yr⁻¹. This mercury is apparently ending up in the lake water, seston or sediments.

According to well established thermodynamic equilibria, pH, together with pCl, govern the speciation of inorganic mercury in freshwater inorganic systems. Under certain specific conditions of pH and pCl, the non-toxic mercury species $Hg(OH)_2^{\circ}$ exists, while under other conditions, most_notably depressed pH, the biologically mobile and easily methylated $HgCl_2^{\circ}$ exists. It is shown

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here that lakes whose pH and pCl are such that the dominant mercury species will exist as $HgCl_2^{\circ}$ contain fish with higher mercury concentrations than lakes whose dominant mercury species exists in the form $Hg(OH)_2^{\circ}$. This suggests that the more $HgCl_2^{\circ}$ that is available, the more mercury will either be methylated and taken up by fish, or taken up directly, and probably methylated <u>in vivo</u>.

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MERCURY MASS BALANCE AND UPTAKE BY FISH IN ACID LAKE ECOSYSTEMS

CHAPTER 1 INTRODUCTION

1.1 · BACKGROUND

Statistical correlations have been made over the last several years linking elevated fish mercury concentrations with acid lakes (Scheider <u>et al</u> 1978). Many of these watersheds appear to have no excess natural or anthropogenic mercury associated with them (Armstrong and Hamilton 1973). Various studies (Jernelöv <u>et al</u> 1975, Scheider <u>et al</u> 1978, McFarlane and Franzin 1980) suggest that high fish mercury levels may result from low pH, low calcium and low alkalinity lake waters. The non-calcareous terrain where the phenomenon has been observed lies in portions of the Canadian Shield, Grenville Province and Appalachian Mountains. These areas contain crystalline rocks which are low or void of calcium carbonate, giving rise to low alkalinity lake waters. These waters' have little or no ability to buffer inputs of acidic precipitation, and hence some of them have depressed pH's (i.e., as low as 4).

Not all low pH (<6) aquatic systems exhibit this phenomenon of increased mercury uptake by fish, and the phenomenon apparently does not exist in any hardwater lakes (i.e., calcium carbonate buffered, pH >7). The lakes in which the phenomenon occurs seem to all have similar characteristics:

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- low pH (<7)

- low alkalinity (<15 mgCaCO₂L⁻¹)

- very soft water (low Ca, Mg i.e., <10 mgL⁻¹)

- background or below background mercury concentrations throughout the abiotic system (<100 μ gkg⁻¹ solids, <0.50 μ gL⁻¹ water)

- possibly acid stressed fish populations

No satisfactory deductive explanation or model for an uptake mechanism of mercury into fish has yet been described for the conditions encountered in these lakes relative to lakes of similar chemistry but without mercury enhancement in fish.

1.2 OBJECTIVES

The objectives of this study include:

- summarizing from the current literature the state-of-the-art knowledge of mercury uptake by fish

- determining the concentration of mercury in various ecosystem compartments of a small, simplified acid lake watershed

- showing that the phenomenon of enhanced mercury uptake in fish in relation to pH and alkalinity actually exists (some recent studies appear to doubt this relationship)

- arriving at a simple conceptual relationship between mercury in fish and pH and alkalinity

- determining what other factors, besides pH and alkalinity, affect

mercury uptake by fish

- explaining how the uptake mechanism, as governed by these controls, might operate

1.3 PROBLEM DEFINITION

Links between low pH and mercury uptake in fish have been described. There are, however, inconsistencies in the various studies.

Konrad (1971) compared the levels of total mercury in sediment against those of fish from the same area in various river systems; he concluded that levels in fish were high whenever the pH of the sediment and water were below 7. Drummond <u>et al</u> (1974) in a study on brook trout, showed that fish had a greater cough frequency (a measure of the fish's response to stress induced by methyl mercuric chloride and other toxic substances) at a pH of 6 compared to a pH of 7.5. Cough response to mercuric chloride was not affected by lowered pH. Fish exposed to methyl mercuric chloride at pH 6 contained more total mercury in their gills and red blood cells than fish tested at pH 9. Mercuric chloride uptake did not significantly differ at pH 6 and 9.

A laboratory study by Tsai <u>et al</u> (1975) also showed a correlation between mercury uptake by fish and ambient solution pH. The results of this experiment are shown in Figure 1.1. Clearly, the uptake changes with pH; uptake increases rapidly as pH is depressed below 6. The water mercury concentrations used in this study were quite high, about 1 mgL⁻¹ and do not



Figure 1.1 The effect of pH on the uptake of mercury by fish, from Tsai <u>et al</u> (1975). For both fish species tested, uptake of mercury increases with decreasing pH. Buffers were used to establish and maintain constant pH in aquaria. Fish were exposed to 1.5 ppm mercuric chloride for 15 minutes.

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Figure 1.2 The effect of alkalinity on fish mercury content, from Scheider <u>et al</u> (1978). Walleye mercury concentrations were determined for 10 soft water lakes and 11 hardwater lakes. For any given fish length; mean fish mercury contents are systematically higher for low alkalinity lakes as compared to higher alkalinity lakes. compare to natural concentrations of water mercury at, typically, less than 0.1 ng g^{-1} .

Kleinert and Degurse (1971) were among the first to infer that low alkalinity favoured mercury accumulation by fish. Scheider <u>et al</u> (1978) showed an inverse correlation between alkalinity and mercury content of fish in Ontario lakes (Figure 1.2); they show that fish in low alkalinity lakes can generally be expected to contain more mercury than fish in high alkalinity lakes. Almer <u>et al</u> (1978) found a negative relationship between pH of lake water and mercury levels in fish for lakes of no known point sources of mercury.

Miller and Akagi (1979) suggested that pH affects <u>distribution</u> of methylmercury in the aquatic environment and not uptake.

A wide range of pHs (4 - 9) and alkalinities (see Figure 1.2) were used in both of the above studies to obtain the correlations with mercury uptake. Suns <u>et al</u> (1980) investigated uptake in a more narrow range of pHs and alkalinities. Except for two hardwater lakes, softwater lakes with pHs between 5.1 and 6.6 and alkalinities between 0.5 and 7.5 mg L⁻¹ CaCO₃ were chosen for study. The lakes, within 20 km of each other in north-central Ontario, had wide ranging fish mercury values. Fish studied were yearling perch. Suns found a statistical correlation between mercury in fish and epilimnetic pH and aluminum. Suns found no correlation between mercury in fish and lake alkalinities, opposite to the Scheider study. Suns also found no correlation between fish mercury and the total organic carbon of the lake water, opposite to a previous study by Cline and Upchurch (1973), and total phosphorus and manganese, as had been

shown by Drummond <u>et al</u> (1974). Further, he found no correlation between mercury in fish and fish weights and sizes, opposite to a study by Scott (1974) or fish lipid contents. The strongest correlations were found between mercury in fish and the ratios derived from drainage area/lake volume suggesting that, besides low epilimnetic pH, terrestrial discharges of mercury to the study lakes have enhanced mercury uptake in the fish. Therefore, correlation of mercury content of fish may reflect merely the importance of terrestrial factors or lake loading.

Although noting the existence of the increased fish mercury versus depressed pH phenomenon, the Suns study offered no reasons to satisfactorily explain the phenomenon. All the above papers were reviewed by Watson <u>et al</u> (1980), who stated succinctly:

"The mechanism(s) by which pH affects mercury uptake of fish..... is not clear."

The Watson <u>et al</u> (1980) study is the most comprehensive laboratory study to date. Watson concluded that there are other factors, besides acidity, that contribute to the accumulation of methyl mercury in the walleye used in their experiments. They suggest unspecified water quality parameters, unknown other factors and methylation rates may affect the accumulation of mercury in fish. They did not investigate these aspects further. Their study was done in lake column simulators containing no sediment or suspended load, and hence they could not evaluate the effect of these important ecosystem niches. They state in their summary:

"Results of this study suggest that mercury uptake by

fish in acid-stressed waters may not be greater than for those in pH neutral areas as currently hypothesized. A more efficient metabolism in fish and zooplankton at neutral pH may have contributed to the enhanced methyl mercury uptake".

On the other hand, Häkanson (1980) states:

"It is well established that the mercury content in fish.....can be qualitatively linked to the pH, trophic level and mercury contamination of the water system."

Wren and MacCrimmon (1982), in a study on sunfish in Ontario Lakes, also found a significant positive correlation between increasing fish mercury levels and decreasing lake water pH.

Megraw and Mathews (1982) in studying lakes in Quebec, also found a similar relationship between fish and pH, and found that lake water calcium concentrations were negatively correlated with fish mercury.

The effect of decreased calcium on increasing fish mercury contents was studied in greater detail by Rodgers and Beamish (1982) who suggest:

"As the principal ions responsible for water hardness, Ca²⁺ and Mg²⁺, also markedly affect cellular permeability, these changes in uptake.....(increased uptake of mercury in soft water).....likely affect

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alterations at the cellular level. The increased efficiency of uptake of methyl mercury observed in soft water suggests that the reported increased methyl mercury concentrations attained by fish in lakes of low alkalinity and pH may be due to the effects of hardness rather than pH."

A further study (Rodgers and Beamish 1983) found that the relative efficiency of methylmercury uptake by rainbow trout in soft water was more than double that measured in hard water. Also, when $HgCl_2$ was added to the system, uptake of CH_3HgCl was further enhanced (in both hard and soft water). They found that zinc sulphate decreased the relative efficiency of methylmercury uptake. Rodgers and Beamish state:

> "....calcium-dependent changes in gill permeability may explain elevated methylmercury residues observed in fish from lakes of low alkalinity and pH."

In review:

1)

2)

- it has been shown that decreasing the pH of a water increases the uptake of mercury by fish (Tsai <u>et al</u> (1975) in a seston-free laboratory system
- but it has also been shown that decreasing the pH of water does not have any significant effect on uptake of mercury by fish (Watson <u>et al</u> 1980) in a seston-free bench-scale system

3) Scheider <u>et al</u> (1978) in a field study have shown that decreasing the alkalinity of a water increases the uptake of mercury by

fish.

4)

5)

Rodgers and Beamish (1982) in a field study, have concluded that decreasing the hardness of a water increases the uptake of mercury by fish

Rodgers and Beamish (1983) in a lab study, have shown that methylmercury uptake efficiency is double in soft waters as compared to hard waters and that this is due to changes in gill permeability

McLean <u>et al</u> (1979) and Tomlinson <u>et al</u> (1980) were summarized by Stokes <u>et al</u> (1983) who state that increases in fish mercury with lower pH may be the result of any or all of the factors listed below: a) chemical

i. increased scavenging of methyl mercury and other mercury compounds from the atmosphere by low pH aerosols, clouds and rain

ii. relatively higher production of the bioaccumulable monomethyl mercury species at low pH compared with the more volatile dimethyl mercury

iii. increased desorption of mercury species from solids into water and resulting increased bio-availability

iv. greater absorption of mercury from the atmosphere by low pH receiving water

v. decreased re-emission to the atmosphere from low AH water b) biological

i. reproductive failure and decreased food supply for fish in acidified water

ii. increase in the amount of water passing over the gills of foraging

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fish with decreased food availability can result in greater methyl mercury uptake per unit weight increase

iii. accelerated biomagnification if piscovores are forced to feed on larger fish which have higher mercury content than small younger fish

iv. decreased biomass of fish per unit volume of water produces greater mercury per unit weight of remaining biomass

There are other variables and processes, besides simply pH, alkalinity and hardness, which may play a role in mercury uptake and retention in fish. These other variables include:

- temperature

- food chain effects

- fish populations stressed by depressed pH lakewaters

- ambient faqueous geochemistry, including amount (concentration and/or activity) and speciation of mercury

- sestonic processes and concentrations, including particulates as substrates for methylation to occur (related to lake trophic state)

- bacterial types and amounts in sediments

- watershed characteristics

- effects of nutrients

This research considers plausible mechanisms connected with depressed pH and the associated hardness and alkalinity which may affect an ecosystem, so that mercury, flowing through the system, is concentrated in the fish. The research is based on the observation that only certain low pH lakes exhibit anomalous mercury elevations in fish.

1.4 APPROACH

In order to arrive at the stated objectives of this study, the following approach was utilized.

A comprehensive literature search was undertaken to determine what the current level of understanding on this subject was. As the study progressed, new research by others was being published, and this information was also reviewed in order to maintain a state-of-the-art understanding of the topic.

A field program was initiated to determine as comprehensively as possible, within the constraints of time and economics, the levels of mercury in various ecosystem compartments in an acid lake watershed. This was considered fundamental in that no further discussion on mercury in acid lakes would be valid without a sound understanding of where, exactly, mercury exists and in what concentration

It was subsequently discovered that, after the initial field survey to determine ecosystem mercury concentrations, a rudimentary mass balance on mercury in this watershed could be done.

The next task was to test whether the relationship between enhanced mercury uptake in fish is related to lake water pH and alkalinity. This was accomplished using Ontario Ministry of the Environment fish mercury data and performing a water chemistry field study on the lakes chosen. The lakes were selected for study on the basis of geological setting and availability of fish ⁹

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mercury data for the fish species walleye.

After showing that the phenomenon clearly does exist, a more detailed study was undertaken to determine the extent of influence of mercury uptake by other factors, those which have traditionally been shown to affect • uptake. In addition, further investigation was carried out to determine the effects of lake trophic state and mercury speciation.

A plausible deductive explanation of the mechanism of uptake is then developed from the study.

CHAPTER 2

CURRENT STATE OF KNOWLEDGE OF MERCURY FLOW THROUGH THE ECOSYSTEM

2.0 INTRODUCTION

The following is a review of the literature pertinent to the present study. As will become apparent, a large amount of work has been performed on the environmental aspects of mercury, especially in fish uptake. In one area of research, food chain versus gill uptake, there appears to be an ongoing controversy. There is disagreement by workers in other areas as well.

This survey briefly looks at cycling of mercury in nature, common means of mobilizing mercury, such as methylation, desorption from sediments or particulates and complexation. Relative to fish uptake of mercury, areas discussed are food chain versus gill uptake, ⁶temperature, age and growth effects, lake water chemistry and acid stress effects.

2.1 SOURCES AND SINKS

A pathway approach is employed in this study. Each portion of the pathway is governed by several factors. As depicted in Figure 2.1, lithology is





Factors affecting mercury distribution in an acid lake interconnected, however only the pathway from source (rocks) to sink (fish) is shown. Feedback mechanisms, such as from fish back to the sediments, are not depicted. All compartments are type ecosystem. Figure 2.1

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the primary stage in this simplified system and is a fundamental source of mercury. Lithology indirectly controls water chemisty, through soil and sediment composition.

Figure 2.1 simplistically depicts the various niches present in an acid lake type ecosystem. Each compartment is a source of mercury for the next more ecologically complex compartment and a sink of mercury for the adjacent less ecologically complex compartment. Mercury is recyled to the sediments by decomposed biota. This is an important feedback aspect of the system. Figure 2.2 depicts how complicated compartment to compartment cycling may be in nature.

2.2 MOBILIZATION, TRANSPORT AND UPTAKE BY FISH

2.2.1 Methylation - A Common Means of Mobilization

Jensen and Jernelöv (1969), Spangler <u>et al</u> (1973a,b) and Hamdy and Noyes (1975) have shown that sediment dwelling bacteria have the ability to methylate mercury. Summers and Silver (1978) indicate that there is still some uncertainty about the actual reaction mechanism involved and whether mono or dimethyl mercury is the primary product.

Fagerström and Jernelöv (1971) found that under aerobic conditions, methyl mercury can be formed from pure mercuric sulphate. Studies stemming from this work (Fagerström and Jernelöv 1972) showed that the pH of the



2. Residence times in years (y) and months (m) are tons/day. Immobilized tonnage (in represent for each of mercury metric t) is shown below each compartment. and arrowpoints are the sink Dots ·are routes cycle (1973). on the above each compartment. The Kothny Numbers from Figure 2.2 sources na ture, route.

Figure 2.3 The effect of pH on the formation of methyl mercury species, (Fagerström and Jernelöv 1972). The more toxic monomethyl species is maximized at a pH of about 5.8 while the less toxic dimethyl form predominates at higher pHs.

water controls the ratio of mono to dimethylmercury. As shown in Figure 2.3, the more toxic monomethyl species is formed preferentially over the dimethyl species under acidic pHs, with the maximum monomethyl form occurring at pH 5.8. Concerning the differences in toxicity between mono and dimethylmercury, Fagerström and Jernelöv (1972) state:

"If monomethylmercury is formed it will be released into the water and accumulated into living organisms. If dimethylmercury is formed it might evaporate to the atmosphere."

Yet less than 1% of atmospheric mercury is in the dimethyl form (Summers and Silver 1978).

There have been numerous studies on the rate of methylation. Methylation rates have been shown to be increased by:

> -increasing microbiological activity (Jensen and Jernelöv 1969) -increasing temperature (Jensen and Jernelöv 1969)

Other controls and their effects are:

-site of occurrence - methylation rate is higher in suspended materials and upper layer of sediment than in deeper sediments (Jernelöv 1970)

-decreasing oxygen content of water (indirect control on microbial activity)

Demethylation can also occur in water and sediments by: -photochemical decomposition (Baughman <u>et al</u> 1973, Inoko 1981) -microbial means (Spangler <u>et al</u> 1973a,b; Billen <u>et al</u> 1974; Batti et <u>'al</u> 1975; Shariot <u>et al</u> 1979; Mason <u>et al</u> 1979)

Inoko showed that ultraviolet light decomposed methylmercury (II) chloride to mercury (I) chloride, metallic mercury, ethane and monochloromethane, the initial first-order kinetic reaction being '

CH₃HgCl ----uv----> CH₃ + HgCl

It appears that UV cannot break the bond between Hg and Cl in the methylmercury (II) chloride molecule.

Jernelöv (1975) summarized the kinetic studies of Bisogni and Lawrence (1973):

a) monomethyl mercury is the predominant form of methyl species near neutral pH values

b) the rate of methylation is higher in aerobic systems than in anaerobic systems for a given inorganic mercury concentration and microbial growth rate (this may be due to anaerobic conditions converting any sulphur present to sulphide, forming HgS, which is extremely insoluble and relatively more resistant to methylation)

c) higher microbial growth produces higher methylation rates under aerobic as well as anaerobic conditions

d) methylation rates could be hampered by the addition of sulphide to some anaerobic systems. Also, under aerobic conditions, HgS may be oxidized to the sulphate, which may then be methylated

e) temperature affects methylation rates in accordance with its effects on the metabolic rate of the methylating organism

Gillespie and Scott (1971) showed that mercuric sulphide in sediment was very slowly mobilized and picked up by fish under aerobic conditions. No mechanism of uptake was described. Gillespie (1972) found that under aerobic conditions fish accumulated little mercury from sediments to which mercury chloride or sulphide had been added, but total mercury rose rapidly in fish exposed to sediments containing metallic mercury. In the presence of metallic mercury, the methyl mercury present in the fish was 30% of the total mercury, for mercuric chloride 40%, and sulphide 45%. In the presence of anaerobic sediments, uptake of mercury by fish was low and only mercuric chloride was significantly methylated, to the extent of 40% of the total mercury in the fish. Furutani and Rudd (1980) showed that there was active methylation in the presence of HgS bound as a sulphide in sediments of mercury contaminated Clay Lake (Ontario).

2.2.2 Other Means of Mobilization

Reimers <u>et al</u> (1974) suggest four aqueous transport mechanisms of mercury in sediments:

1) natural solubility of mercury

2) complexation of mercury with chloride, sulphur, clays and organics, and hence possible physical transport

3) changes in dissolved oxygen content causing minimal release of mercury and increased solubility of elemental mercury

 changes in pH causing the solubilization of mercury-humate complexes

An extensive study on the kinetics of mercury adsorption and desorption in sediments has been carried out by Reimers and Krenkel (1974). In reference to the work of Trost and Bisque (1970), and Andersson (1970), they state that if mercury is in a nonpolar and nonionic form, organic humus in the sediments tends to adsorb the mercury. Ionic mercury tends to be adsorbed by clays. For studies on the effect of organics on sediments, the Reimers group investigated carboxyl, amine and mercaptan groups. Each of the organic chemicals were long chain alkanes, which are insoluble in water, with a single functional group. The compounds used were stearic acid $(R-C^{=O}_{-H})$, octadecylamine $(R-NH_2)$ and dodecanethiol (R-SH).

Reimers and Krenkel (1974) arrive at the following conclusions:

I. at a constant pH value, the adsorption of inorganic mercury is definitely affected by the chloride concentration with a 20% to 100% loss in sediment adsorption capacity, depending on the constituents of the sediments (sands, clays or organics)

2. for the materials listed, the uptake rate and capacity of inorganic mercury is given in the following order:

R-SH >> illite > montmorillonite > R-NH₂ > kaolinite >

 $R-C^{=O}_{-H}$ > fine sand > medium sand > coarse sand

3. four materials found in natural sediments were observed to absorb methyl mercury, and they did so in the following order:

R-SH >> illite > montmorillonite >> fine sand

4. amines and carboxyl functional groups on organics have a lower capacity for binding inorganic mercury than do the natural clays, illite and montmorillonite

Hydrogen sulphide may be evolved in anoxic, sulphur-containing lake sediments (Aston and Chester 1976). To this end, Craig and Bartlett (1978) found that monomethyl mercury species in sediments may be mobilized into the atmosphere as dimethyl mercury if H_2S is generated in the sediments.

Furutani and Rudd (1980), in studying a mercury contaminated system (Clay Lake, Ontario), found that periods of methylation in the water column coincided with surface sediment methylation and appeared to be related to overall microbial activity. They found that, in at least one anoxic area of this lake, mercury entering on particulates was probably methylated before it could form mercuric sulphide.

Several studies have been performed on the relationship between mercury and humic acid. Bongers and Khattak (1972) have shown that anaerobic sediments treated with ionic mercury release elemental mercury. Also, Strohal and Huljev (1971) have shown that mercuric ions form a strong but reversible complex with humic acid. Alberts <u>et al</u> (1974) combined the results of these two studies, and with further experimentation, concluded that elemental mercury is formed in aqueous solution by the chemical reduction of mercuric ion in the presence of humic acid. This was corroborated in a later study by Miller <u>et al</u> (1975), who observed the mobilization of mercury from freshwater sediments.

Cline <u>et al</u> (1973) studied mercury mobilization as organic complexes. The following conclusions were reached:

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- low specific gravity organic flocs may be as important as soluble organic metal complexes with respect to mobilization and transport of mercury

in natural waters

- mercury concentration and organic carbon content of sediment pore water were directly correlated

In a study by Hahne and Kroontje (1973), it was shown that little or no Hg(II) is adsorbed by montmorillonite, illite or kaolinite from water containing $HgCl_2^{\circ}$. (predominantly) at [Cl⁻] between $10^{-4.4}$ and $10^{-3.4}$ M (1.4 to 14 mgL⁻¹) and pHs between 3.7 and 4.9.

Inoue and Munemori (1979) showed that at [CI] less than $10^{-3.5}$, Hg(II) is likely coprecipitated with iron(III) hydroxide. It appears that larger amounts of chloride (> 10^{-3} M) suppressed coprecipitation and favoured the formation of HgCl₂° which remained in solution.

These same conclusions were also reached by Avotins <u>et al</u> (1975) who used a simple ion exchange isotherm based on the process

 $2H^{+}_{adsorbed} + Hg^{2+}_{aq} = 2H^{+}_{aq} + Hg^{2+}_{adsorbed}$ to account for absorption density quantitatively onto hydrous ferric oxide for equilibrium total dissolved mercury concentration from 10^{-4} to 10^{-9} M (20 mgL⁻¹ to 200 ngL⁻¹), [CI⁻] from 0 to 1.0 M and pH from 4 to 11 in an organic free water solution.

Armstrong and Hamilton (1973) found in a study on the Wabigoon River that up to 75% of the total mercury in the water was associated with the particulate fraction and "the correlation of mercury and iron may result from a coprecipitation phenomenon, or more likely from the fact that both metals are associated with organic matter".

James and MacNaughton (1977) suggest that uptake of mercury onto clays is strongly pH dependent and usually occurs over a narrow pH range. Inoue and Munemori (1979) found that as pH decreased in the range 10 to 4, the percentage of particulate sorbed mercury dropped from about 90% to about 10%.

Ion exchange onto a substrate such as humic acid would occur with the release of an H^+ -ion (Gjessing 1975), a typical reaction being: $(OH)^R^{(CO OH)} + Hg ----> (OH)^R^{(COO - Hg)} + H^+$ humic acid humic-mercury complex

Kerndorff and Schnitzer (1980), in a more detailed study on the sorption of metals on humic acid found that at pHs of 2.4, 3.7, 4.7 and 5.8 mercury (and iron) were most readily sorbed by humic acid of 11 metals studied. They found no correlation between metal sorption affinity to humic acid and atomic weight, atomic number, valency or crystal and hydrated ionic radii.

2.2.3 Factors Other Than pH, Alkalinity or Hardness Which Control the Uptake of Mercury by Fish

2.2.3.1 Foodchain versus gill uptake

Other aspects such as food chain versus gill uptake, temperature effects, age and growth effects and water chemistry effects affect mercury

uptake by fish. Huckabee et al (1975) summed up the literature thusly:

"Where do fish get their methyl mercury body burdens; from the water, from their food, from their own bacterial flora independent of the sediment, or any combination of these?".

Evidence for the magnification of mercury concentrations through the trophic levels has been reported by many investigators (Peakall and Lovett 1972, Klemmer and Luoma 1973, Cunningham and Tripp 1975a, Caracciolo <u>et al</u> 1975). Others, however, suggest that biomagnification of mercury through the food chain does not occur to any significant extent (Jernelöv and Lann 1971, Leatherland <u>et al</u> 1973, Williams and Weiss 1973, Westoo 1973).

Jernelöv (1972) established that non-predator fish, such as the whitefish, obtain about 10% of their mercury body burdens through food and 90% through their gills. In predator fish, such as pike, Jernelöv concluded that about 50% is taken up by food, most of which is fish. Since 90% of the mercury present in the ingested fish had been taken in through the gills, and at least half of the mercury in the predator fish, he concluded that the important primary mechanism of intake is through the gills.

Studies at lower trophic levels, such as bacterial or protozoan (Colwell <u>et al</u> 1975) suggest the food chain is the most important route at these levels. Colwell's group showed that an Hg-labelled bacterim, <u>Pseudomonas</u>, can be taken up by a bactiverous ciliate, <u>Keronopsis pulchra</u>, with a resultant increase in mercury concentration in the ciliate. Huckabee <u>et al</u> (1975) also

suggest that direct uptake is predominant at lower trophic levels (i.e., zooplankton) but food chain uptake is more significant at higher (fish) trophic levels.

Olson <u>et al</u> (1973) showed that uptake of $HgCl_2$ or CH_3HgCl by trout can be largely through the gills since uptake was not affected by esophetigeal ligation. They also showed that methyl mercury enters the fish at a faster rate than the inorganic form and anomalous tissue distribution of these two forms suggest that inorganic mercury does not require methylation prior to entry into the fish. On the other hand, Lock (1975) has an opposite view. He states:

> "Although aquatic organisms are capable of rapidly removing methyl mercury from water, it is concluded that organisms accumulate most of their methyl mercury burdens from food since practically all methyl mercury is complexed to organic matter. Dissolved methyl mercury in water is only present in extremely low concentrations (below 1 ng HgL⁻¹) and cannot account for the methyl mercury burden found in organisms of higher trophic levels."

Lock suggests that the rate of direct uptake is faster than food chain uptake, but food chain uptake accounts for 5 - 10 times the total amount of methyl mercury transferred, when compared to gill uptake.

In vivo methylation was studied by Rudd <u>et al</u> (1980b). This group studied pristine and mercury polluted lakes and found that intestinal contents of

fish from these lakes were capable of converting Hg^{2+} to methylmercury. It is suggested that bacterial activity in the intestinal material is the likely cause of this methylation. These findings were contrary to a previous study by Pennacchioni <u>et al</u> (1976).

Olson <u>et al</u> (1975) studied uptake of methyl mercury by fathead minnows and found that as the nominal concentration of mercury in the test water increased, so did the mean mercury concentration of the fish, but non-linearly. This is opposite to findings others discussed earlier. Olson's group concluded that the uptake was via food since it was observed that the minnows were eating periphyton growing in the test chambers, and periphyton are known to concentrate mercury (Johnels <u>et al</u> 1968). Huckabee <u>et al</u> (1975), in studying zooplankton, <u>Daphnia pulex</u>, found that uptake of methyl mercury increased non-linearly with increased concentration of methyl mercury in water.

Kramer and Neidhart (1975) studied direct (non-food chain) uptake of mercury by fish and found that methyl mercuric chloride was taken up 4 times faster than mercuric nitrate. Accumulation rates decreased in the presence of EDTA, cysteine and glutathione. These complexing groups may have a screening effect, so that desorption at the surface of the cells is insignificant or does not take place at all. Kramer and Neidhart suggest that only the mercury which is not complexed is accumulated. This means that the accumulation rate should depend very strongly on the concentration of "free mercury" in the water, and this was the effect that was found after further experimentation.

Release or depuration of inorganic mercury from fish into distilled
water was also studied and it was found to be a two step process. The first, rapid step has a half life of about 4 days and the second step about 68 days. When methyl mercury was allowed to depurate from the fish so treated, a one step reaction with a half life of 69 days occured. Huckabee <u>et al</u> (1975) found a rapid loss at first, followed by a steady, slow, long term loss. The good agreement between the two longer half lives led Kramer and Neidhart to conclude that the release of incorporated methyl mercuric chloride, and accumulated inorganic mercury that is methylated in the fish (as previously stated by Jensen and Jernelöv (1969) and Bertilison and Neujahr (1971)) follows that of methyl mercuric chloride. In an earlier field study on depuration, Lockhart <u>et al</u> (1972) transferred mercury laden pike from a contaminated lake and discovered that after one year, only 30% of the total mercury had been eliminated from the fish. The foregoing suggest that mercury is a persistant chemical, especially once incorporated into a fish.

Hildebrande <u>et al</u> (1976) suggest that food chain uptake is most important in a study they performed in a contaminated system. In an area where sediments contained less than detectable amounts of methyl mercury, about 80% of the mercury in the fish was methyl, as was about 50% of the mercury in benthic invertebrates.

A study was undertaken on the behavior of mercury in laboratory biosystems. The various aspects of the study were: 1) uptake and concentration in the food chain (Prabhu and Hamdy 1977), 2) depuration of radio-labelled Hg^{2+} in various trophic levels (Hamdy and Prabhu 1978), and 3) biotransference of mercury through food chains (Hamdy and Prabhu 1979). The study was conducted

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to follow the biotransference of radioactive mercury in a simple model food chain which consisted of four trophic levels: from mercury resistant bacteria, toge mosquito larvae; then from larvae to guppies (i.e., small fish); and finally from guppies to Cichlids (i.e., large fish). Data on the dynamics of mercury uptake, depuration and biotransference revealed that these various processes are affected by many factors, particularly those altering metabolic rates. In the system studied, mercury was concentrated by the lower organisms - the bacteria and the larvae. These were the only systems that exhibited magnification of mercury. This substantiates work done by Colwell and Nelson (1974). Evidence against magnification of mercury was shown to occur in the higher food food chain guppies feeding on larvae and then being eaten themselves by Cichlids.

The pathways for mercury uptake by fish from bed sediments was studied by Kudo and Mortimer (1979). They wanted to determine whether the pathway was

or

bed sediment -----> water ----> fish

bed sediment -----> fish

The bed sediments, amended with $HgCl_2$ were screened off with netting. In one system, the fish and sediment were together in one tank, while in the other system, the fish and water were in one tank connected by screened pipes to a tank with water and sediment. The water was circulated between the two tanks in the second system. Mercury concentration in the sediment was $1.023 \ \mu gg^{-1}$, and the mercury concentration of the water was $2 - 5 \ \mu gL^{-1}$. Fish in both systems accumulated mercury continuously. Fish in association with

bed sediments reached equilibrium (about $0.2 \ \mu gg^{-1}$) before fish not in contact with bed sediment (equilibrium mercury concentration about $0.02 \ \mu gg^{-1}$). This suggests that mercury accumulated by the route: sediment ----> fish, is about $0.18 \ \mu gg^{-1}$ while mercury accumulated by the water route is about $0.02 \ \mu gg^{-1}$. Thus the mercury accumulated by the fish from the bed sediments was nine times greater than that accumulated from water alone, and was accumulated at a more rapid rate.

2.2.3.2 Temperature

Temperature affects the rate of uptake of methyl mercury into fish. MacLeod and Pessah (1973) studied accumulation of mercury in muscle of rainbow trout and found that at 5, 10 and 20°C, and for 0.1 mgL⁻¹ Hg concentration (as $HgCl_2$), biological magnification factors (concentration in fish/concentration in water) were 4, 10 and 22 respectively.

Burkett (1974) subjected bluntnose minnows to radio-labelled methyl mercury at temperatures of 18, 21 and 24°C. Burkett found increased uptake of methyl mercury at 18 and 21° but not at 24°. One of three hypotheses may serve to explain why the increased uptake trend did not continue beyond 21°C: 1) equilibrium may be achieved between uptake and excretion of Hg at about 21°, 2) methyl mercury has a depressant effect on metabolic rate above 21°, or 3) routine activity, and therefore routine metabolic rate of the test fish peaked at 21° or slightly above. In a somewhat more quantitative study, Cember <u>et al</u> (1978), as a follow-up to an earlier experiment by Blaylock and Huckabee (1974), studied methyl mercuric chloride uptake in fish at water temperatures of 9, 21 and 33°C and mercury concentrations of 0.2, 0.5, 5 and 50 μ gL⁻¹. The bioconcentration factor was found to increase exponentially with water temperature at a rate of 0.066 per C°. Mercury concentration in the water did not influence the bioconcentration factor.

Ribeyre <u>et al</u> (1980) studied the effect of temperature (10, 18 and 26°C) on the uptake of methy mercury in a freshwater trophic chain. This food chain consisted of Chlorella vulgaris, a producer, Daphnia magna, a primary consumer, Gambusia affinis, a first rank carnivore, and Salmo gairdneri, a second rank carnivore. At 18°C, the "global" rate of trophic transfer of mercury between the water and the terminal consumer was about 15%. Terminal consumer mercury levels showed a reduction in the transfer rate when the water temperature was raised from 10° to 26°C.

2.2.3.3 Age and Growth

Age and growth effects on mercury uptake have been studied. Johnels and Westermark (1969) showed that mercury uptake in fish increased linearly at a given concentration until death occurred. Bache <u>et al</u> (1971) carried out analysis of total mercury and methyl mercury in lake trout of precisely known ages from 1 to 12 years. They found that the concentrations of both total mercury and methyl mercury increased with the age of the fish. Also, the

proportion of methyl mercury to total mercury increased with age: about 30 to 35% methyl for 1 year old fish, and 80 to 90% methyl for fish 7 to 12 years old. In a similar study, Kerfoot and White (1972) studied striped bass ranging up to 12 years of age and found that the mercury content of the axial muscle exhibited an annual increase of $0.0\frac{19}{9}$ µg Hg g⁻¹ of wet weight tissue.

Blaylock and Huckabee (1974) found that fish from an uncontaminated system had about 93% of their mercury in the methyl form, unlike benthic invertebrates which contained around 76% of their mercury as methyl mercury (Huckabee and Hildebrand 1974). Another portion of this study showed that, in a lake ecosystem, seston was the major reservoir of methyl mercury.

Scott and Armstrong (1972) showed that a positive correlation exists between mercury concentration and fish length. Scott (1974), in his study on four species of fish in heavily mercury contaminated Clay Lake (Ontario) found that older fish and faster growing fish contained generally more mercury. Also, as previous findings have shown, the larger the fish, the greater, was its white muscle mercury concentration, both within species and within populations. Scott found a contradiction to previous studies in that relatively heavier fish tended to have lower mercury concentrations. Scott states:

> "The various statistical relationships do not appear to be simple, first-order regressions; rather, there appear to be significant interactions between age and growth, and age and condition (weight) which tend to change the partial slopes with age."

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More recently, Phillips <u>et al</u> (1980), in studying various trophic levels of fish in Montana, also found that the mercury content of fish flesh increased with size and age. These workers found that the rate of mercury accumulation was faster in piscivorous species (northern pike, sangers, walleye) than in planktivorous species (black crappies and white crappies).

MacCrimmon <u>et al</u> (1983) studied the growth of lake trout in Precambrian Shield Lakes and found that fish mercury content was well correlated ($r^2=0.92$) with fish length. They also found substantial among-lake differences in fish mercury contents occuring in fish of comparable ages.

2.2.3.4 Lake water chemistry

Drummond <u>et al</u> (1974) state that some mercuric compounds, such as . methylmercuric chloride and mercuric chloride, are readily absorbed by the gills of fish where they are transferred to the blood and subsequently distributed to other body tissues. Fang (1974) and others have suggested that mercury enters the fish during gill uptake because it is in a lipid soluble form. Fish gill membrane is composed partially of lipid, or fat, which is non-polar in nature. Thus only non-polar solutes are significantly soluble in the non-polar solvent, which is the lipid. Assuming that toxic substances pass directly through the lipid portion of the gill (some may pass through the water-filled pores), the toxic substance must be non-polar. This leads to speculation on whether or not mercury, inorganic or organic, exists in polar or non-polar species under the chemical conditions existing in acid lake ecosystems.

It has been shown (Reimers, Krenkel and Englande 1974) that sulphate, nitrate, nitrite and other ligands do not form stable mercury complexes. Only under anaerobic conditions is mercury stable as elemental mercury or as mercuric sulphide. Other ligands such as I⁻, Br⁻, CN⁻, NH₄⁺ and especially S²⁻ form more stable complexes with both inorganic and organic mercury than Cl⁻, and CN⁻ and S²⁻ form more stable mercury complexes than OH⁻. The concentrations of these other ligands in natural (oxidizing) waters, however, are considered totally negligible. Mercury complexes formed by these species, therefore, are not important compared to complexes formed by chloride and hydroxide. Thus the only two common ligands which form important mercury complexes are OH⁻ and Cl⁻. This has been shown experimentally by Ciavatta and Grimaldi (1968). The hydroxide-chloride equilibrium diagram for mercury is shown in Figure 2.4.

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As shown in Figure 2.4, the predominant inorganic mercury species at the pHs and pCls found in many Precambrian Shield lakes are predicted to be HgCl₂°, HgOHCl° and Hg(OH)₂°. Calculations show that the predominent organic mercury species is CH₃HgCl°. In terms of inorganic mercury, the species most likely to occur in acid lakes is HgCl2°. It is of special consequence that this particular species be prevalent, since, although it is linear, non-polar (Pauling 1970) and electrically neutral (Ciavatta and Grimaldi 1968) like the other inorganic species, this species is only weakly bonded to water. (CH₃)₂Hg° is also linear (Spice 1966). The other species are more heavily hydrogen bonded and generally not mobile with respect to fish uptake. Hydrolysis of HgCl₂° occurs to form HgOHCl°. Cotton and Wilkinson (1972) suggest there is no proof of a true hydroxide, however the weak base Hg(OH)₂° is commonly assumed to exist. This species may exist simply as a heavily hydrolyzed form of HgO. Thus the HgCl2° species may be more readily assimilated by fish, where it may or may not get methylated on the gill surface or in vivo, compared to other inorganic species.

Shield lakes where the phenomenon of increased mercury uptake by



Figure 2.4 Predominance diagram for inorganic mercury species as a function of pH and pCl. Under high pHs and high pCls (i.e., low chloride concentrations), the neutral hydroxide species $Hg(OH)_2^\circ$ predominates, while at lower pHs and pCls, the neutral and more biologically available chloride species $HgCl_2^\circ$ predominates. The neutral hydroxo chloride complex is depicted as a narrow strip between these two species, but the hydroxo chloro complex never exists in concentrations greater than about 20 % of the other two species. The dashed lines, indicating 1 % concentration limits depict the rapidity that the non-predominant species decreases in concentration in the predominant species' field.

fish has been shown to occur, are typically low in calcium. This is a common occurence in lakes of low pH and alkalinity. These lakes have also been shown to have elevated metal concentrations (National Research Council of Canada 1981).

Hunn and Allen (1974) showed that lipid solubility and degree of ionization of, in their experiments, a drug, play a significant role in the movement of compounds across the gills of fishes. In general, any substance that is distinctly charged, or otherwise fat-insoluble, and has a molecular weight in excess of 100 is almost certain to be virtually excluded from entering cells from the outside unless the particular cell is equipped with a specific transport system for that particular substance (Le Fevre 1972). Many substances appear to penetrate cells by diffusion at rates that could be correlated with their solubility in fat solvents. Hunn and Allen state that it is the un-ionized form of most drugs which penetrate cell membranes most readily.

Calcium concentrations in natural waters (Ogawa 1974; Isaia and Mansoni 1976; McWilliams and Potts 1978) and waterborne zenobiotics (Jackson and Fromm 1977) have been shown to affect gill permeability of freshwater teleosts to water and ions. Gill permeability varies inversely with calcium concentration.

> In their recent work, Rodgers and Beamish (1983) state: "Changes in efficiency of methylmercury uptake in hard and soft waters are consistent with the effects of ambient calcium concentration on gill permeability and

electric potential.Although the mechanisms through which calcium affects gill permiability are poorly understood, calcium influences fluxes across the gills of both polar and non-polar molecules (tritiated water) and ions (Na⁺, H⁺ and Cl⁻), and changes in both active and passive transport processes are implicated (Ogawa 1974; Isaia and Mansoni 1976; McWilliams and Potts 1978). In addition, the electrical charge of the gill becomes more positive at higher calcium concentrations (McWilliams and Potts 1978), consequently, uptake of cations, such as CH₃Hg⁺, should decrease in waters of elevated calcium concentration. The observed changes in the uptake of methylmercury with water hardness would thus. seem to result from Ca²⁺-induced changes in gill permeability and charge. Although changes in water hardness also involve a slight decrease in pH, at pH than 6.0, pH had little effect on gill greater permeability and charge (McWilliams and Potts 1978).

"The increased efficiency of methylmercury uptake relative to oxygen in soft water is consistent with and may in part explain the common observation of degreased toxicity of metals in hard water (Sprague 1970). Unfortunately, data on the effects of water hardness on toxicity of waterborne methylmercury are currently not available.

"The increased efficiency of methylmercury uptake in soft water is also consistent with the observation that fish from lakes of low alkalinity and pH contain higher concentrations of methylmercury than fish from adjacent waters of higher alkalinity and pH (Jernelöv <u>et al</u> 1975; Scheider <u>et al</u> 1979). Our results would suggest that the higher methylmercury residues in fish from softwater lakes could result from the effects of ambient Ca^{2+} on uptake of waterborne methylmercury. The effects of pH on methylmercury uptake by fish have yet to be defined."

Various studies have attempted to describe changes in mercury toxicity due to synergistic and antagonistic effects of other materials, especially selenium (Parizek and Ostadalova 1967; Ganther <u>et al</u> 1972; Huckabee 1974; Kim <u>et al</u> 1977), copper (Roules and Perlmetter 1974) and zinc (Gale 1973). Rodgers and Beamish (1983) found that the addition of zinc sulphate decreased the relative efficiency of uptake of methylmercury by rainbow trout.

Rodgers and Beamish further state:

"Short-term exposure to concentrations of mercuric chloride as low as $12 \ \mu g L^{-1}$ increased mucus production of rainbow trout (Lock and van Overbeeke 1981). Mercuric chloride has also been reported to change the structural properties and permeability of trout mucus (Varanasi <u>et al</u> 1975). Changes in the rate of production

and structural properties of the mucus covering the gill epithelium may thus account for the increased efficiency of methylmercury uptake with coincident exposure to mercuric chloride. Sublethal concentrations of zinc have also been reported to increase mucus production in trout (Sellers et al 1975), yet the addition of zinc with labelled methylmercury decreased rather than increased the effeciency of methylmercury uptake relative to oxygen [in the Rodgers and Beamish study]. The mechanisms by which inorganic mercury and zinc affect uptake of waterborne methylmercury thus remain undefined. The reduction in the efficiency of methylmercury uptake with the addition of inorganic zinc may indicate a competition for sites of uptake on the gill. This interpretation is consistent with observations that another divalent metal, copper, was antagonistic to methylmercury in toxicity tests with the blue gourami, Trichogaster trichopterus (Roales and Perlmutter 1974)."

Varanasi <u>et al</u> (1975) found that the introduction of selenium-to water caused an increased production of mucus by the fish. This mucus may readily absorb mercury from the water and render it immobile in this relatively harmless location. Rudd <u>et al</u> (1980a) found that selenium and mercury did not move through the ecosystem either chemically or biologically and that 0.1 mgL^{-1} Se stabilized the movement of mercury among the various water column

compartments. Elevated selenium appeared to retard the rate of mercury bioaccumulation by fish, crayfish and haptobenthos.

2.2.4 Acid Stressed Fish Populations

• When dealing with acid stress, apparently two possible situations may exist, independently or together. These situations are:

 "apparent" increase in fish population mercury content due to the modification of the population itself because of bio-stress induced by lake water acidification

2) actual or "real" increase in fish population mercury content due to increased uptake of mercury by fish, which may be related to changes in fish physiology induced by lake water acidification

Apparent increases in fish mercury content for a population relate to a statistical phenomenon only. Lake water acidification may inhibit spawning at certain low pHs. It may also increase recruitment failure and diminish or eliminate young-of-the-year for a given year. This form of acid stress, if it occurred several times in succession, would cause a statistical change in the fish population. That is, the smaller size classes would be missing, with only the older and larger fish present. As previously stated, older and larger fish generally contain more mercury (within lake, within species) than do younger, smaller fish. Therefore, even if the older, larger fish contained "normal" amounts of mercury, for their size class, when the mean is calculated for a population, it would appear that the mean mercury content for that species in that lake was inordinately high. That is, the mean would not be weighted by the missing smaller, low mercury content size classes of fish.

Physiological or "real" effects of acid stress may occur concommittantly. Inputs of slugs of acidic snowmelt into a lake in the spring, when fish are most susceptable to pH depression, may occur, and eliminate or reduce the number of small fish for that year. A chain of events can then occur, as hypothesized here. With no young fish, competition for food is decreased. Larger fish can eat more. At the same time, predator fish, relying to some extent on the young fish for food, must now either choose larger fish to prey on, or change their eating habits. The following possibilities may result:

1) with less competition for food, large fish may grow larger, and may even grow disproportionately large or fat (heavy); larger fish, of course, contain proportionately more mercury as well

2) predator fish, having to eat larger fish than before, are increasing their food chain body burdens of mercury, because these larger prey contain more mercury than the original and now absent smaller prey

3) the predator fish may also change its eating habit to, say zooplankton, from small fish; plankton may contain more mercury, for the same weight, as small fish, and thus the predator body burden of mercury may increase

Some substantiation of this hypothesis already exists in the literature (Jernelöv and Lann 1971, Lockhart <u>et al</u> 1972, Fagerström and Asell 1973, Cox <u>et al</u> 1975, Jernelöv <u>et al</u> 1975, Ollson and Jensen 1975, Phillips <u>et al</u> 1980).

SUMMARY

2.3

Mercury exists in all compartments of the ecosystem. Cycling between these niches, or compartments, depends upon the nature of the compartment, the type of pathway and the form in which mercury exists. Mercury can be readily mobilized from relatively secure compartments by the process of methylation. This process is controlled by various factors, most notably pH, microbial activity, temperature and site of occurrence. Mercury can also be mobilized by other means. Complexation appears to be the most prevalent. Common complexers which have been shown to mobilize inorganic mercury include chloride, sulphur, clays and organics. Complexation reactions are also largely controlled by pH and Eh. Iron hydroxide may also be an important complexer or scavenger of mercury.

Once in a mobile form, it is not clear whether or not uptake of mercury by fish occurs via the food chain or by gill uptake. Some studies have shown very clearly that uptake occurs primarily through biomagnification, while • • others studies show just as convincingly that 100% of the uptake can occur through the gills. Other studies suggest that the likely route of uptake is some combination of the two processes.

Various parameters have been shown to affect uptake of mercury by fish. These include temperature, age and growth and lake water chemistry.

As uptake of mercury progresses in a population of fish, the statistics which govern fish numbers and sizes may be altered. Lake water acidification

may alter the population to show an apparent increase in fish mercury concentration because the population contains only larger fish, which typically contain greater mercury body burdens. On the other hand, real increases in fish mercury may exist due to changes in fish feeding habits, etc. caused by lake water acidification.

There emerge from the literature two distinct areas of research need. The first is the study of the initial mobilization and transport of the mercury to a location and state available for fish uptake. The second is the determination of the mechanism of uptake itself.

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Certain concepts appear to be common to most studies found in the literature. Mercury must first be complexed in order to be mobilized. Mercury does not persistering in the aqueous phase. Sorption of mercury onto a substrate followed by physical particle movement appears to be the most efficient transport mechanism. This sorption reaction is strongly pH, and to some extent pCI dependent. It also depends on the amount of mercury available and the amount of substrate available. Likely substrate candidates in natural systems include clays and other fine inorganic particulates, such as iron hydroxides. Other potential substrates include organic materials such as large, high molecular weight materials and other organic matter including detritus and fish mucus.

The principal processes influencing the behavior of mercury include methylation, demethylation, oxidation, reduction, sorption, sediment/water exchange, volatilization and longitudinal transport (Lassiter et al 1976). The

environmental factors of importance include pH, concentration of suspended particulates, depth of water and depth of sediment. The flow of mercury may be controlled largely by the mercuric mercury form sorbed to the sediments as opposed to elemental or methyl forms. This partitioning to the suspended particulate and sediment phase is generally understood to occur soon after the mercury is mobilized into an aqueous form. Thus sorption is likely to be the single most important control on mercury in an aquatic system.

• Once situated in the particulate phase, a mechanism is required to remobilize the mercury and move it into the fish:

-the particulates could act as a substrate for methylating bacteria to act upon the inorganic mercury, producing for example methyl mercuric 'chloride, which is soluble and very mobile in the aqueous phase; this reaction also appears to be very pH and temperature dependent

-the particles could be taken up on the gill surfaces where the fish's own bacterial flora could methylate it, or ingested where in vivo methylation could occur

-the particles could be consumed by lower trophic level biota, and the mercury then could be biomagnified up the food chain.

-the particulate mercury could be remobilized by changes in pH or pCl and taken up by the fish in the inorganic form.

It is still not clear in the literature as to which of these processes, acting singly or in combination, is the most likely to effect the transport of mercury from particulates into fish.

CHAPTER 3

MERCURY IN AN ACID LAKE ECOSYSTEM - CONCENTRATION AND MASS BALANCE

3.1

GENERAL STATEMENT

A fundamental understanding of mercury concentration in an acid lake type ecosystem is a prerequisite before attempting any further study on the uptake of mercury by fish. In this portion of the research, sampling and analysis of mercury concentrations in various ecosystem compartments of such an uncontaminated system is undertaken. These concentrations are compared to other systems in the literature.

Enough data is generated here to allow for a very rudimentary mass balance to be calculated for the small watershed chosen for study.

3.2 STUDY AREA

3.2.1 Site Selection

Certain criteria were used to find a suitable site for this study. A suitable site would be:

logistically small

- geologically and biologically simple

⁷- geomorphologically simple with respect to lake inlet and outlet

streams

- preferably contain a headwater lake

- be remote from population yet reasonably accessible

- be in an area in which some background data already existed

- the lake itself would have to be acidified or susceptible to acidification, by having a low or depleted alkalinity but would not be so acidified that it would not contain fish

Several possible lakes, mostly un-named, were investigated, all in the LaCloche Mountains, south-west of Sudbury, Ontario. One of the larger of these, Wright's Lake, most closely met the criteria listed. Unfortunately there were no fish mercury concentration data available for this lake, because of its remoteness and small size. The compliance to the other criteria outweighed this one negative aspect.

3.2.2 General Description

Figure 3.1 shows the location of Wright's Lake with respect to the surrounding area. Figure 3.2 is a map of Wright's Lake Watershed. The lake is located as follows:

- latitude 46°6'30" N - longitude 81°54'20" W



Figure 3.1

Location of Wright's Lake.

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- altitude

- within the LaCloche Mountains

- 85 km SW of Sudbury, Ontario

- 14 km W of Whitefish Falls, Ontario

- access is achieved by boat from Whitefish Falls and a one mile hike along a trail west of Flat Point, on the Lake Huron shoreline

Table 3.1 depicts the physical aspects of Wright's Lake and its watershed.

The lake sits entirely within the same rock formation, an orthoquartzite and aluminous orthoquartzite unit of the Lorraine Formation. The bedrock geology is described in detail by Card (1978). This essentially monomineralic rock is up to 99% SiO_2 . The lake's watershed is almost completely enclosed by this same rock unit. A micaceous and hematitic sandstone is found in the most southerly portion of the watershed. This simple geology reduces the number of variables in the system since:

- basically there is only one rock formation to deal with, and it contains two very similar rock types

- the two similar rock types are chemically very simple ,

Overburden in the watershed is thin, probably averaging about 1 m in flat areas to perhaps several metres in valleys. Rock outcrops are common; most topographic highs lack any overburden veneer. The overburden is composed largely of glacial outwash silts and sands. A soil is developed in the upper 25 cm of the overburden.

Table 3.1 watershed.	Physical	aspects	of	Wright's	Lake	and	its
size of lake, NS and EW dimensions			500 x 750 m [`]				
approximate area of lake			26 ha (260,000 m^2)				
approximate volume of lake				$2.81 \times 10^6 \text{ m}^3$ (2.81 x 10 ⁹ L)			
probable maximum depth				. 26 m			
area of lake which is <2 m deep >2 but <10 m deep >10 but <23 m deep >23 m deep			30 % 30 % 40 % <1 %				
area of watershed	drained by Wrigh	it's Creek	:	3.5	km ²		
area of watershed which is lake surface			9 %				
area of watershed draining into lake			3 km^2				
outcrop area			. 60	% (1.8	km ²)		
stream flows				_			
main inflow	May 1980 August 1980			75 0	Lsec ⁻¹		
west inflow	May 1980 August 1980	-		7 0			
outflow May 1980 early August 1980 late August 1980			900 5 25			-	
	•						

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As shown in Figure 3.2, the lake has only one major and two minor inlet streams. All the streams are seasonally intermittent. The lake has one outlet stream.

The main inlet stream is partially fed from two small ponds (surface area 25 m² and 300 m²) situated on a quartzite ridge. The ponds are almost completely enclosed by bedrock, with small outlets which, in part, run underground along joints in the bedrock. The smaller of the ponds contains only 5 to 10 cm of sediment which lies directly on bedrock. No open water is found in either of the ponds during the driest part of the summer. The west inflow is little more than a ditch draining a pine covered hillside. The east inflow was never observed in any detail, but appears to have an insignificant flow.

On a gross scale, the vegetation in the watershed is almost as simple as the geology. About two thirds of the trees in the flat areas and gentle slopes are white birch, with some oak and maple. The rest of the trees in these areas, and most of the trees on the steeper slopes and topographic highs are pinetrees. In low lying areas of the valleys, particularly the swampy area near the outlet stream, cedar is the predominant tree type.

The small swamp at the southern end of the lake, just below the outfall, is valuable in that besides providing another niche in the ecosystem, it possesses the only area found so far in the watershed which is chemically reducing. The rest of the near surface environment of the watershed, as well as the lake water and surface sediments, is oxidizing. The physical appearance, as well as the composition of the organic-rich lake sediments, is similar to other lakes situated in the Lorraine Formation. With respect to the composition of the surrounding soil, from which they most likely are derived, the sediments appear somewhat depleted in SiO_2 and enriched in Fe_2O_3 . Nodules rich in Fe and Mn were present in the upper sediments, typically in the top 5 cm. No attempt was made to quantify the nodules, however, "several" per square metre of sediment were observed. The rough textured, porous, low density concretions were 0.5 to 2 cm in length, in the rough shape of oblate spheroids and rust to reddish brown in colour.

Sulphur content is highest in the quartzite ridge pond sediments. This suggests that either these topographically high structures are more effecient in \sim trapping airborne SO₄²⁻ or their sediments contain traces of FeS₂ or other sulphur containing minerals.

The physical limnology of the lake is described in Table 3.2. The lake - is thermally stratified in the summer.

Biological and microbiological parameters are shown in Appendix A.

Water chemistry is described in detail in Appendix B.

Assuming an acid lake is one with a pH below about 6 and/or having very low alkalinity, less then about 5 mgCaCO₃L⁻¹ for a non-calcareous regime (Kramer 1977), and thus being susceptable to acidification, then Wright's Lake can be called an acid lake.

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Parameter	Units	Compartment	Time	Value
Secchi				
depth	m	whole lake	August 1979	9.20
			early Aug 1980	9.35
temperature	°C	epilimnion	early Aug 1980	['] ~21
		hypolimnion		4.3 (minimum)
		central surface	August 1979	21.8
		•	May 1980	8.8
		south shore		
		surface		8.8
		outflow		8.8
		•	,	
specific				
conductance	uScm ⁻¹	epilimnion	August 1979	29.4
		•	May 1980	25.9
	-	hypolimnion	August 1979	30.3
		central		
		surface	May 1980	25.9
		south shore		2000
		surface	-	35.8
		outflow	·	32.0
		main inflow	,	30.7
		west inflow		39.5
		Lake Huron outle	et . '	
		of Wright's Cree	k	30.0
		SWAMD		41 7
		large pond		35 0
		small pond		28 5
		Saure pour	. •	20.0
particulates	1		•	· ·
1	mgL ^T '	epilimnion	early Aug 1980	3.9
		hypolimnion	- · · -	4.8

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Wright's Lake is compared in Table 3.3 to other nearby and somewhat larger Lacloche Mountain lakes studied by Sprules (1975). This table suggests that Wright's Lake is typical with respect to the parameters listed for the area in which it resides.

Analysis for snow and rain are shown in Appendix C along with winter conditions for nearby meltwater streams and lakes.

Anthropogenic influences on the lake are minimal as there are no cottages in the watershed, and the lake is more than 10 km away from any permanent and readily accessible habitation.

In 1972, the Ontario Ministry of Natural Resources stocked Wright's Lake with 2000 speckled trout, (<u>Salvelinus fontinalis</u> [Mitchill]). A very high winter fishery depleted this stock quickly. Further to this, there are no suitable places to spawn in the lake-stream system (N. Conroy, personal communication) thus it is unlikely that new fish were generated from this initial stocking. Scott and Crossman (1973) suggest that an average life span for speckled trout is 5 years, with none living more than 8 years. This indicates that the lake would contain very few of the original speckled trout.

3.2.3 History

A north-south trending fault (Card 1978) extending about 4 km from the Bay of Islands appears to be responsible for causing the depression which

Table 3.3Comparison of Wright's lake to other LaclocheLakes in terms of surface area, maximum depth, total dissolved solids,Secchi depth and pH.

	Surface Area	Maximum Depth	TDS	Secchi Depth	рН
	ha	m	mgL ⁻¹	m	
47 other Lacloche			•		
Lakes	3.4-1088.3	2.7-61.0	13-37	1.9-20.9	3.8-7.0
Wright's Lake	26	26 (+?)	~20	~9	5.4-6.2

forms Wright's Lake basin. The steep west shoreline and cliffs may be the fault surface.

Four or more periods of Pleistocene glaciation scoured the basin. Glacial outwash sands and other materials were deposited in post-glacial lakes which covered the entire area following the most recent ice recession. This is described in considerable detail by Prest (1970).

The area was dewatered about 5800 years B.P. and Wright's Lake 'proper was formed, probably with a surface elevation about 2 m below present. This would have been the elevation of the original outlet. The lake therefore would have had a smaller surface area, about 400 x 500 m.

As beavers started to populate the area in the years following . dewatering, the lake basin again began to change. A large beaver dam was built at the south end of the lake, at the outlet. This raised the water level about 1.5 m. The remains of this dam indicate that it was at least 1.5 m high, 2 mwide and about 50 m long, and may be a combination of many smaller dams. The building of this dam caused a swamp about 50 x 50 m in area, to be formed immediately below the dam. A breaching of the dam occured, probably in the last decade and the water level receded to a temporarily constant level about 0.5 m below the top of the large beaver dam. This conditions remained until the fall of 1979 or the very early spring of 1980 when another beaver dam was built atop the old, established dam, and the water level was raised another 0.5 m.

3.3 SAMPLING & ANALYSIS

A total of 5 field surveys were conducted in Wright's Lake Watershed. Appendix D lists these surveys and the principal work performed each time.

Standard sampling techniques were employed in all phases of this study.

Water samples at depth were retrieved with 1 L and 2L Van Dornbottles. Surface water samples were taken directly into storage containers, where the samples were required for laboratory analysis, or into a plastic bucket, when filtering or other-steps were to be performed immediately. Sampling and preservation of the water samples for the various parameters was performed according to established methods as outlined in Analytical Methods Manual (Environment Canada 1979). The only deviation from these methodologies was that linear polyethylene bottles were used in place of glass for the mercury samples. This was necessitated by the remoteness of the site causing problems in safe sample transportation.

Sediments at depth were sampled with an Ekman dredge. Shallow sediments and soils were sampled with a small stainless steel scoop.

Fish were sampled by gill and dip nets, supplied by the Ontario Ministry of the Environment at Sudbury.

All samples were kept on ice (approximately 0° C) until brought back to the laboratory. At this time, the waters were refrigerated and the soils, sediments and biological materials were frozen at -20° C.

Standard analytical techniques (Environment Canada 1979) were employed in all phases of this study. See Appendix L. Plankton studies were performed independently, by R. Playle and bacteriological work was performed by the Ontario Ministry of Health in Sudbury.

Elemental characterization of soils and sediments was performed using standard XRF techniques.

Standard quality assurance/quality control procedures were employed in all phases of analysis. Blanks, duplicates and replicates were analysed to assure the quality of analytical results. For all parameters error was estimated to be in the range depicted by the Analytical Methods Manual (Environment Canada 1979). Detection limits for all parameters were similar to values described by Environment Canada (1979) except for mercury, where the detection limit varied between 0.02 and 0.05 ng g⁻¹, depending on the day, operator and other unknown influences. See Appendix L.

3.4

RESULTS

Mercury concentration data for the various compartments in Wright's Lake ecosystem are reported in Appendix E. To simplify compartment to compartment comparisons, and comparisons to the literature, all results are reported in ng Hg g^{-1} of material.

3.5 DISCUSSION

3.5.1 Mercury in Wright's Lake Ecosystem

3.5.1.1 Comparison to other systems

Table 3.4 summarizes the results of Appendix E and depicts how mercury concentrations in various ecosystem compartments in Wright's Lake watershed compare to literature value ranges. Wright's Lake values generally within the range of literature values for the various compartments. The literature values are based on a wide variety of ecosystem types and are used here for broad reference only.

3.5.1.2 Wright's Lake ecosystem mercury concentrations

3:5.1.2.1 Bedrock



Table 3.4 Comparison of mercury concentrations to literature values. Table 3.4 Wright's Lake ecosystem

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mercury concentration in ng g^{-1} compartment

Wright's Lake

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	· · ·	ture value for an unpolluted system
•	r	•••
lake water	0.025 - 0.05	0:005 - 0.1
lake_sediments	10 - 164	4 - 9500
soils	11 - 244	55 - 815
biològicals	. <5 - 246	5 - 199
lake particulates	261 - 339	90 - 220
fish	160	100 - 1200
snow	0.042 - 0.084	0.11
- rain	0.025	0.005 - 0.5
Lorraine Quartzite	10	

litera-

10 - 100 average

sandstone

typical

and K. Although the data are based on only 3 samples, it appears that mercury is also lower in concentration in the weathered surface of the rock. This weathering process, therefore, represents a primary natural source of mercury which may enter the rest of the ecosystem.

3.5.1.2.2 Snow

Mercury contents of snow are similar to values found by other workers. The lowest 15 cm of the snow profile, resting on bedrock at the particular location that it was sampled, was already recrystallized and partially melted at least once, and was likely about 3 months old. This snow had a mercury content of 0.08 ng g⁻¹. This value likely does not represent the mercury concentration of the snow during deposition, due to the metamorphism that takes place during freeze-thaw, recrystallization and compaction.

The 15 cm of snow on top of the bottom 15 cm was also partially crystallized, and at the time of sampling, starting to melt. This horizon contained about half of the mercury that the lower horizon contained. This may be due to the mercury being partitioned during melting and percolating down to lower depths in the snow profile, where it may be fixed upon refreezing.

¹ The surface 2 cm of snow, representing the previous days's snowfall, and also in a state of melting when sampled, contained 0.05 ng g^{-1} mercury, just slightly higher than the old snow it was resting on.

3.5.1.2.3 Meltwater

Upon the thawing of snow, meltwaters percolate through the snow profile to the ground surface. Here, most of the water appears to percolate through the matte of leaves and humus, into the sandy soil, where it proceeds downslope and exits at stream banks. Some of the meltwater also enters the streams by overland flow and some of it enters directly.

61

Although the (melted) snow has in the order of 0.04 to 0.08 ng g⁻¹ mercury in it, the meltwater streams have <0.025 ng g⁻¹ mercury in their water. This suggests that upon coming in contact with the ground surface, or very shortly thereafter, the meltwater gives up a portion of its mercury burden, which is likely temporarily retained by organic matter and fine particulates in the soil. This further suggests that the acidic snowmelt, with a pH of around 4.5, is not leaching mercury from the ground materials. This is substantiated by the higher levels of mercury found in the snow, and the relatively lower levels found in the meltwater stream after the water has come in contact with the soil.

3.5.1.2.4 Rain

Except for higher values of mercury found at the beginning of rain storms, rain is fairly dilute with respect to mercury, when compared to snow which has already accumulated on the ground. A single rain sample used in this study was <0.025 ng g⁻¹ mercury, similar to the meltwater streams; however, the rain was also about 10 times more acidic, with a pH of about 3.75. Wright's Lake water itself has a mercury concentration at or below 0.05 ng g⁻¹. It has already been shown that meltwater is less than this value.

There exists the possibility that rainwater, although low in mercury with respect to snow and lake water, may increase its mercury burden upon becoming runoff by leaching mercury from the soil (unlike snow which appears to give up its mercury burden). The runoff may in fact leach a portion of the mercury originally deposited by the snowmelt. This will not be further considered here.

3.5.1.2.5 Water

For most of the samples taken in August of 1979 and May af 1980, water mercury concentrations of inflows, outflow and lake water were below the detection limit of 0.05 ng g⁻¹. An improvement in the analytical technique to a detection limit of about 0.02 ng g⁻¹ allowed better resolution for the August 1980 sampling. Here epilimnion water was shown to be 0.05 and hypolimnion water 0.025 ng g⁻¹ in mercury.

Pore waters were somewhat higher in mercury than the lake and streams waters. Pore water in the swamp was 0.25 ng g⁻¹. Pore water in the surface sediments was 0.60 ng g⁻¹, some 24 times higher than the water of the

62.
adjacent hypolimnion. Pore water mercury concentration approached that of the lake water with sediment depth.

3.5.1.2.6 Sediments

Sediment sampling locations are shown in Figure 3.2. Lake sediment mercury concentration ranged from 10 to 164 ng g⁻¹ depending on location and depth. The ridge pond sediments were also in this range. The highest sediment mercury value was found in the swamp sediment, in a sample taken just below the surface. This value was around 440 ng g⁻¹, which was about 10 times higher than overlying or underlying sediment.

3.5.1.2.7 Surficial Materials

The bulk of the surface materials in the watershed are unconsolidated sands of glacio-fluvial origin, and to a much lesser extent, sand and gravelerosion broducts of in situ bedrock. These glacio-fluvial materials are likely derived from a fair distance up-ice-direction from the present site of deposition. An unknown percentage of the glacio-fluvial debris represents Lorraine quartzite, but this percentage is not known. In any event; the overburden, whose composition and mercury content are taken to be those of the lowest parts of the soil profile (C horizon), is largely SiO₂ (80%), with Al_2O_3 (10%) and Fe₂O₃ (3%), and mercury contents in the range of 30 to 90 ng g^{-1} . The range of mercury levels in the overburden is 3 to 9 times higher than the levels found in the bedrock. This may be due to the scavenging effect of organic matter, fine particulates or oxidized iron on mercury. These components are not present in any significant amount in the bedrock, but abound in the surficial materials.

Mercury in the soil profile varies within, the range of other workers; and is higher in the soil profile relative to the unconsolidated materials below the soil horizons. Except for soil location #1, shown in Figure 3.2, mercury appears to be concentrated in the uppermost 5 cm of the soil, and is in the range of 95 to 250 ng g⁻¹ of dry soil. This is the part of the soil which contains the most organic matter, and also the part, along with the humus matte, that first comes into contact with meltwaters, as described previously.

Forest litter, or humus, lying on the soil at location #2, had a mercury content of 60 ng g⁻¹ of dry litter. This material was lying on the upper soil horizon which, at this location contained about half of this amount of mercury.

The mercury may enter the humpes and soil horizons by several possible means or a combination of them:

a) the mercury may be indigenous to the parent material

b) the mercury may be originally derived from the plant materials, which are now decaying; the mercury is now being sequestered by organics and fine particulates

c) the mercury was derived from rain, snow and dry deposition

The bedrock, which is the original parent material may contribute up to 10 ng g^{-1} of mercury to the overburden. The overburden, or soil parent material, may contribute up to 90 ng g^{-1} . The surface soils, however, are all higher than this. It is possible that the mercury may be upwardly mobilized from the overburden to the soil tile, accumulating in the soil. More likely, the mercury in the bedrock and are due to other inputs.

These other inputs may include the decay of biological materials. Trees growing in the area contain 40 ng g^{-1} mercury (cedar, pine and birch wood). The leaves and pine needles make the most important contribution to the forest litter. These components contain <5 ng g^{-1} mercury. Of course, decomposition and removal of volatiles may increase the ratio of mercury to mass of dead material. This is indicated by the mercury concentration of the forest litter, which, at 60 ng g^{-1} , is 12 times more concentrated in mercury than its source materials, the leaves and pine needles. This suggests the validity of possibility "b", listed above (mercury derived from plant materials). Thus the plant materials may contribute a small but significant amount of mercury to the soil.

Atmospheric input may also be a plausible source. Note however that acidic rain, in the pH range of 3.75 may cause leaching instead of deposition of mercury in the soil. The two processes may in fact occur concommittantly. This will be discussed further in 3.5.2 Mass Balance. /

3.5.1.2.8 Flora

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The mosses appear to be the best terrestrial accumulators of mercury • in the system, ranging in mercury concentration from 100 to 250 ng g⁻¹ of dry moss. Lichens and fungi were only slightly higher in mercury concentration than the major flora.

Macro flora growing in water showed the greatest variation in mercury content. Of the sparse assemblages of plants growing in Wright's Lake, lily pads had 4 ng Hg g⁻¹ of dry material and bottom plants 24 ng Hg g⁻¹ of dry material. In the small ponds the water plants were relatively low in mercury at 5 ng g^{-1} .

The highest mercury concentrations in the biological-system occur in the seston of Wright's Lake. Two samples of material retained on a phytoplankton net, and taken to represent phytoplankton, contained 240 and 520 ng Hg g^{-1} , the highest value found for plants in this watershed.

Zooplankton, or material retained in a zooplankton net, contained up to 850 ng Hg g^{-1} of dry material. Although the number of samples taken limits the interpretation, it appears that samples of both phytoplankton and zooplankton taken in May of the year contained less mercury than samples taken in August of the year.

It has been shown (Stumm and Morgan 1970, p455) that algae are negatively charged down to a pH of about 3. This suggests that there may be

some attraction of any positively charged mercury species to the algae. pH and chloride levels encountered in this lake would cause the mercury to exist largely in the uncharged complexes HgCl₂° and HgOHCl°. The algae may also be taking up methyl mercury from the water. The water is at the optimum pH for methylation to occur (Fagerström and Jernelöv 1972). Herbivorous zooplankton consume phytoplankton. This may account for the higher levels of mercury found in the zooplankton (food chain biomagnification). Herbivorous zooplankton grazing on phytoplankton throughout the summer, and being grazed up themselves by carnivorous zooplankton may account for the apparent net increase in plankton mercury concentration over the summer period.

3.5.1.2.9 Lake suspended load

Particulates retained on 0.45 μ m Millipore filters had mercury concentrations around 300 ng Hg g⁻¹ of dry particulate. Phytoplankton and zooplankton are also retained on the filters, therefore, the concentration of non-planktonic seston mercury is probably somewhat lower than reported. This non-planktonic seston is likely composed largely of clay size inorganics, large organic molecules and debris and large colloidal particles, such as Fe(III) hydroxides.

Sorption of mercury complexes_onto the particulates is suspected to be the reason for the relatively high concentration of mercury found in the seston.

3.5.1.2.10 Fauna

In the ecosystem studied here, the final or receptor stage is the fish, the last compartment of the food chain. The fish examined in this study did not appear to have overly enhanced mercury burdens, and certainly showed no biomagnification of mercury up the food chain with respect to plankton or lower versus higher trophic level fish.

The minnows, at 160 ng g^{-1} in mercury, were much higher than the water they live in (0.05 ng g^{-1}) and somewhat higher than the sediment (20 to 80 ng g^{-1}), two parts of the ecosystem with which they are intimately associated. These values represent concentration factors of 3200 (water) and 2 to 8 (sediment).

In a study by Keast and Webb (1966) whose work was conducted in Lake Opinicon (Ontario), it was found that bluntnose minnow stomach contents consisted almost entirely of:

organic detritus (bottom ooze) 20 - 50 % by volume

chironomid larvae 5 - 30 % cladocera 10 - 75 %

Samples from Kearny Lake, Algonquin Park contained mostly chironomid larvae and algae.

Scott and Crossman (1973 p.483) report that fathead minnows eat organic detritus, bottom mud, aquatic insect larvae and zooplankton. With respect to the minnows, on a dry weight basis, phytoplankton in Wright's Lake are 2 to 4 times more concentrated in mercury and zooplankton are 4 to 6 times more concentrated. This suggests either that the minnows do not consume much plankton, or that food chain biomagnification does not occur between these two trophic levels in this system.

The single large predator fish caught, a speckled trout, had 180 ng Hg g^{-1} of fish in the white muscle. This species of fish has been shown to eat a large variety of foods, including minnows. Other foods eaten by the speckled trout are adult and immature insects, snalls, leaches, various fishes such as the sand lance, smelt, blackfish, stickleback and a variety of invertebrates such as stoneflies, beetles, amphipods, ostracods, spiders, gastropods and earthworms, as well as mice, moles, frogs and birds (Scott and Crossman 1973).

Of the possible food sources listed, minnows (160 ng g^{-1} mercury), gastropods (<5 ng g^{-1}) and water beetles (<5 ng g^{-1}) were analysed in this study. The gastropods and beetles were captured at nearby LaCloche Lake, and are expected to have mercury contents similar to those of Wright's Lake.

There is not enough data to show clearly the effect of food on the concentration of mercury in a single fish, or the effect of gill uptake of mercury directly from the water. However, this large (3.12 kg), old (~8 years) fish has a white muscle mercury content similar to the small (4 g), young (<1 year) minnows.

Compared to similar size fish from nearby lakes which are somewhat larger than Wright's Lake, the mercury concentration of the Wright's Lake trout

appears to be low. Only data for walleye exist for nearby lakes, and comparisons between species may not be valid, but in the same size range as the trout from Wright's Lake, the walleye from nearby lakes are more than 1 order of magnitude more concentrated in mercury.

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Distribution coefficients (K_d) are listed in Table 3.5. The coefficients for phytoplankton coincide well with the range of 4000 to 14500 found by Stokes <u>et al</u> (1983) as bioconcentration factors in waters of soft water lakes in Ontario.

The K_d values suggest 3 levels or plateaus of mercury mancentration in this particular system. Level I could be described as the aqueous mercury system, with a concentration around 0.05 ng/g^{-1} . This level would include rain, snow, meltwater, runoff, streams, lakewater and lake outflow. With a $K_{d} = 1$, there appears to be little partitioning of mercury between these warious compartments. The second level might be the terrestrial flora, fish, soil, overburden and sediments, which also have K values among them of around 1. The concentration of this level is around 100 ng Hg g^{-1} of material. The components of these first two levels appear. Within a level, to be in some type of equilibrium with each other, and the levels appear to be in equilibrium with each other. The third level, with K_d values in the hundreds and thousands, appears to be out of equilibrium. This could be termed an "accumulator" level and consists of mercury sequestering components such as seston, phyto and Mercury concentrations of these third level compartments are zooplankton. much more varied than the other two levels, and range, in this system from 250 to 850 ng g^{-1} ,

Table 3.5Distribution coefficients (Kd) for mercurybetween various ecosystem compartments in Wright's Lake Watershed

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aqueous system

rain/snow:streams:lake:outflow

à biota

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fish:water	•	•	3400
zooplankton:water			17000
phytoplankton:water			5000-10000
flora:water		4	300

fish:sediment flora:sediment flora:soil

abiotic

soil:sediment		÷,	1	
SOILTOCK	÷.	• •	10	%
particulates:water	٠.	-	6000	\$
sediment:water		ż	3000	•
sediment pore water:w	ater		12	

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3.5.1.3 Summary

For most of the ecosystem compartments studied here, mercuryconcentrations are not out of line with studies of other systems. For the most part, this suggests that this watershed is indeed a typical watershed and may also suggest that acid lake type watersheds are not grossly different from hardwater lake type watersheds in terms of their mercury contents. Concentration factors between mercury in various compartments and water and sediment are also within the range of factors found by other workers.

Figure 3.3 depicts the concentrations of mercury in each of the ecosystem compartments studied.

3.5.2 Mercury Mass Balance

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The masses of mercury found in each compartment of Wright's Lake ecosystem, as described in the previous section are determined and compared.

A mass balance equation for mercury sources and sinks in the watershed can be written thus:

frx

fo

Sources of Mercury

weathered from rock weathered from overburden

weathered from soil fs rain fr

dry deposition fdd

fsn

Sinks of Mercury

snow

Contributed to overburdentocontributed to soiltscontributed to lake (all compart-
ments)tllost from the systemlst

then

 $[Hg_{frx}] + [Hg_{fo}] + [Hg_{fs}] + [Hg_{fr}] + [Hg_{fsn}] + [Hg_{fdd}]$

= $[Hg_{to}] + [Hg_{ts}] + [Hg_{tl}] + [Hg_{lst}]$

With direct atmospheric contribution, a simple aquatic system mass balance equation can be depicted as follows_____

fw

fa

Sources of Mercury

from watershed directly from atmosphere

Sinks of Mercury

retained in aquatic system lost from the system then

entering lake remaining in lake leaving lake

 $[Hg_{fw}] + [Hg_{fa}] = [Hg_{as}] + [Hg_{lst}]$

These units can be further broken down:

as

lst

$$[Hg_{fa}] = [Hg_{fr}] + [Hg_{fsn}] + [Hg_{fdd}]$$

 $[Hg_{as}] = [Hg_{aq}] + [Hg_{p}] + [Hg_{sed}] + [Hg_{biota}]$

[Hg_{lst}] = [Hg_{ao}] + [Hg_{po}] + [Hg_{oul}] where particulates p aqueous aq sediments sed aqueous outflow ao particulate outflow po other unaccountable losses out

3.5.2.1 Watershed

Assuming that only the outcrop portion of the bedrock is weathered, and that this weathering is 2 mm deep, then the total rock weathered since glaciation is 3600 m^3 . At a nominal density of 2.65 g cm^{-3} , the weight of this volume of rock is 9.54×10^9 g, and the 2 ng Hg g⁻¹ of rock lost represents 19 g of mercury contributed by the rock. Strict temporal confinements to this loss 'are not possible. However, glacial striations on the bedrock surface suggest that all previously weathered surfaces were removed during the last glaciation.' Therefore the 2 mm thick weathered zone occurred since the last glaciation.

 1^{4} m of overburden over 30% of the watershed (0.90 km²) represents 9 x 10^{5} m³ of material, and with a density of about 2.65 g cm⁻³, the mass of overburden is 2.38 x 10^{12} g. At a nominal [Hg] of 55 ng g⁻¹, the overburden contains 131,175 g of mercury. For soil, the mercury concentration is about 100 ng g⁻¹. This assumes that the soil covers 30% of the watershed to a depth of 15 cm and therefore represents 135,000 m³ of material. At a density of 2.65 g cm⁻³, this yields 3.57×10^{11} g of soil and this represents 35,775 g pf mercury. If the overburden and the soil contained the same amount of mercury as the bedrock they were derived from (i.e., 10 ng g⁻¹), then this combined phase would contribute 27,732 g of mercury. Therefore there are 166,950 g in the system now, less 27,732 g from rock weathering leaves 139,218 g coming from outside the rock weathering reaction.

Total precipitation for this area is 0.84 m yr^{-1} (Brown <u>et al</u> 1968).

This includes 2.04 m yr⁻¹ of snow. At a 10:1 ratio of snow to meltwater, the snow represents about 0.2 m of precipitation, or about 24% of the total precipitation. Discounting direct contribution to the lake itself, the volume of rain coming in contact with the overburden and soil is 1.74×10^6 m³ or 1.74×10^{12} g of water. Assuming that the rain has a nominal mercury composition of 0.025 ng g⁻¹, this represents about 43.68 g yr⁻¹ of mercury added to, or flowing through the overburden which is contributed by rain. This does not take into account the mercury which may be leached from the soil and the overburden by the rain.

Each spring, about 0.20 m of water in the form of snow sits on top of the watershed surface and melts. This represents a mass of 5.46×10^{11} g of meltwater. Before melting, the snow has a nominal mercury concentration of 0.05 ng g⁻¹. Therefore, the contribution from the snow is about 27.3 g yr⁻¹, and as previously described, most of this is probably immediately taken up by, or flows through the soil upon melting.

Now, to account for the 140,000 excess grams of mercury in the overburden and soil and assuming that the 19 g of rock-derived mercury is negligible, it would take 139,218 g / 70.98 g yr⁻¹ = 1961 yr to account for this buildup by precipitation. Input to the overburden was actually occuring for some 5800 years since dewatering therefore one can assume that pre-industrial inputs may have been lower. The 70.98 g yr⁻¹, over the 3 km area of watershed draining into Wright's Lake, represents a wet deposition input of about 2400 ng $m^{-2}yr^{-1}$. This compares favorably with the value of 4400 found by Bloomfield et al (1979) for a watershed in the Adirondacks, and the range of 2000 to 3000

found for Ontario by Barton et al (1982).

3.5.2.2 Aquatic System

The lake represents about 9% of the watershed, with a surface area of 0.26 km² (actually 260,000 m² or about 26 hectares) and an estimated volume of 2.8 x 10^6 m³. This is 2.8 x 10^9 L or 2.8 x 10^{12} g of water.

At a nominal mercury concentration of 0.050 ng g⁻¹ of water, the aqueous mercury in the lake is about 140 g. Ignoring for now mercury in runoff, assume the precipitation falling into the lake is the major source of mercury into the lake. For a rain of 0.025 ng Hg g⁻¹ of rainwater, at 0.7 m yr⁻¹ over an area of 26 hectares, the 1.66 x 10^5 m³ of rain (which is about 1/20th the volume of the lake) inputs about 4.16 g of mercury per year directly to the lake. Also, about 0.20 m yr⁻¹ of meltwater contributed by snow falling directly on the lake is 5.2 x 10^4 m³. With a nominal snow concentration of 0.050 ng Hg g⁻¹ of meltwater, the snow contributes about 2.6 g of mercury per year to the lake.

Thus each year precipitation contributes about 6.76 g of mercury directly to the lake. Assuming no other inputs, no outflow and no other interactions, it would take about 21 years to fill the lake with its present burden of aqueous mercury.

The 4 mg L^{-1} concentration of particulates represent a mass of 1.12

x 10^7 g. At a nominal mercury concentration of 300 ng g⁻¹ the particulates represent about 3.36 g of mercury sequestered in the seston. The total mercury in the lake water column, therefore, is 143 g.

This mercury enters the lake at a minimum of 6.76 g yr^{-1} directly from precipitation. An estimate can now be made of how much mercury enters the lake by runoff. This calculation is based on many assumptions and only a small amount of data.

About 0.84 m yr⁻¹ total precipitation falls on the watershed, which has an area of about 3 km². Thus about 2.18 x 10¹¹ g of water enters the sytem in 1 year. Evapotranspiration and other effects may account for some 36.36 % (Brown <u>et al</u> 1968; Phillips and McCulloch 1972) of the water lost from the system. Thus about 1.25 x 10¹¹ g of water may actually reach the lake, and, taking the watershed:lake areas into account, 90% of this can be considered runoff (including shallow groundwater flow), the other 10% added directly to the lake, as discussed previously. This calculation assumes no difference in mercury concentration between precipitation which drains directly overland and into the lake and that which soaks into the ground and travels via groundwater to the lake.

In May 1980, during the wettest season, inflow streams contributed water to the lake at about 82 L sec⁻¹. Since outflow at this time was about 900 L sec⁻¹, more than 800 L sec⁻¹ entered Wright's Lake by overland flow and interflow. Both inflow streams were dry in August but outflow continued at a greatly reduced rate, suggesting only groundwater interflow as a water source

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(the lake level remained constant).

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Assuming for the streams, 6 months of flow at a nominal flow rate of $8 \text{ L} \text{ sec}^{-1}$, this is 1.24×10^{11} g of water. At a mercury concentration of 0.050 ng g⁻¹ of water, the amount of mercury entering the lake via the streams would be 6.22 g yr⁻¹. Assuming the interflow or groundwater input averages 0.02 L sec⁻¹(calculated from inflow and outflow data) and its mercury burden is similar to that of the streams, the contribution from this source would be 0.033 g yr⁻¹ of aqueous mercury. Assume groundwater inflow has negligible particulates.

80

If stream inflow water has a similar particulate load as the epilimnion of the lake, then 4.85×10^8 g of particulates enter the lake in a year. With a mercury concentration of 290 ng g⁻¹ (i.e., similar to the epilimnion), the particulates bring in about 146 g of mercury per year. Therefore the amount of mercury contributed to the watershed each year is 6.22 g of aqueous mercury from streams, 0.033 g of aqueous mercury from groundwater and 143-g of mercury associated with stream particulates for a total of 152 g.

As shown in the previous section, the watershed is gaining mercury at the rate of about 71 g yr⁻¹ and losing it to the lake at the rate of about 152 g yr⁻¹. This suggests that there is a net loss of mercury from the watershed to the lake of about 81 g yr⁻¹. This may imply that acidified precipitation may be leaching mercury from the watershed materials. At this rate of accumulation, it would take ~1.5 years to fill the lake to its present burden of mercury.

With the watershed contributing about 152 g of mercury per year to

the lake and about 7 g is added directly to the lake by precipitation, about 159 g is the total yearly input.

81

A rough estimate of the outflow from the lake on yearly basis can be made. Taking evapotranspiration and evaporation from the lake surface into account, and assuming that the rest of the water added to the watershed reaches the lake $(1.25 \times 10^{11} \text{ g yr}^{-1})$ then about this same amount of water plus the amount of precipitation which falls directly on the lake surface itself, must leave the lake each year via Wright's Creek. Assuming outflow from the lake occurs only 300 days yr⁻¹, then the average outflow is about 4 L sec⁻¹. This seems to be a reasonable estimate of the average outflow, since the measured value for May 1980 was 900 L sec⁻¹ and in August 1980 about 5 L sec⁻¹ and 25 L sec⁻¹ measured on two different days, three weeks apart.

The ~4 L sec⁻¹ of water leaving the lake via Wright's Creek represents a net outflow of about 5 g yr⁻¹ of aqueous mercury.

The outflow stream is tapping only the epilimnion of the lake, which has a particulate concentration of 3.9 mg L⁻¹. Thus the outflow stream, which can be expected to have a similar particulate concentration is removing 3.86 x 10^8 g of particulates per year and at a mercury concentration of 290 ng g⁻¹ then about 116 g yr⁻¹ of seston sequestered mercury leave the system via the creek. This value is close to the 146 g yr⁻¹ of particulate bound mercury entering the lake each year.

Total yearly output of mercury from the lake is, therefore, 121 g.

The total amount of mercury entering the lake and watershed system in one year is about 158 g and the amount leaving is 121 g resulting in a net increase to the system each year of 37 g. Further, the watershed is gaining mercury at the rate of about 71 g/yr but losing it to the lake at the rate of 152 g/yr meaning the watershed is becoming depleted in mercury at the rate of 81 g/yr presently. The overburden contains somewhat higher mercury concentrations than the bedrock from which it was derived. This suggests that the opposite of the above phenomenon must have previously been taking place, that is, the overburden must at one time have been an accumulator of mercury. At the present rate of depletion, it would take about 860 years to completely void the overburden of mercury.

152 g of mercury are added to the lake each year, while about 121 g are lost each year meaning that 38 g of mercury are retained each year by the lake. Predictions can be made on future concentrations and masses of this burden if the present trend continues. Refer to Appendix F. Aqueous and particulate mercury masses increase in the lake while the ratio of aqueous to particulate mercury mass decreases. The concentration of total mercury can also be expected to increase, from the present 0.05 ng g⁻¹ to almost 0.08 in ten years and almost 0.34 ppb after 100 years.

Surface sediment is likely largely composed of previously suspended material. The lake particulates gain 30 g of mercury per year. To force this mercury into a sediment to an average value of 134 ng g⁻¹, it would require 3.3 $x 10^8$ g of sediment. In this lake this mass of sediment is approximately equal to , 1.3 mm yr⁻¹ of sedimentation. At any given time/the take contains 1.12 x 10⁷ g

of seston. This represents about 0.05 cycles per year. The upper 3 cm of sediment represents a repository of mercury estimated to be about 1600 g.

The watershed loss of 152 g yr⁻¹ to the lake represents a loss of 8.43 x 10^{-5} g of mercury lost per m² of watershed. For a nominal overburden depth of 1 m, the loss in this mass is 0.031 ng g⁻¹ yr⁻¹. One metre of watershed is leached by 3.3 x 10^{5} g of precipitation in one year. Therefore the mercury concentration of the runoff would be 0.096 ng g⁻¹. This value is within the range measured experimentally in this study (<0.05 ng g⁻¹).

3. 2.3 Summary of mass balance

The major repositories of mercury in Wright's Lake and its watershed can now be established:

143.4

1600

compartment

mass of mercury in grams

soil overburden aqueous, in lake 140 particulate, in lake 3.4 total, in lake upper 3 cm of sediment also

36000 rounded off

131000 😱 📝

weathered out of bedrock 19 from outside this system 139000 and on a yearly basis (g yr^{-1}) . rain 44 to watershed snow 27 to watershed total 71 to watershed rain to lake L snow to lake 3 total 7 to lake streams 152 to lake groundwater negligible to lake total input ·159 · to lake total to lake and watershed 230 from lake ् 121 left in system 109 retained by lake 38 lost by watershed 81

The overburden and soil are by far the most significant sinks of mencury in this system. For the lake itself, the mass of aqueous mercury outweighs the mass of particulate mercury in this clear, oligotrophic lake by a margin of about 43 to 1.

The fundamental source of mercury in this system; the bedrock, was shown to have contributed only 19 g of mercury since glaciation. This is 7200

times less mercury than that which was atmospherically derived (or at least, entered the system from without).

85

The mass balance is depicted schematically in Figure 3.4.

As shown, the most important sink for atmospheric mercury appears to be the soil and overburden veneer of the watershed. However, this veneer appears to decrease its mercury burden as time goes on, at the rate of about 81 $g yr^{-1}$ As previously mentioned, this could not have always been the case. The most significant fluxes of mercury through the system appear to be the initial precipitation (source) input and then runoff (streamflow) fluxes to the lake. The lake water column is gaining mercury at the rate of about 38 g yr⁻¹.

A typical watershed in non-calcareous terrain was chosen for this study. Mercury analyses were performed on various ecosystem compartments in the watershed. For each compartment, mercury concentrations were within the ranges found by other workers in other systems.

3.6

SUMMAR Y

A mass balance on mercury was performed. This calculation showed that most of the mercury in the watershed is sequestered in the soil and overburden materials. In the lake itself, aqueous mercury accounted for about 2.3% of the total found in the water.



Figure 3.4. Summary diagram of fluxes and sinks of mercury in Wright's Lake ecosystem. Numbers in shaded background represent the approximate mass of mercury in the compartment. Other values are nominal rates of movement or retention of mercury.

The main flux of mercury appears to be from precipitation to overburden, and via stream flow (and precipitation directly) to the lake. Although the watershed is receiving an annual increment of mercury from precipitation, the net mercury flux is out of the watershed, to the lake, so that the watershed is actually losing mercury and the lake is gaining mercury. The mass balance depicted here shows that more mercury is leaving the watershed materials and flowing via streams to the lake, than what is being added to the watershed materials via atmospheric deposition.

watershed (all values in g of Hg/year)

rain + snow + watershed losses = streams .

+ 27 + x = 152x = 81

where x is the yearly watershed loss to the lake

lake

rain (on watershed) + snow (on watershed) + rain (on lake) + snow (on lake) + mobile watershed losses = retained in lake + lost from lake via stream

44 + 27 + 4 + 3 + 81 = 38 + 121 159 = 159

This mass balance is based on only one full year of data. Although the geological materials and flora are not expected to change very much in mercury concentration from year to year, stream flows, etc. with their mercury loadings can change drastically, even from one season to the next. More data is required to better estimate mercury fluxes in the system studied here.

CONTROLS ON THE UPTAKE OF MERCURY BY FISH .

CHAPTER

SELECTED ONTARIO LAKES

IN

4.1 GENERAL STATEMENT

As described in Chapter 1, some studies have shown that fish mercury levels increase with decreasing alkalinity (Scheider <u>et al</u> 1978), increase with decreasing pH (Tsai <u>et al</u> 1975), and increase with decreasing hardness (Rodgers and Beamish 1982). Other studies (Miller and Akagi 1979; Watson <u>et al</u> 1980; Suns <u>et al</u> 1980) suggest that other factors may be more important, and ascribe less significance to the effects of pH and alkalinity. It is therefore necessary to show that the phenomenon of increased fish mercury concentration with decreasing pH and alkalinity does in fact occur, and this must be proven before any explanation on how *i*t occurs can be put forward. Once this has been shown, a relatively simple explanation can be made as to why it occurs.

4.2

SELECTION OF STUDY LAKES

Three areas in Ontario were chosen for study. Groups of lakes were chosen in each area. Group 1, just west of Espanola, and Group 2, in Central



Ontario south of Lake Nipissing, were chosen to represent softwater lakes, as would be expected in light of the geology in both areas. These lakes would also be expected to have low alkalinities and possibly depressed pHs due to lake water acidification. Group 3, also in Central Ontario, but south of Group 2 (except for Vermilion Lake, northwest of Sudbury) were chosen to represent lakes of moderately hard to hard water. This is expected due to the carbonate terrain in which these lakes reside. These lakes would have somewhat higher alkalinities and pHs than the lakes in Groups 1 and 2, and serve as a controlgroup. The 17 lakes are listed and located in Table 4.1. Also shown is the year that the lake's fish were sampled by the Ontario Ministry of Natural Resources. Also refer to the map, Figure 4.1

After reviewing Ontario Ministry of the Environment (MOE) fish mercury data (Ontario Ministry of the Environment 1977) it was found that the fish species walleye appeared to exist in the most number of lakes, both hard and soft. Therefore, a primary criterion for selecting a lake for study was that it had fish mercury data for walleye. In this way all 17 lakes eventually chosen could be compared by at least one species of fish. Several of the lakes chosen also had fish mercury data for small mouth bass.

Another criterion for choosing this particular set of lakes is that they were expected to represent a wide range of water chemistries, and this in fact was found to be true.

Table 4.1

Group

Lake

ι.

. County or District Lat/Long

Group 1 - Espanola Softwater

		<i>,</i> ·	- •		
Agnew _e Evangeline Gough (Lacloche	Sudbury Sudbury Sudbury Sudbury		4622/8145 4608/8152 4618/8158 4610/8204	1975 1976 1975 1975	•

Group 2 - Central Ontario Softwater

CaribouParry SoundCecebeParry SoundCommandaParry SoundMemesaugamesingParry SoundRestouleParry SoundSkeletonMuskoka	4555/8005 1976/1977 4538/7933 1971/1977 4601/7943 1977 4600/8000 1975 4603/7946 1976/1977 4515/7927 1971/1077	
--	---	--

Group 3 - Central Ontario Hardwater

Balsam	Channel)	Victoria	4435/7850	1977
Dalyrmple		Ontario	4438/7907	1977
Huron (North		Algoma	4612/8239 •	1976
Scugog		Victoria	4410/7850	1970/1977
Sparrow		Muskoka	4447/7924	1971/1977
Vermilion	*	Sudbury	4447/7924 4630/8126	1971/1977 1977

· Year Sampled

ONTARIO MINISTRY OF THE ENVIRONMENT FISH MERCURY DATA

4.3.1 Description

4.3

MOE tish mercury concentration data (Ontario Ministry of the Environment 1977 and Neary <u>et al</u> 1980) are used exclusively herein. Since this research is based largely on the MOE data, a review of its structure is in order.

For a given lake, mercury data is presented by species. The number of specimens collected of each species is given, as well as the arithmetic mean and ranges of the fish mercury concentration in $\mu g g^{-1}$. Also given are the means and ranges of the length (cm) and weight (g) for each fish species. For samples with 5 or more specimens of the same species, regression analysis is performed on mercury and length using natural logarithm transformations.

The coefficients for the mercury versus length regression are given, as well as the correlation coefficient and the mercury concentration of a "standard length" fish. The report (Ont. Min. of the Environment 1977) states:

"The standard length of 50 cm for a walleye was selected as being a common size encountered in most collections. The mercury concentration at this length has been used to compare fish from year to year and area to area, eliminating variability due to differences in the average size of walleye making up the sample. Walleye collections were not available for all lakes, but

it was found that 60 cm lake trout and pike had levels similar to those of a 50 cm walleye. These "standard" mercury concentrations permit comparison of mercury levels between lakes, and offer a very approximate indication of relative mercury from one lake to another, or one year to another."

Mean fish mercury concentration within a lake, within species, is an average of all the mercury concentrations of all of that species captured. When the length and mercury concentration data of each fish captured is known, the amount of mercury in a standard length fish can be predicted. Both mean and standard length mercury values are used in this study. Mean values can be used to make comparisons between lakes (within species) and between species. When population differences (weight and length) of a species are comparable between lakes, standard length mercury concentrations can be used to compare lake to lake populations, even when a particular size class may be absent. Thus both systems give useful information, depending on how they are used.

MOE fish mercury data for the 17 study lakes is shown in Appendix

4.3.2 Pitfalls and Problems

Some problems are associated with using the MOE data in its present form, but these are either far outweighed by the usefulness of the data base or

are shown to be inconsequential. One major drawback is that the data, presented as "standard length" fish mercury concentration does not adequately account for the differences in growth rate, from lake to lake, in that there may be differences in the time required for fish to reach the standard length in different lakes. This will be shown not to be a problem in the lakes chosen for this study by analysis of Lake Memesaugamesing data (see Section 4.5.3.3).

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Another problem is that mercury enhancement due to acid stress on the fish population (resulting in absent size classes, for instance) may not be recognizeable in this type of data reporting. As will be shown, one lake, Memesaugamesing, was discovered to have a fish population affected, possibly, by acid stress, but the population differences between this lake and the other lakes showed up very clearly in a graph of fish length verses weight, for walleye.

Some lakes were sampled by the Ontario Ministry ON Natural Resources more than once. In these cases, MOE records give data for both sampling periods. For the lakes in this study which were sampled more than once, the data is compared in Appendix H.

As shown, there is a slight temporal increase in fish mercury in several of the lakes, while others show a slight decrease. Differences in the mean size of fish caught during a particular sampling event may account for some of this difference. Only one particular year of data is used in this study. Usually, the data set for the latest year is the data set chosen, however, if that data set is small compared to the previous set, the larger data set is chosen.

FIELD WORK AND LABORATORY METHODS

No water chemistry data suitable for use in this study, previously existed for these lakes. For this reason a general water chemistry reconnaisance was undertaken.

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All 17 water bodies were sampled during the early part of May, 1980, and the Central Ontario softwater group were resampled in August of 1980 in more detail. Littoral zone surface water, near shore sediment and adjacent soil samples were collected from each site. Water samples were collected from docks and other nearshore structures, usually directly into sample containers or with Van Dorn bottles in the case of boat sampling. The August sampling was done from a boat so that bottom waters and sediments in the central portions of the lakes could be collected. Sediment samples were taken with a stainless steel scoop, and in cases where this was not practical, by an Eckman Dredge. Soil samples were taken with a small stainless steel scoop. All samples were kept cool until shipment to the laboratory, where they were kept refrigerated. Analysis commenced immediately after the samples arrived at the laboratory.

For the lake waters, pH, conductivity and temperature were measured on site. pH was measured again in the laboratory under constant ionic strength conditions. The addition of a salt to bring all the samples to a constant ionic strength enables lake to lake pH comparisons to be made more easily; field pHs in very dilute softwater systems at natural ionic strength are approximations at best. Laboratory analysis were also performed for alkalinity, chloride, hardness (magnesium and calcium) sulphate, etc. Sediments and soils were analysed for

4.4

pH, mercury and other parameters.

Analytical methods followed those described in Analytical Methods Manual (Environment Canada 1979). See Appendix L.

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4.5 RESULTS AND DISCUSSION

4.5.1 Results

Results of the field and laboratory investigation are shown in Appendix I for all 17 lakes in the preliminary survey, and in Appendix J for the second survey on the Central Ontario softwater group. The data for pH, specific conductance, hardness, and alkalinity indicate a wide variety of lake water chemistries, from hard water, carbonate buffered lakes such as Scugog and Dalyrmple.to very dilute, soft water lakes such as Ahmic and Skeleton, as expected.

4.5.2 Data Reduction

In order to better evaluate the field and laboratory data in light of the MOE fish mercury data, certain data reduction procedures have been employed.

Appendix K depicts correlation coefficients between fish mercury

concentration and water chemistry parameters. As shown, the various water chemistry parameters having the greatest influence on mean and standard length fish mercury concentrations have the highest coefficients. These include field and laboratory pH, specific conductance, alkalinity and total hardness. The other parameters investigated do not appear to have as great a correlation with the fish mercury concentrations and therefore will not be considered further. An exception to this is surface sediment mercury concentration, which correlates highly with small mouth bass mean mercury.

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Table 4.2 describes, for the highly correlating-parameters only, within region means and standard deviations. pH and alkalinity are plotted graphically in Figures 4.2 and 4.3. The best fit curve through the data is calculated using the information shown in Table 4.2. The curves are generated using data from all 17 lakes, not the three lake groups.

4.5.3 Discussion

4.5.3.1 Alkalinity and pH effects on fish mercury concentrations

Standard length fish mercury verses alkalinity is plotted in Figure 4.2 for the three groups of lakes. Clearly, the relatively high alkalinity (~50 mgCaCO₃L⁻¹) lakes have fish with relatively low mercury contents (~400 ng g⁻¹), and relatively low alkalinity (~2 mgCaCO₃L⁻¹) lakes have fish with relatively high mercury contents (~600 - 1800 ng g⁻¹). The low alkalinity Central Ontario softwater lakes also show the greatest variation, 1 x S, where

Table 4.2	Solutio	n to y =	= a + b(lnx)	équations	for graphs.
У	x	a	b	r ²	
mean Hg	lab pH	8244	-3892	. 91	
mean Hg	field pH	5132	-2371	- 5.5	
mean Hg	alkalinity	413	-215	.84	
mean Hg	spec. cond.	2679	-456	.83	•
mean Hg	tot. hardness	2079	-454	.70	•
std. length Hg	lab pH	9558	√ -4495	.99	, r
std. length Hg	field pH	6486	-3021	.73	
std. length Hg	alkalinity	507	-253	.95	
std. length Hg	spec. cond.	3182	-539	.95	•.
std. length Hg	tot. hardness	2529	-556 .	85	•
lab pH	alkalinity.	-11.69	6.34	.90	
lab pH	spec. cond.	-1184	660	. 9 <u>4</u>	
lab.pH	tot. hardness	-290	162	.90	• •
alkalinity	tot. hardness	37.7	9.6	.95	•
alkalinity	spec, cond.	147	38.6	98	

98

 r^2 = coefficient of determination

Except for mean Hg and field pH most pairs of parameters had $r^2 > 0.80$. Poorly correlating parameters were mostly well below 0.50. A cutoff value of 0.50 was chosen because r^2 values from approximately 0.5 (actually 0.485) and above are considered significant when applied to a Student's t-distribution at the 5% level of significance. Also, a natural break, or void, occured in the r^2 values around 0.05.






Figure 4.3 The effect of decreasing pH on walleye mercury contents. For each lake group, the mean and one standard deviation is represented. Clearly, from lake group to lake group, as the pH decreases, the means of the standard length fish mercury contents increase.

S is sigma (standard deviation), of fish mercury concentration. As shown in Table 4.3, the standard deviation for these softwater lakes is actually less than that of the hardwater, but in terms of absolute range, softwater lakes have more variability with respect to fish mercury concentration.

The greater range in the alkalinity of the hardwater lakes is likely a direct artifact of the lake population chosen. This further emphasizes the point that fish mercury contents for these lakes vary only slightly with large changes in the relatively migh alkalinity range, while the softwater lakes exhibit large scale changes in fish mercury concentration in light of relatively small variations in the lower alkalinity range.

Figure 4.3 is similar to 4.2 but depicts lab pH rather than alkalinity. As shown, groups of lakes with lower pH exhibit higher fish mercury contents, as opposed to high pH lakes. This is shown more clearly with lab pH, taken at a constant ionic strength, rather than field pH taken at natural (very low for these lakes) ionic strength, which causes variability in pH readings when it is very low.

These two graphs show very clearly the relationship between alkalinity and pH and fish mercury contents for these particular groupings of lakes. Similar graphs can be made for specific conductance and hardness. These four parameters are all related, in that they are all a measure, in some way, of a watershed's ability to impart ionic strength to a lake water. As shown in Table 4.2, these parameters all correlate above 0.90 with each other.

100

Table 4.3 Within region means and standard deviations of highly correlating parameters.

Hgmean Hgstln pH lab pH fld alk sp.cd.T-hard Hgsfsed

Region lake

•

Espanola So Agnew Evangelin Gough Lacloche	oftwate ne	T							
Mean	710	960	6.68	5.77	.107	49.8	12.0	45	
Std. Dev.	159	116	.26	.09	.031	8.9	2.8	39	
% C.V.	22	12	4	2 -	29	18	23	87	

Central So	ftwater					-		
Ahmic	•							••
Caribou								
Cecebe						•		
Commanda	•							
Memesaug	amesing							
Restoule						•		
Skeleton								
Mean	1231	1396	6.20	5.84	041	32 3	10 2	110
Std. Dev.	514	634	.41	.19	.019	63	7	212.
% C.V.	42	45	7	3	46	12	• /	240
			•	5	. +0	1.	. ′	208
		· · · · · ·						

7.26

.58

8

1.244

91

•

159.0 41.0

37

1.133 94.7 15.1

60

107

66

67

Central Hardwater Balsam Dalyrmple North Channel of Lake Huron Scugog Sparrow Vermilion Mean 418 483 7.57 Std. Dev. 245 252 .42

59

% C.V.

% C.V. - Coefficient of Variation in %

52

6

t

4.5.3.2 Mathematical Relationships

Figure 4.2 suggests that, as lake water alkalinity decreases, standard length walleye mercury content increases, roughly according to the equation

xHg = 507 ~ 253InxALK

which is based on all 17 water bodies, where

xHg = mean of the standard length fish mercury

concentrations for a given group of lakes

xALK = mean of the alkalinities for a given group of lakes

The equation governing the pH relationship is

xHg = 9558 + 4495InxLABpH

where

ог

xLABpH = mean of the lab pHs for a given group of lakes

Consistent with the effects of alkalinity, low pH lakes, like low alkalinity lakes show more variability in fish mercury concentrations than do the higher pH (and alkalinity) lakes. As expected, and depicted in Table 4.2 (coefficient of determination = 0.90) the low alkalinity lake groups are also the low pH lakes. The statistical equations governing this relationship are

xALK = -11.69 + 6.34lnxpH

xpH = exp[(xALK + 11.69)/6.34]

4.5.3.3 Lake Memesaugamesing - An Acid Stress Anomaly?

Since uptake of mercury appears to be at least partially, controlled by pH, and pH is the primary control on acid stress in fish, this phenomenon may account in part for the higher levels of mercury in fish residing in acid lakes. Acid stress causes the fish population of a lake to generally be depleted with respect to young fish. Since older fish tend to have higher concentrations of mercury than younger fish, this would cause (statistically) the population to show greater average mercury concentrations in a fish species for a given lake.

Basically, if a fish population is skewed towards larger and heavier fish, with an absence of smaller fish, this may be an indication of acid stress in the fish population. Recruitment failure due to spawning and hatching problems associated with depressed pH environments, would eliminate the small fish subclasses. With less competition for food, the larger established subclasses of fish may have the tendency to grow larger and/or heavier.

Figure 4.4 depicts the 3 groups of lakes in relation to walleye weight and length. This envelope type diagram is constructed from data for each individual fish captured (MOE, raw data). The fish population of Lake Memsaugamesing, of the Central Ontario softwater group, is shown separately.

As shown, the walleye length-weight relationships in the population of all three lake groups generally overlap. The Espanola softwater lakes contain somewhat heavier but shorter fish in the heavier subclasses. This may be a result of factors such as water temperature, which are unrelated to acid stress.



Figure 4.4 - Group to group comparison of walleye lengths and weights. For each lake group, all walleye lengths and weights. For each lake group, all walleye captured in all lakes of the group are used to represent the field. Lake Memesaugamesing data is left out of the Central Ontario Softwater group and shown separately. The three lake groups generally have fish of similar weight to length relationships, while Lake Memesaugamesing appears to have walleye which are somewhat heavier than the other lakes, for a given size class.



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Figure 4.5 Group to group comparison of small mouth bass lengths and weights. For each lake group, all bass captured in all lakes of the group are used to represent the field. No bass were captured in the Espanola Softwater lakes. The length to weight relationships between the hardwater lakes and the softwater lakes are similar. 104

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Acid stress among this lake group may also be ruled out by the fact that the Espanola softwater lakes are well represented in the shorter and lighter size ranges, even more so than the hardwater lakes.

A similar comparison is shown in Figure 4.5 for small mouth bass. Again the fish populations of both Central Ontario groups are similar with respect to length and weight (no small mouth bass were captured by MNR in the Espanola softwater lakes).

Frequency diagrams, Figure 4.6 and 4.7, further establish that acid stress is not affecting the fish populations of these lakes. Figure 4.6, length versus frequency of that length occurring, shows that the Espanola softwater lakes and the hardwater lakes have the same mode. The Central Ontario softwater lakes peak one size class shorter. It appears that the opposite is occurring from what would be expected with acid stress, particularly with respect to the Espanola softwater Lakes, since the bulk of their population lies to the short end of their mode, and contains the smallest fish of all three groups. The Central Ontario softwater lakes show some skewness 'to the longer size end, but this is largely due to the effect of the Lake Memesaugamesing population.

When comparing weight versus frequency of that weight occurring, the populations are all skewed to the heavy fish, but modes are all within the first two (lightest) subclasses. Again, the Lake Memesaugamesing population exerts influence on the skewness of the Central Ontario softwater lakes.

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Figure 4.6 Walleye size distributions for the three lake groups. Modes are within one size class of one another between the groups, suggesting that there is little or no difference in walleye population condition among the groups.

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It appears from the diagrams that acid stress does not affect the fish populations of these three groups of lakes, with the exception of Lake Memesaugamesing. This lake, as shown in Figure 4.4, retains a population of relatively large and fairly heavy walleye, as compared to the other lake groups.

Figure 4.8 shows this effect as a frequency diagram for length subclases for walleye and small mouth bass in Lake Memesaugamesing. The population for walleye is skewed to larger fish, with the two smallest subclasses void. The effect is not so-clear with small mouth bass, but the smallest subclass is still empty. Figure 4.9 depicts similar results for weight versus frequency.

It can be concluded therefore that acid stress may be at least partly responsible for Lake Memesaugamesing fish containing statistically high mercury contents, compared to hardwater lakes. There appears to be sufficient evidence to state that acid stress does not affect fish populations of the other lakes in this study.

The acid stress on the fish population of Lake Memesaugamesing is the likely cause of "statistically high" mercury in the fish of this lake. This is only an artifact of the lake containing larger, heavier fish, which contain more mercury, generally, than lighter fish. For a given fish length, however, mercury concentrations in the fish of Lake Memesaugamesing are not out of line with other similar lakes which do not show acid stressed fish populations, as shown in Appendix G. Standard length walleye (50 cm) for Lake Memesaugamesing contain well within one standard deviation of the mean of mercury content for its group



Figure 4.8 Fish population length distributions for Lake Memesaugamesing. For both small mouth bass and walleye, the smallest size classes are absent, and for walleye, the population is skewed towards longer fish.



Figure 4.9 Fish population weight distributions for Lake Memesaugamesing. The walleye population is clearly skewed towards heavier fish.

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of lakes. The mean mercury value for this lake, as expected, is at the high end for this group, being one standard deviation above the mean, of the mean mercury values.

4.6 Summary

The preceeding has shown definitively that the phenomenon originally described by Scheider <u>et al</u> (1978), whereby low alkalinity lakes exhibit high fish mercury concentrations actually is true, at least in the lakes chosen for this study. The effect has also been shown here to occur for pH as well as hardness and specific conductance. This combined relationship is not unexpected since these four parameters are all related.

This preliminary field study raises several conclusions and questions.

Fish mercury concentration is definitely influenced in some manner by pH and possibly by the other water quality parameters associated with ionic strength.

Although the field sampling for sediment and soil mercury carried out in this phase of the study was performed as a quick survey only, it appears that absolute levels of mercury in the various sediments and soils have perhaps only marginal influence on fish mercury concentrations.

The lakes chosen for study, except Lake Memesaugamesing, do not

show signs of acid stressed fish populations. Lake Memesaugamesing show's signs of "apparent" acid stress induced enhanced fish mercury contents. Standard length mercury content of walleye for this lake indicates that enhancement is not "real", that is acid stress has caused the fish population to be skewed to heavier, larger fish (which contain more mercury), giving rise to the "apparent" or "statistically high" population mercury levels. However, acid stress has not caused any size classes of fish to uptake more than the amount of mercury they would have if they had been in a similar water chemistry lake which did not have an acid stressed fish population.

4.7 FURTHER DISCUSSION

Now that the phenomenon of increased uptake of mercury by fish with decreasing pH has been clearly established, the controls governing this uptake can be studied.

Two main controls are considered here. These are lake trophic state and the chemical speciation of mercury.

4.7.1 Lake Trophic State Considerations

The trophic state of a lake may influence the flow of mercury through the ecosystem.

Oligotrophic lakes are clear, as a result of low biomass, and hence low total suspended load. Eutrophic lakes, being rich in nutrients, generally have elevated biomass. Since lake eutrophication is a major source of adding total particulates to a lake, there may be some relationship between trophic state, particulate mass and fish mercury content. More eutrophic lakes would contain more seston and hence more sites for both water column methylation of mercury and inorganic speciation changes of mercury to occur.

A eutrophic lake expected to contain greater masses of phytoplankton and zooplankton, which, as shown for Wright's Lake in Chapter 3, contain relatively high amounts of mercury.

Various studies (Armstrong and Hamilton (1973) and literature reviewed in Chapter.3 of the present study) have shown that particulates account for a large percentage of water column mercury. This phenomenon may cause the following possible reaction to occur. The particulates would likely adsorb a portion of the available mercury. Rather than immobilize the mercury, it would be in more intimate contact with methylating bacteria, which are also associated with the seston. The particulates would act as sites for the methylation process to occur, and soluble methylmercury would be released to the water. Other inorganic processes may also occur on the particulate sites, as described in the next section.

The Central Ontario softwater lakes were studied with respect to their particulate masses and mercury contents in relation to fish mercury concentration. On a lake to lake basis, the amount of surface water particulates

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does not appear to affect mercury concentration in fish. However, on samples taken 1 m from the bottom of each lake the amount of particulates does appear to be related to fish mercury content. As particulate mass increases, from lake to lake, fish mercury concentrations also show an increase, according to the equations

r² = 0.62

 $r^2 = 0.41$

X = 0.05(P) + 0.66 and

Y = 0.05(P) + 0.82

where

X = mean walleye mercury concentration in $\mu g g^{-1}$ Y = standard length walleye mercury concentration in

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µg g⁻¹

P = concentration of particulates in mgL⁻¹ 1 m from lake bottom

Is this phenomenon a cause of fish mercury uptake or an effect from some other reaction taking place at the same time? That is, do increased bottom water particulates, because they increase the number of possible methylation sites, cause more mercury to accumulate in fish, or does the same factor that causes bottom water particulates to increase, also increase fish mercury contents?

It has already been shown that depressing the pH of a lake water has an effect on the fish mercury content, directly or indirectly. Deductively, one of the above mentioned alternatives can be discarded.

Particulate mass is controlled by several factors:

-decomposition and resuspension of sediment and sestonic material -in situ colloid formation

Will depressing the pH enhance any of the above?
-productivity - no, acidification has been shown to cause a decrease in biomass concentration in Ontario lakes
-debris input - no, this is a physical process
-decomposition - no, depressed pH inhibits organic decomposition by affecting anaerobic decay rates
-colloid formation - no, solubility of i.e. iron hydroxides increase with

This suggests that no relationship should exists between pH and particulates, but for this particular group of lakes it was found that the total particulates actually do increase slightly with decreasing pH.

decreasing pH

The amount of mercury associated with the seston may also be of some consequence. In this set of lakes, however, there is almost no correlation $(r^2 = 0.01)$ between fish mercury content and particulate mercury content.

Relationships can now be constructed (in context to this setting): -as pH decreases, particulate mass increases (probably not related) -as particulate mass increases, fish mercury content increases -as pH decreases, fish mercury content increases

therefore

-fish mercury content increases as pH decreases and particulate mass increases

Concerning the first point above, the effects of bottom invertebrates which might disturb and resuspend the sediments, as well as the topography of the area surrounding the lakes, which may allow wind to affect bottom mixing and currents, is not considered here.

Skeleton Lake, which has the hardest water and highest pH of the Central Ontario lake group chosen, conforms to this hypothesis in that it also is the most oligotrophic lake and contains fish with the lowest mercury contents. At the same time, however, Skeleton Lake also contains particulates with the highest per unit mass of mercury and water with the highest concentration of mercury. This suggests that water mercury concentration is not a significant factor in determining the amount of mercury taken up by fish living in the water. Since there are fewer sites for mercury to bind to, because of the lower particulate mass, each site will contain proportionately more mercury. Because of the pH, the mercury appears to be in a relatively immobile form, as suggested by the low fish mercury contents in this lake.

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The total particulate mass of a lake is controlled to a certain extent by the trophic state of the lake. The Central Ontario softwater lakes and their rank in terms of trophic state and mean and standard length fish mercury contents are depicted in Table 4.4. As shown, the most eutrophic lakes are associated with the highest fish mercury contents. Ranking of the bottom water

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Bottom Water Lab pH Rank	2		Three	PH's	ß	ĸ	Ф
Mass of Bottom Water Parlculate Rank		Highest	1 Mass of Bottom	 Particulates (except Restoule) 		4	5 Mass of Particualtes
Mean Hg Rank	Э		Three 1. Highest	FISH Hg	4	3	5 Lowest Fish Hg
Std. Length Hg Rank	Three	1 Highest		2	4	£	Lowest 5 Fish Hg
Trophic State Rank	Throo	1 Most	Eutrophic	2	ß	4	5 Most Oligotrophic
Trophic State	Eutrophic	· Eutrophic	Eutrophic .	ng Eutrophic Mesotrophic	Mesotrophic	Mesotrophic- Oligotrophic	Oligotrophic
Lake	Cecebe	commanda	Restoule	Memesaugamesir	Ahmic	caribou	Skeleton

Table 4.4The relationship between a lake's trophic characterand mean and standard length fish mercury concentrations for for the lake'swalleye population. The most eutrophic lakes generally have the highest masses These euatrophic lakes are also the ones with the highest fish mercury contents. More contents, as well as higher bottom water pHs and less bottom water particulate oligotropic lakes have fish populations with relatively lower fish mercury of bottom water particulates and the lowest bottom water pHs. mass.

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particulates and the bottom water pH are also closely related to each other and the other parameters described.

This evidence tends to support the hypothesis that more particulates are related to increased fish mercury contents. This may occur as a result of the particulates sequestering inorganic aqueous mercury and making it available, either by methylation or speciation change, and re-emitting it in a more readily taken up form.

As shown in Table 4.4, there is also some relationship between trophic ranking and water pH. Cecebe Lake appears anomalous. It appears that, for this set of lakes, lower pHs are associated with more eutrophic conditions.

Nutrients control the trophic state in a lake. Generally, the higher the available nutrients, the higher the biomass in a lake, and the higher the trophic state. Lake acidification may affect nutrients and trophic state by decreasing the biomass faster than it can be regenerated. This phenomenon is not apparent in this set of lakes, suggesting pH and trophic state do not together affect fish mercury concentrations, but rather trophic state may affect the amount of mercury which is available, while pH may control the rate of production of available mercury, as well as speciation, as described in the next section.

Mercury contents of phytoplankton and zooplankton were determined for each lake. Highest levels of phytoplankton mercury are associated with Skeleton Lake, which has the lowest fish mercury. As fish mercury levels increase, mercury in phytoplankton generally decreases. Although not conclusive, this suggests that, as for particulates, the less sites available for mercury to go into, the more will go onto the available sites. Even though mercury is elevated in the phytoplankton, this is not reflected in the fish mercury contents. There is no relationship with zooplankton, either. This suggests that there is no observable food chain link between phytoplankton and fish for this set of lakes, for walleye. There does appear to be a food chain link of mercury between phytoplankton and zooplankton. This is consistent with the literature.

4.7.2 Thermodynamic Speciation of Mercury

As described in Chapter 2, certain species of mercury are more mobile than others, and are more readily able to transfer themselves from one ecosystem compartment to another. Although many ligands can associate themselves with mercury, it can be generally concluded that the most important ligands, in the natural system studied here, are chloride and hydroxide.

Fish mercury contents have been shown to vary with pH. pH is also a master variable in the speciation of mercury. It can be hypothesized therefore, that as long as mercury is available in aqueous form in the water, pH and pCl will control what form it is in. It is generally understood that the species of mercury most readily absorbed by fish are non-polar, non-ionic forms, not heavily hydrogen bonded to water. $HgCl_2^{\circ}$ and to a lesser extent $HgOHCl^{\circ}$, would be most mobile and thus biologically available, while $Hg(OH)_2^{\circ}$, although

non-ionic, is heavily hydrogen bonded to water and thus less mobile.

It would be reasonable to assume, therefore that as the chemistry of a lake water approaches conditions depicted for pH and pCl in the $HgCl_2^{\circ}$ field, the more $HgCl_2^{\circ}$ will be available, compared to the other relatively less available species, and the more potential mercury there would be to enter the fish.

Figure 4.10 shows the three groups of lakes and how their surface pHs and pCls coincide with the predominence fields of mercury. Clearly the softwater groups, which also have the highest fish mercury values, tend to be closer to the $HgCl_2^{\circ}$ field while the hardwater lakes, which contain fish which are low in mercury content, coincide with the $Hg(OH)_2^{\circ}$ field.

This same test of a lake's closeness to the $HgCl_2^{\circ}$ field with respect to its mean and standard length fish mercury contents was also applied to the individual in the Central Ontario Softwater group. Referring to Figure 4.11, for this group of lakes, two of them, Skeleton and Ahmic, which contain fish with lowest amounts of mercury, have pHs and pCls which cause their inorganic mercury to exist as the species $Hg(OH)_2^{\circ}$. The other lakes, with Higher fish mercury contents, have more of their mercury as the complex $HgCl_2^{\circ}$ or $HgClOH^{\circ}$.

The ranking of fish mercury contents versus closeness to the $HgCl_2^{\circ}$ field in Figure 4.11 is shown in Table 4.5. Except for lakes Caribou and-Commanda being transposed, the closer a lake's mercury tends to be in the



Figure 4.10 Mercury species predominance diagram with lake group water chemistries superimposed. The Central Ontario Hardwater Lakes have pHs and pCls such that they lie well into the biologically non-mobile Hg(OH)₂° field. These are the lakes with relatively low fish mercury contents. Both softwater lake groups, on the other hand, lie nearer the HgCl₂° field. HgCl₂° is considered biologically mobile and capable of entering a fish. The lake groups lying close to this field contain fish with relatively higher mercury concentrations. Table 4.5Comparison of increasing fish mercury contentsto mercury speciation.

Standard length fish mercury

content, ranked highest to lowest

Lake

HgCl₂° field Restoule 1 1 Commanda 2 4 Cecebe 3 3 Caribou 4 5 2 Ahmic 5 Skeleton 6 6 Lake Mean fish mercury content, ranked highest to lowest Mercury species, HgCl₂° field C

Commanda Restoule Caribou	1 2 3	4 — 1 2
Cecebe Ahmic	4 5	3 4
Skeleton	6	6

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Mercury species,

closeness to.



seven Central Ontario Softwater lake chemistries superimposed. The lakes with the lowest mean and standard length fish mercury contents lie well into the non-toxic Hg(OH)₂° field (the upper shaded area). Lakes with higher fish mercury contents lie closer to the $HgCl_2$ ° field (the lower shaded area).

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complex HgCl₂°, the greater is its standard length fish mercury burden. The same appears true for mean fish mercury, again with Commanda Lake out of order. Lake Memesaugamesing was left out of this ranking, as its fish mercury burden may have been at least partially influenced by acid stress rather than mercury speciation effects.

4.8 Summary

In this chapter it has been shown that:

1. The lakes chosen for study do exhibit the phenomenon whereby decreasing the pH (and alkalinity and hardness) is associated with increase fish mercury concentrations, on a lake to lake basis.

2. One of the lakes, Memesaugamesing, appears to contain fish affected by acid stress, which may be at least partially responsible for fish in this lake having elevated fish mercury concentrations.

3. This acid stress effect does not appear to affect any of the other lakes in this study.

4. The amount of bottom water particulates may affect fish mercury concentrations in that, in the Central Ontario Softwater Lakes, as bottom water particulates increase, so did the fish mercury content, on a lake to lake basis.

5. Of the Central Ontario Softwater Lakes studied, the most eutrophic lakes contained fish with the highest fish mercury content, while the most oligotropic lake had fish with the lowest mercury concentrations.

6. The pH and pGI of a lake govern the chemical species that mercury will exist in. The hardwater lakes, whose mercury is predicted to be in the form

 $Hg(OH)_2^{\circ}$, which is not considered biologically available, contain fish with the lowest fish mercury content. The Espanola and Central Ontario Softwater Lake groups, whose mercury is predicted to be in the relatively easily uptaken form $HgCl_2^{\circ}$, contain higher fish mercury contents.

7. When observing individual lakes in one group, the Central Ontario Softwater, except for one misfit lake, the more $HgCl_2^{\circ}$ predicted for that lake, as opposed to $Hg(OH)_2^{\circ}$, the greater is the fish mercury content of that lake.

CHAPTER 5

CONCLUDING STATEMENTS

5.1 GENERAL SUMMARY

The state-of-the-art literature on environmental mercury has been summarized. There appears to be some controversy over several aspects of fish uptake of mercury, including gill uptake versus foodchain biomagnification and whether or not mercury uptake by fish is affected by depressed pH. The most recent literature addresses the effects of water hardness on gill permeability to mercury. The control of fish uptake of mercury by chemical speciation, as proposed by the present study, was not discussed in any of the literature found to date. It is suggested therefore, that this thesis presents a unique approach to the phenomenon of increasing fish uptake of mercury with decreasing pH (and increasing $HgCl_2^{\circ}:Hg(OH)_2^{\circ}$).

The mass and concentration of mercury in various ecosystem compartments were determined for Wright's Lake (Ontario) and its watershed. This small, geologically simple, acidified watershed has most of its mercury mass sequestered in its overburden, soil and sediments. As shown in Figure 3.3, the highest concentrations of mercury are found in the lake's particulates, phytoplankton and zooplankton. The main source of mercury to the watershed appears to be from atmospheric deposition. Flux calculations suggest that the

watershed materials are now losing mercury to the lake and its seston and sediments and that these three receptor compartments are increasing in mercury concentration. Refer to Figure 3.4. This was likely not always the case, as the overburden must have at one time, been a net accumulator of mercury, since its present mercury concentration is about 10 times higher than its parent material. It is not known whether the relatively recent phenomenon of acid precipitation is causing the watershed materials to purge themselves of mercury.

The present study has clearly shown that there is a relationship between enhanced mercury uptake in fish and decreasing lakewater pH and alkalinity, on a lake to lake basis (Figures 4.2 & 4.3). Other relationships were also encountered. On a lake to lake basis, fish mercury concentrations were higher when the lake was more eutrophic and the bottom water particulate mass was higher, as shown in Table 4.4. These two factors are probably related and suggest perhaps that increasing the eutrophic character of a lake (and its particulate mass burden) increases the sites for mercury methylation to occur on. Then, the methyl mercury may or may not be made available for uptake by fish.

In the lakes chosen for study, once the phenomenon of increasing fish mercury concentration with decreasing pH was clearly shown to exist, the effect of thermodynamic speciation of mercury on upfake could be established. pH, together with chloride concentration, governs what chemical species or complex mercury will exist in. Previous workers have often suggested in the literature that inorganic aqueous mercury exists as Hg^{2+} and that this is the inorganic form taken up by fish. The non-biological literature has clearly

established this not to be the case. Using well documented equilibrium constants, a pH/pCI mercury species predominance diagram can be constructed (Figure 2.4) to show that, under typical lake water conditions of pH and pCl; inorganic mercury will exist as either $Hg(OH)_2^\circ$ or $HgCl_2^\circ$ with a possible HgOHCI° subcomponant. The $Hg(OH)_2^\circ$ is not considered toxic while the $HgCl_2^\circ$ is easily taken up by fish. Lakes whose pH and pCl are such that their mercury is in the $Hg(OH)_2^\circ$ form contain fish with relatively low fish mercury content. Lakes with lower pHs, the acid lakes or acid susceptable softwater lakes, have their mercury in the $HgCl_2^\circ$ form. These lakes contain fish with relatively higher fish mercury contends. (See Figures 4.10 & 4.11.)

The concepts developed in the present study depend upon the inter-relationship of the physical chemistry concept of thermodynamic chemical speciation of mercury with the fisheries science concept of non-polar, uncharged and biologically mobile chemical species, such as $HgCl_2^{\circ}$, having a greater efficiency to be absorbed by fish lipid, as opposed to a biologically non-mobile species like $Hg(OH)_2^{\circ}$.

This thesis puts forth the aforementioned hypothesis of thermodynamic speciation for further consideration. This does not suggest that the process defined here acts independently to produce the effects shown in nature. It is most likely that this process acts together with other processes described in the literature to increase mercury burdens in fish with decreasing pH, alkalinity and hardness.

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APPENDICES

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Appendix A

Phytoplankton and zooplankton in Wright's Lake.

Organisms caugth in a phytoplankton net towed along the surface of mid-lake, August 1980

organism counts/10mL Ankistrodesmus falcatus (var. acicularis?) 600 Denobryon sp. 6. T. flocculosa present T. fenestrata present solitary flagellates 8,500 solitary non-flagellates Merismopedia sp. 17,500 Chroococcus sp. 2,800 other 31,400 Cyclotella sp. 5 Navicula sp. present Peridinium and/or Glenodinium spp. 6 Frustulia sp. 1 Pinnularia sp. present Cosmarium sp. present miscellaneous diatoms 3 Eunotia sp. present Stauroneis present Tetraedron regulare (?) present

Organisms caught in a zooplankton net at 10 m depth, August 1980

Organism

counts/100 mL

Cyclotella spp. 155 Bambusina sp. 15 Cosmarium 15 Miscellaneous diatoms 15 miscellaneous phytoplankton (Chroococcus turgidus?) 15-

Organisms caught in a zooplankton net at 25 m depth, August 1980

Organism

counts/100 mL T. flocculosa 300 Cyclotella spp. 320 Dinobryon sp. 17 T. fenestrata 17 Eunotia spp. 5 Gomphonema sp. 17 Gomphonema acuminatum 17 miscellaneous diatoms 32 miscellaneous phytoplankton 17

		•		
parameter .	units	epilimnion	hypolimnion	when sampled
temperature	°C	21.8	,	August 1070
		21.8	43	August 1979
		22.0		lato August 1980
field pH	рН	6.21	6.23	August 1970
		5.57	0.25	May 1080
		5.75	5 08	
		5.39	5.00	late August 1980
lab pH	рН	6.60	6 35	face August 1980
	•	6.21		May 1080
•		6.27	6 11	
conductivity	µScm ⁻¹	29.4	30 3	August 1980
		25.9	20.3	Mar 1080
alkalinity	megL ⁻¹	0.028	0.028	May 1980
	•	0.023	0.020	August 1979
calcium	mgL ⁻¹	1.95		May 1980
	9-	2.15		August 1979
		1.90	1 09 1	May 1980
magnesium	mgL ⁻¹ .	0.71	1.90	early August 1980
-		0 71		August 1979
•	\frown	0.82	0 00	May 1980
total hardness	mel-1	7 70	0.82	early August 1980
	-6~	8 20 °		August 1979
		0.29		May 1980
PO. (unfilt.)	1. ⁻¹	<u>/ 0</u>	0 5	early August 1980
P0,(filt.)	-	1 0	9.J	early August 1980
$NO_{4}^{4} + NO_{4}$	⁻¹	27	4.0	early August 1980
sio 3	· ^{µg1} -1	21 ·	50	early August 1980
chloride		2.7	1 1 5	early August 1980
sulphate		1.13	1.15	early August 1980
	ш8т <i>•</i> ′	10.0	,	August 1979
	, · .	9.J 9.pr	0.00	Мау 1980 .
$A1^{3+}(unfilt.)$		0.20	8.25	early August, 1980
$A1^{3+}(fi1t)$	на п ,	11 .		early August 198 9.
chlorophyll a	ma m-3	11		early August 1980
narticulates	^{wg} ^w l	2.03		early August 1980
pur creditates	шĞГ	3.9	4.8	August 1979
bacteria	• • •			
fecal coliform	counte / 100-1	•	•	·
total coliform	counts/100mL	0	0	early August 1980
	Counts/100mL	U	U	early August 1980
Secchi desth				
,	ш.	9.20		August 1979
	•	A 22 .		early August 1980

Appenix B

Rain, snow and meltwater analytical results.

Location	Sample	Field pH	Lab pH	Alkalinity (µeqL ⁻¹)
500 m north of Wright's Watershed	snow upper 2 cm 2-17 cm 17-32 cm	4.67 4.57 4.53	5.75 5.58 6.02	0.120 0.096 0.145
. .	meltwater stream	4.75	6.04	0.145
Evangeline Lake	outflow		6.47	0.230
Restoule Lake	rain	3.75	,	÷



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Field surveys of Wright's Lake Watershed.

Appendix D

Survey

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<u>Period</u> mid August 1979 early May 1980 early August 1980

> late August 1980 late February 1981

preliminary reconnaissance of water, sediment and soil

Principal Work Performed

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comprehensive sampling of ecosystem

resampling some ecosystem compartments, seston investigation, gill netting

4

gill netting

snow and meltwater survey

	<u>`</u>	•		· · ·
	·			
	<u>.</u>	• • /	•	154
•		\bigcirc	•	
	ecosystem compartments.	ercury concentrations	of various Wright's	Lake
	Ecosystem Compartment	Total [Hø	Month Sampled	·.
	•	ng g	, nonch Sampied	
	0 45 um filtored labe and			
	epilimnion	3r 0.05	May 1080	•
	• • • • • • •	0.05	August 1980	· •
	hypolimnion	0.025	August 1980	,
	lake sediment		\sim	•
	location #1 - 2.53 r	n depth	·	
	0-5 cm	. 20	August 1980	· ·
·	5-10	164		• .
	location #2 23 m (lepth ()	• ·	•
	. 0−5 cm.	82 \	•	
	5-10	77	•	
	10-15 location #3 - 10.7 r	25 1 depth		3
· · · · ·	0-5 cm	300 .		
	5-10	390		· ·
	10~15	220		
	13-20			
	sediment pore water (locat	:ion #3), 0.45 µm filt	ered.	
	0-5 cm	0.60 •	August 1979	•
, .	10-15	0.05	•	•
-	15-20	<0.05	· · · · · · · · · · · · · · · · · · ·	
	moin inflam ann an fa			
	main initow, stream surface	sediment (sampled 10) m upstream from mou	th) .
			May 1900	. • .
	swamp sediment		`	
	0-3 cm 3-8	39 443	May 1980	•
	8-15	45		
	, 15-20	48	· •	
• •	augenteito mideo anal - li	ient ,	57 .	
· · . 2 .	YUALLZILE TIOVE DODA SEATE		May 1980	
···. 	small pond 0-5 cm	. 95	110 1 1 1 1 1 1 1 1 1 1	
•	small pond 0-5 cm large pond 0-4	95 1356	May 1900	
•••••••••••••••••••••••••••••••••••••••	small pond 0-5 cm large pond 0-4	95 1356	nay 1900	
	watershed soils location #1 (near Wr	95 1356 ight's Lake outlet)		
	watershed soils location #1 (near Wr 0-8 cm	95 1356 ight's Lake outlet) 110	August 1979	
	watershed soils location #1 (near Wr 8-11	95 1356 ight's Lake outlet) 110 490	August 1979	
	watershed soils location #1 (near Wr 0-8 cm 8-11 11-15 15-46	95 1356 ight's Lake outlet) 110 490 560 770	August 1979	· · · · · · · · · · · · · · · · · · ·
	watershed soils location #1 (near Wr 0-8 cm 8-11 11-15 15-46	95 1356 ight's Lake outlet) 110 490 560 770	August 1979	
	watershed soils location #1 (near Wr 0-8 cm 8-11 11-15 15-46	95 1356 ight's Lake outlet) 110 490 560 770	August 1979	
	watershed soils location #1 (near Wr 0-8 cm 8-11 11-15 15-46	95 1356 ight's Lake outlet) 110 490 560 770	August 1979	
	watershed soils location #1 (near Wr 0-8 cm 8-11 11-15 15-46	95 1356 ight's Lake outlet) 110 490 560 770	August 1979	

location #2 (10 m south of Wright's Lake south shore) 0-2 cm 29 May 1980 2-5 244 5-10 32 10-15 .90 location #3 (watershed west flank) 0-5 199 August 1980 5-10 115 10 - 1528 0 location #4 (south of location #1) 0-2 cm 135 August 1980 2 - 4112 4-7 16 7-20 27 location #5 (near large pond, quartzite ridge) 0-3 cm 128 May 1980 3-7 35 location #6 (near small pond, quartaite ridge) . 1-5 cm 178 May 1980 bedrock (Lorraine Formation) orthoquartzite from quartzite ridge near ponds 10.9 May 1980 micaceous and hematitic sandstones (quartzites) from south of Wright's Lake pink 10.2 August 1979 white 8.5 weathered surface (2 mm) of white sample 7.9 . feldspathic sandstone 10.4 diabase dyke sampled 12 km east of Wright's Lake, intruding Lorraine quartzite 5.5 August 1979 . *1*. forest litter from soil location#2 60 May 1980 forest moss 177 May 1980 water plants from small pond <5 May 1980 water plants from large pond 245 May 1980 ground moss from near near pond <5 May 1980 pine needles <5 May 1980 cedar leaves <5. May 1980 : rock lichen from near large pond 64 . May 1980 swamp moss May 1980

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bi	rch wood		· •		· ·
	10 year ol	.d tree 🤺 🚩	43	May 1980	•
	sapling		41		•
• •	The second se	🔍 🖕 🙀			۰.
ce	dar wood (grow	ving in swamp)	45	May 1980	
		_	•		
tr	ee fungus	. G	56 .	May 1980	
			り		•
ne	ar shore plant	S		- *	
•	growing on	bottom ôf lake	24	August 1980	-
	water kily	pads	4	Magdot 1900	
	$\langle \cdot \rangle$	-			
ct	am (from nearb	y Lacloche Lake)	<5 -	May 1980	· · · · ·
	- 1	•	-)	• ¹
wa	ter beetles	r.	<5	[`] • • • • • • • • • • • • • • • • • • •	
~	•				
- 5 p	eckled trout (0.6 m length 3.1	2 kg weight)		
•	white musc	1e 😽		_	
-		anterior 🗡	268 -	- August 1980	
	· ` ` ` ``	central -	165	. August 1900	
		Dosterior	100		
🕜 🔥 🛣 🖓			109		
T	<u> </u>	average	181	• •	
		p-1			
	2 C			•	
- · ·	3.0 Cm	U.33 g	. 135	August 1980	
	4.0	0.72	166	د.	-
. Lot	<u> </u>	0.72	· 171	•	
R m	4.5	0.93	143		
	4.4	0.75	165	•	
	4.8 _r	1.14	180		
ave	erage	,		1	
	. 4.4 لر	0.76	157		· •
		•		. /	•
phy	toplankton	sample #1	240	May 1980	•
	-	sample #2~	523	Anonet 1020	4
			~ ~ ~	AUGUST 1200	
200	plankton	sample #1	530	Man 1090	
	\$	sample #2	850	MBY 1980	•
N	\sim	sample #?	8/2		•
· · · · ·		sample #/	04Z	August 1980	,
· · · · · · · · · · · · · · · · · · ·		Sembre 14	020		
. ה פו	ticulates	anilimnian			
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Appendix r. Sprea	dsheet ou	itput	tor m	ercury	mass	balance.
measured values	-				•	•
watershed area			~ -			_
lake untorchod anos	·.	.•	3.5			sq km
lake area			ک			sq. km
lake to lake meteraked			. 26			sq. km
dopth of moch mathematic			10		•	z
depch of rock weathering			.002	•		m
density of Dedrock			2.65			g/cc
precipitation			•84			m/yr
			.64			
SnowIall		•	2.04			m/yr
snow as liquid			.2			m/yr .
escimated values						
lake volume						
lake volume		28	500000			cu. m
voight of water		28000	00000			L
		2	.8E12			g
Juccrop	:		60			z
Dutcrop area			8.1			sa km
overburden			30			вц. кш 7
overburden area			0			A a.a. 1
average overburden thickness			.,			вq.кш —
average soil thickness			15			ш
snow:melted snow			10			ш
land surface area in waterche	a	J	01			~
lake surface area in watershe			91	*		4 ' ¥
vater lost from system by	•		,			*
vapotranspiration etc. in 1	VAAT		60 G			•••
lake particulates	year		00.0 /-			A /-
pilimnion particulates			2 0			mg/L
partacutates			2.9			mg/L
nercury contents (nomin	nal)		•			
edrock "			10	•		nala
weathered surface of bedrock		•	20 20	••		ug/g
.oss in-surface	•	•	2			
overburden	•		4 55			
oil			001			
ain			100		\sim	
now on ground			1023		. `	\sim
ake water			.05			
ake particulates fever	(مور		200			

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•	· · ·		158 •
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	assumed values		
	1 ga		
	inflow streams flow	180	d/yr
	inflow rate	8	L/sec
	outflow rate (oplowland)	300	d/yr
· •	outrow rate (carculated)	3.818690467	L/sec
			· /
	calculations	~	-
•	· ·	\	· ·
	tot. rock weathered since glaciation	3600	си т
-	weight of rock weathered	954000000	o
	amount of mercury released	19.08	о g /
		· • • •	
	volume of overburden	900000	eu. a
	emount of more and	2.385E12	8 -1
	amount of mercury	131175	8 .
	Volume of soil	135000	•
-	weight of soil	3 5775811	cu. m
•	amount of mercury	35775	8
	·	00770	8
	soil & overburden volume	1046500	cu. m
• •	weight	2.773225E12	g
	amount of mercury if all	_	.
	at bedrock concentration	27732.25	8
	therefore	· · · · ·	- N .
	amount of mercury in soil and	•	
	overburden less mercury derived	130217 75	¥
	from rock weathering	i.e. entered from oute	g the succession
7			The cire system
· · · · ·	entering the system on a yearly basis	s (watershed)	
	rainraii	.64	m/yr
	soil and everywhere		2 *
	weight of rain	1747200	cu. m
	amount of mercury	1./4/2612	g · J
	· · · · · · · · · · · · · · · · · · ·	42.00	g 🔹
	snowfall	. \	1
	volume of melted snow in contact	546000	Cu. m
	with soil and overburden	-	G.
	weight of melted snow	5.46E11	g ^{Ye}
	amount of mercury	27.3	8
e	mercury from roin and anon		
	in one year	70.00	
	···· ,	/0.98	g/yr
	years of precipitation to vield	10 c	
	139217.75g of mercury	1961.365878	Vr
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	entering the lake directly	•	
		`	
` _	volume of rain	166400	cu. m
	weight of rain	1.664E11	g
	amount of mercury	4.16	с С
- ·	•	•	D
	volume of snow ,	52000	C11 m
	weight of snow	5200000000	са. щ с
	amount of mergury	2.6	8
	•	2.0	8
	direct confribution by precipitati	on 6.76	g/yr
ł	mercury in lake (aqueous)	140	
· ·		140	1 S
. 🖡	particulate mercury		, .
A.	weight of particulates	11200000	` - ·
V(S	amount of mercury		g
1 Martin) g-
×.	total mercury in lake	•	
10		143.30	S S
· · · · · · · · · · · · · · · · · · ·	Rough estimate of amount of mercur	· ·	
~		y entering lake from 1	runoff and ground
	weight of precipitation		. •
	60 67 even of range on eventuation	2.184E11	g .
	607 overburden n 60 6	y (bedrock =40%)	
•	less 36 367 augustant	36.36	% lost
	10:1 lond to water mat a	1.389898E11	+ 8 .
•	Turoff and moust to the		
.,	runori and groundwater	-1.250908E11	g/yr
$\mathcal{I}_{\mathcal{A}}^{(1)} = \mathcal{V}_{\mathcal{A}}^{(2)}$	•		•
5	streams	1.24416E11	g/yr
!	mercury added	6.2208	g/yr
	groundwater	674784000	g/yr
1	mercury added	.0337392	g/yr
	total aqueous	6.2545392	g/vr
	stream particulates	485222400	g/vr
	mercury	145.56672	g/vr
	total	151.8212592	g/yr
	•		0197
•	total input of mercury to lake	158.5812592	. g/vr
	(includes precipitation directly)		o, 1 -
•	outflow inc 60.67 evapotrana	98980456896	a/wr
			R\lar
•	mercury aqueous	4,949022845	o/ww = 1
•	mercury aqueous particulates	4.949022845 · · · · · · · · · · · · · · · · · · ·	g/yr
· · ·	mercury aqueous particulates mercury	4.949022845 386023781.9 115.8071346	g/yr g/yr
~	mercury aqueous particulates mercury total leaving	4.949022845 386023781.9 115.8071346	g/yr g/yr g/yr
\sim	mercury aqueous particulates mercury total leaving	4.949022845 386023781.9 115.8071346 120.7561574	g/yr g/yr g/yr g/yr
~	mercury aqueous particulates mercury total leaving total mercury entering lake and	4.949022845 386023781.9 115.8071346 120.7561574	g/yr g/yr g/yr g/yr
~~	mercury aqueous particulates mercury total leaving total mercury entering lake and lake watershed in 1 year	4.949022845 386023781.9 115.8071346 120.7561574	g/yr g/yr g/yr g/yr
· · · · · · · · · · · · · · · · · · ·	mercury aqueous particulates mercury total leaving total mercury entering lake and lake watershed in 1 year leaving lake	4.949022845 386023781.9 115.8071346 120.7561574 158.5812592 120.7561574	g/yr g/yr g/yr g/yr
· · · · · · · · · · · · · · · · · · ·	mercury aqueous particulates mercury total leaving total mercury entering lake and lake watershed in 1 year leaving lake left in everem	4.949022845 386023781.9 115.8071346 120.7561574 158.5812592 120.7561574 27.8051010	g/yr g/yr g/yr g/yr g/yr g/yr
•	mercury aqueous particulates mercury total leaving total mercury entering lake and lake watershed in 1 year leaving lake left in system	4.949022845 386023781.9 115.8071346 120.7561574 158.5812592 120.7561574 37.8251018	g/yr g/yr g/yr g/yr g/yr g/yr g/yr
•	mercury aqueous particulates mercury total leaving total mercury entering lake and lake watershed in 1 year leaving lake left in system	4.949022845 386023781.9 115.8071346 120.7561574 158.5812592 120.7561574 37.8251018	g/yr g/yr g/yr g/yr g/yr g/yr g/yr
· · · · · · · · · · · · · · · · · · ·	mercury aqueous particulates mercury total leaving total mercury entering lake and lake watershed in 1 year leaving lake left in system	4.949022845 386023781.9 115.8071346 120.7561574 158.5812592 120.7561574 37.8251018	g/yr g/yr g/yr g/yr g/yr g/yr g/yr
•	mercury aqueous particulates mercury total leaving total mercury entering lake and lake watershed in 1 year leaving lake " left in system	4.949022845 386023781.9 115.8071346 120.7561574 158.5812592 120.7561574 37.8251018	g/yr g/yr g/yr g/yr g/yr g/yr g/yr
•	mercury aqueous particulates mercury total leaving total mercury entering lake and lake watershed in 1 year leaving lake " left in system	4.949022845 386023781.9 115.8071346 120.7561574 158.5812592 120.7561574 37.8251018	g/yr g/yr g/yr g/yr g/yr g/yr g/yr
•	mercury aqueous particulates mercury total leaving total mercury entering lake and lake watershed in 1 year leaving lake " left in system	4.949022845 386023781.9 115.8071346 120.7561574 158.5812592 120.7561574 37.8251018	g/yr g/yr g/yr g/yr g/yr g/yr g/yr

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	· · · · · · · · · · · · · · · · · · ·			
1	added to lake each year leaving	158.5812592	g/yr	
÷)	retained	-37.8251018	g/yr	
	added to lake watershed each year	- 70.98	a /	
· · · · · · · · · · · · · · · · · · ·	less amt entering lake from	~	R) AT	
6	watershed	151.8212592	g/yr	
\sim		-80.8412392	g/yr	
	time required to fill lake to 143.36g of mercury	3.790075722	yr	æ
	further calculations			
1	veerly net loss from unterched		-	16
•••	yearly net gain by lake	-80.8412592 ^37.8251018	g	•
	for lake	0.045514055	8	
· · · · ·	particulate net gain	29.75958544	g	
	aqueous/particulate gain	.2710224701	to one	
- · · ·	at this rate of gain: mass	grams		
· · ·	at this fate of gain: mass	grams	total rati	io
~ `	at this rate of gain: mass aqueou now 14 after 1 year 168 06514	grams us particulate 40 3.36 1	total rati 43.36 41.6666666	io 57
· `)`	at this fate of gain: mass aqueou now 14 after 1 year 148.065516 10 years 220.65516	grams 18 particulate 10 3.36 1 14 33,11958544 181.18 16'300.9558544 521.61	total 43.36 41.6666666 51018 4.47063314 10180 .733181163	io 57 43 37
·	at this fate of gain: mass aqueou now 14 after 1 year 148.065516 10 years 220.655163 100 years 946.55163	grams 18 particulate 40 3.36 1 54 33.11958544 181.18 55 2979.318544 3925.8 55 2979.318544 3925.8	total rati 43.36 41.6666666 51018 4.47063314 10180 .733181163 70180 .317707429	io 57 43 37 92
.) .	at this fate of gain: mass aqueon now 14 after 1 year 148.065516 10 years 220.655163 100 years 946.55163 1000 years 8205.5163	grams 18 particulate 40 3.36 1 54 33,11958544 181.18 36 300.9558544 521.61 55 2979.318544 3925.8 55 29762.94544 37968.	total rati 43.36 41.6666666 51018 4.47063314 10180 .733181163 70180 .317707429 46180 .275695709	io 57 43 37 92 93
	at this fate of gain: mass aqueon now 12 after 1 year 148.065516 10 years 220.655163 1000 years 946.55163 1000 years 8205.5163 inorease in concentration	grams gr	total 43.36 41.66666666 51018 4.47063314 10180 .733181163 70180 .317707429 46180 .275695709	io 57 43 37 92 93
·	at this fate of gain: mass aqueon now 14 after 1 year 148.065516 10 years 220.655163 100 years 946.55163 1000 years 8205.5163 inorease in concentration now	grams 18 particulate 40 3.36 1 54 33,11958544 181.18 56 300.9558544 521.61 55 2979.318544 3925.8 55 29762.94544 37968. 05 ng/g	total rati 43.36 41.6666666 51018 4.47063314 10180 .733181163 70180 .317707429 46180 .275695709	io 57 43 37 92 93
	at this fate of gain: mass aqueon now 14 after 1 year 148.065516 10 years 220.655163 100 years 946.55163 1000 years 8205.5163 inorease in concentration now 6 after 1 year .052880543	grams gr	total rati 43.36 41.6666666 51018 4.47063314 10180 .733181163 70180 .317707429 46180 .275695709	io 57 43 37 92 93
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	at this fate of gain: mass aqueou 14 now 14 after 1 year 148.065516 10 years 220.655163 100 years 946.55163 1000 years 946.55163 1000 years 8205.5163 inorease in concentration 00 now 00 after 1 year .052880541 10 years .078805415 100 years .338054155 1000 years 2.93054155	grams gr	total rati 43.36 41.6666666 51018 4.47063314 10180 .733181163 70180 .317707429 46180 .275695709	io 57 43 37 92 93
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	at this fate of gain: mass aqueou now 14 after 1 year 148.065516 10 years 220.655163 100 years 946.55163 1000 years 8205.5163 increase in concentration now 4 after 1 year 052880541 10 years 07880541 10 years 07880541 100 years 2.93054155 mercury flux to sediment average surface sediment Hg conc	grams 18 particulate 40 3.36 1 54 33,11958544 181.18 56 300.9558544 521.61 55 2979.318544 3925.8 55 29762.94544 37968. 05 ng/g 16 ng/g 134	total rati 43.36 41.6666666 51018 4.47063314 10180 .733181163 70180 .317707429 46180 .275695709	io 57 43 37 92 93
	at this fate of gain: mass aqueon now 14 after 1 year 148.065516 10 years 220.655163 100 years 946.55163 1000 years 8205.5163 inorease in concentration now 6 after 1 year 052880541 10 years 078805415 100 years 2.93054155 1000 years 2.93054155 mercury flux to sediment average surface sediment Hg conc force 29.75958544 g into sed to average value - need	grams gr	total rati 43.36 41.6666666 51018 4.47063314 10180 .733181163 70180 .317707429 46180 .275695709	io 57 43 37 92 93
	at this fate of gain: mass aqueou now 14 after 1 year 148.065516 10 years 220.655163 100 years 946.55163 1000 years 8205.5163 increase in concentration now 0 after 1 year 0.52880541 10 years 0.7880541 10 years 0.78805415 1000 years 2.93054155 mercury flux to sediment average surface sediment Hg conc force 29.75958544 g into sed to average value, need i.e. this is amt of sed required if	grams gr	total rati 43.36 41.6666666 51018 4.47063314 10180 .733181163 70180 .317707429 46180 .275695709 46180 .275695709	io 57 43 37 92 93
	at this fate of gain: mass aqueon now 14 after 1 year 148.065516 10 years 220.655163 100 years 946.55163 1000 years 8205.5163 inorease in concentration now 0 after 1 year 0.52880541 10 years 0.78805415 100 years 0.78805415 1000 years 0.78805415 1000 years 0.38054155 1000 years 0.38054155 mercury flux to sediment average surface sediment Hg conc force 29.75958544 g into sed to average value, need i.e. this is amt of sed required if contains 134 ng of Hg/g	grams gr	total rati 43.36 41.6666666 51018 4.47063314 10180 .733181163 70180 .317707429 46180 .275695709 	io 57 43 37 92 93
	at this fate of gain: mass aqueou now 14 after 1 year 148.065516 10 years 220.655163 100 years 946.55163 1000 years 8205.5163 inorease in concentration now 0 after 1 year 052880541 10 years 078805415 100 years 0.78805415 100 years 2.93054155 mercury flux to sediment average surface sediment Hg conc force 29.75958544 g into sed to average value, need i.e. this is amt of sed required if contains 134 ng of Hg/g volume of sed density	grams gr	total rati 43.36 41.6666666 51018 4.47063314 10180 .733181163 70180 .317707429 46180 .275695709 46180 .275695709 mg/g g of sed ation g/cc	io 57 43 37 92 93
	at this fate of gain: mass aqueou now 14 after 1 year 148.065516 10 years 220.655163 100 years 946.55163 1000 years 8205.5163 inorease in concentration now 0 after 1 year .052880541 10 years .078805415 100 years .338054155 1000 years 2.93054155 mercury flux to sediment average surface sediment Hg conc force 29.75958544 g into sed to average value, need i.e. this is amt of sed required if contains 134 ng of Hg/g volume of sed density volume	grams gr	total rati 43.36 41.6666666 51018 4.47063314 10180 .733181163 70180 .317707429 46180 .275695709 46180 .275695709 mg/g g of sed ation g/cc cc	io 57 43 37 92 93
	at this fate of gain: mass aqueou now 14 after 1 year 148.065516 10 years 220.655163 100 years 946.55163 1000 years 8205.5163 inorease in concentration now 0 after 1 year .052880541 10 years .078805415 100 years .338054155 1000 years 2.93054155 mercury flux to sediment average surface sediment Hg conc force 29.75958544 g into sed to average value,: need i.e. this is amt of sed required if contains 134 ng of Hg/g volume of sed density volume spread over 26 hectares 12812680.30 cc/hectare 12812680.30 cc/hectare 1281268030 cc/square m	grams gr	total rati 43.36 41.6666666 51018 4.47063314 10180 .733181163 70180 .317707429 46180 .275695709 46180 .275695709 mg/g g of sed ation g/cc cc	io 57 43 37 92 93 7
	at this fate of gain: mass aqueou now 14 after 1 year 148.065516 10 years 220.655163 100 years 946.55163 1000 years 8205.5163 inorease in concentration now 0 after 1 year .052880541 10 years .078805415 100 years .338054155 1000 years 2.93054155 mercury flux to sediment average surface sediment Hg conc force 29.75958544 g into sed to average value, need i.e. this is amt of sed required if contains 134 ng of Hg/g volume of sed density volume spread over 26 hectares 1281268030 cc/square m .1281268030 cc/square cm	grams gr	total rati 43.36 41.6666666 51018 4.47063314 10180 .733181163 70180 .317707429 46180 .275695709 46180 .275695709 mg/g g of sed ation g/cc cc	io 57 43 37 92 93
	at this fate of gain: mass aqueon now 14 after 1 year 148.065516 10 years 220.655163 100 years 946.55163 1000 years 8205.5163 inorease in concentration now 0 after 1 year .052880543 10 years .078805415 100 years .338054155 1000 years 2.93054155 mercury flux to sediment average surface sediment Hg conc force 29.75958544 g into sed to average value,: need i.e. this is amt of sed required if contains 134 ng of Hg/g volume of sed density volume spread over 26 hectares 12812680.30 cc/square m .1281268030 cc/square cm	grams gr	total rati 43.36 41.6666666 51018 4.47063314 10180 .733181163 70180 .317707429 46180 .275695709 46180 .275695709 mg/g g of sed ation g/cc cc	io 57 43 37 92 93 7
	at this fate of gain: mass aqueou now 14 after 1 year 148.065516 10 years 220.655163 100 years 946.55163 1000 years 8205.5163 inorease in concentration now 0 after 1 year 0.52880541 10 years 0.78805415 100 years 0.78805415 1000 years 0.78805415 1000 years 0.78805415 1000 years 0.78805415 mercury flux to sediment average surface sediment Hg conc force 29.75958544 g into sed to average value, need i.e. this is amt of sed required if contains 134 ng of Hg/g volume of sed density volume spread over 26 hectares 12812680.30 cc/square m .1281268030 cc/square cm	grams gr	total rati 43.36 41.6666666 51018 4.47063314 10180 .733181163 70180 .317707429 46180 .275695709 46180 .275695709 mg/g g of sed ation g/cc cc	io 57 43 37 92 93
	at this fate of gain: mass aqueou now 14 after 1 year 148.065516 10 years 220.655163 100 years 946.55163 1000 years 8205.5163 inorease in concentration now 0 after 1 year 052880541 10 years 078805415 100 years 2.93054155 mercury flux to sediment average surface sediment Hg conc force 29.75958544 g into sed to average value, need i.e. this is amt of sed required if contains 134 ng of Hg/g volume of sed density volume spread over 26 hectares 12812680.30 cc/square m .1281268030 cc/square cm	grams gr	total rati 43.36 41.6666666 51018 4.47063314 10180 .733181163 70180 .317707429 46180 .275695709 46180 .275695709 mg/g g of sed ation g/cc cc	io 57 43 37 92 93

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i.e. 1.281268030 mm/year of se need 222086458.5 g of seston/y at any given time lake contains cycles per year	dimentation ear 11200000 g of seston
finally watershed loss	504308100
net to lake 15 area loss occurs in 8.434514E-5 g of Hg lost per square men for nominal overburden depth of 1 m	l.8212592 g/yr l.8 square km tre
8.434514E-5 g/cubic m = 3.1 at 2.65 g/cc density 3.1	18284E-11 g of Hg/g
this is a loss of .03 in l cubic metre .03	318283562 ng/g/yr
loas per cubic metre 3.1 or 318 precipitation leaching 1 m concentration of Hg if	82836E-5 g/yr 28.35623 ng/yr 330960 g/yr
31828.35623/precipitation .09 compare to runoff at .05 ng	161697976 ng/g

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162 Appendix G. MOE data on walleye and small mouth bass for study lakes. Lake (Yr) N Mean Hg Std.Ln.Hg Mean Len Mean Wt A В R species ng/g ng/g 亻 сm g Agnew (1975) walleye 26 660 870 36.3 576 .009649 1.15211 .520 Ahmic (1977) 1 walleye 331 910 1120 41.0 787 .002520 1.55866 .643 s.m.bass 20 620 30.1 465 . .006060 1.35184 .884 Balsam (1977) walleye 14 360 **8**60 47.8 1114 .000036 2.35654 .908 s.m.bass 20 270% 35.8 804 .000205 1.98121 .₁952 Caribou (1976) walleye 7 1190 1180 49.2 1293 .000000 4.12038 .900 s.m.bass 11 490 49.2 635 .000207 2.23159 .817 Cecebe (1977) ~ 1 walleye 38.9 30 990 1260 702 .007774 1.30074 .745 s.m.bass 19 590 31.1 613 .000152 2.37515 .909 Commanda (1977) walleye 6 1830-2190 42.8 717 .019054 1.21332 .789 s.m.bass 3 970 . _ 31.0 450 Dalyrmple (1977) walleye 30 590 700 44.1 870 .000050 2.43889 .826 s.m.bass 20 560 36.5 785 .000241 2.12103 .944 Evangeline (1976) walleye 24 540 1130 32.7 403 .000666 1.90136 .873 . . Gough (1975) 40.4 walleye 67 720 910 836 .004537 1.35397 .832 Lacloche (1975) walleye 32 920 930 ⁵1688 48,.5 .003379 1.43546 .903 Memesaugamesing (1975) walleye 34 1750 1420 53.1 2164 .000224 2.23754 .932 s.m.bass 19 760 28.9 558 .004405 2.82939 .892 North Channel of Lake Huron (1976) walleye 10 220 390 39.4 731 .000006 2.85232 .945 2

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Restoule (1976) walleye 26 1550 2200 36.3 .025456 1.13938 .615 729 Scugog (1977) walleye 20 100 · 100 45.5 1140 .002577 0.93922 .729 Appendix G. (continued) Skeleton (1977) 2 walleye. 28 400 400 -48.0 1400 .000005 2.87788 .923 Sparrow (1977) walleye 15 770 s.m.bass 15 590 790 35.6 957 .000407 1.93693 .727 -35.6 610 .002353 1.53605 .602 Vermilion (1977) walleye 30 470 560 43.1 653 .003441 1.30090 .719

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 $Hg(fish) = A \times L^B$ with R = correlation coefficient

s.m.bass 8

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.004527 1.25643 .874

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330 (51) 370 (48)

Appendix H. Comparison of fish mercury data for lakes sampled two different years. Mercury data is in ng/g. For walleye, standard length mercury concentration is given first, followed by mean mercury concentration. For other fish, mean mercury concentration only is given. Mean length, in cm, of the sample caught in the stated year is given in brackets.

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Lake year	Walleye	Small Mouth Bass	Lake Trout
Caribou		•	
1976		490 (32)	600 (49)
1977	· ·	470 (31)	480 (50)
Cecebe			
1971	1150/930 (35)	370 (22)	
1977	1260/990 (38)	590 (31)	
Restoule		•	,
1976	2200/1550 (36)	•	
1977 .	/1300 (38)		
Scugog			-
1970 🦟	/80 (54)		
1977	100/100 (45)	· · · ·	•

Skeleton 1971 ` 1977

Sparrow

1971 1977

•	۰.			
/380	(43)	360	(33)	+
790/770	(48)	590	(35) 1	

Appendix I.

Analytical results of preliminary field survey.

Lake	Field pH	Lab pH	Sp. Cond. µmho-cm	Alk. meq/L	Temp. °C	Cl mg/L	
Agnew	5.83	6.61	53	0.099	11.2	8.	
Ahmic	5.82	6.24	31.5	0.033	10.0	8.5	
Balsam	7.69	7.77	150	0.786	15.3	12.	
Caribou 🦯	5.98	. 6. 71	40.7	0.069	11.2	6.	
Сесеве	5.83	5.74	30.1	0.018	10.0	3.	
Commanda	5.87	5.60	30.5	0.023	11.0	3.	
Dalyrmple	7.75	7.99	217	2.347	14.5	14.	
Evangeline	5.85	6.63	47	0.144	7.2	3.	
Gough	5.70	6.42	39	0.069	15.9	<3.	
Lacloche	5-68	7.04	60	0.116	13.9	<3.	
Memesaug.	5.45	6.16	28.2	0.052	6.7	<3.	
N. Channel	7.27	7.77	119.5 '	0.886	12.0	10.	
Restoule	5.91	6.34	29.8	0.033	11.0	<3.	
Scugog	7.74 _	7.81	318	2.940	19.5	30.	
Skeleton	6.05	6.61	35	0.057	5.5	<3.	
Sparrow	6.43	7.00	60.7	0.154	14.0	[`] 7.	
Vermilion	6.69	7.06	89	0.350	10.5	7.	
Tako	Ма			áo.	·		
Durc	^{rig}		I. Hard	so ₄	Sf.Sed.	Hg Lw.Sed.Hg	
•	- тау т	шg/ L	mg/L	mg/L	ng/g	ng/g	
Agnew	1.01	2.63	10.72	7.3	30	85	
Ahmic	0.89	2.41	9.68	8.4	13	-	
Balsam	2.05	13.45	42.02	9.5	142	- ·	
Caribou	1.21	2.60	11.49	10.0	35		
Cecebe	0.88	2.22	9.47	7.9	<5 [']	- .	
Commanda	0.91	2.63	10.31	9.0	680	. 69	
Dalyrmple	3.30	21.60	67.52	8.4	44	197	
Evangeline	1.43	3.21	13.90	10.0	96	40	
Gough	0.86	2.10	8.78	6.8	49	48	
Lacloche	1.51	3.42	14.75	9.0	<5	124	
Memesaug.	1.01	2.60	10.65	9.5	- 30	-	
N. Channel	4.41	11.40	46.62	13.9	- -	-	
Restoule	0.89	2.52	9.96	8.4	36	15 .	·
Scugog	6.54	2.53	32.87	10.6	61	-	·
Skeleton	0.81	2.81	10.35	8.4	31 ·		
Sparrow	1.36	7.50 😒	24.33	7.3	182	<5 ·	
Vermilion	2.35	9.30	32.89	-	-	-	

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Sf.Sed.Hg = surface sediment Hg $(0 - ^2 \text{ cm})$ Lw.Sed.Hg = next lower sediment layer Hg $(^2 - 5 \text{ cm})$ <5 = less than the 5 ng/g detection limit - = no sample available

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	Lake	Sf.Soil.Hg	Lw.Soil.Hg
		ng/g	_ng/g
	Agnew	12	85
	Ahmic	76	126
•	Balsam	12	85
	Caribou	≺5	<5
	Cecebe	276	321
	Commanda	57 ·	58 ·
	Dalyrmple	<5	22
	Evangelene	<5	<5
	Gough	521	168
	Lacloche	<5	×5
	Memesaug.	57 -	13
	N. Channel	-	-
	Restoule	281	-
	Scugog	205	-
	Skeleton	56	54
	Sparrow	103	63
	Vermilion	133	64

Sf.Soil Hg = Surface soil Hg (0 - 3 cm) Lw.Soil Hg = Next lower soil layer (3 - 8 cm) <5 = less than the 5 ng/g detection limit - = no sample available

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Central Ontario Softwater Lakes water chemistry (August 1980). (s-surface, b-bottom 6.8 6.3⁻ 065 9.7 2.5 Memesaug. s b 8.3 49 5.1 6.0 6.0 9.7 9.7 1.0 1.0 1.6 4.36 7.8 18.9 2 .025 320 ۰. 9000 141100 141100 24 24 8.9 8.9 7.3 7.3 8 8 390 370 170 25. 38 5.7 6.2 22 8.3 11.6 05 120 17.4 53 5.7 6.1 6.1 10.4 10.4 1.0 1.0 4.3 3.92 Cecebe 24.7 17.4 24.7 17.4 24.7 17.4 48 53 6.3 6.1 6.3 6.1 10.3 10.2 10.3 10.2 10.3 10.2 10.3 10.2 1.0 1.0 4.0 4.3 3.95 3.95 1.0 4.3 4.0 4.3 3.95 3.95 1.0 1.0 8.6 11.6 2.8 245 1.4 5.5 Caribou 8 b 22.7 4.6 48 48 6.3 5.4 6.3 5.4 6.3 5.4 6.3 5.4 1.0 11.1 2.4 2.5 1.2 1.2 2.8 2.8 4.10 4.10 4.10 4.10 4.10 4.10 2.6 2.6 3.9 6.5 4.4 6.5 4.4 6.5 20 3.0 280 370 280 . . 31 7.7 7.7 0 240 L.0 ' 24 7.2 7.5 9.8 9.8 4 4 4 93 4. °T µS/cm µ8/Г µ8/Г п8/с в8/с пеq/L пg/L mg/L mg/L mg/L lg/L J/SI пg/L 1g/L 3q.ka ng/g I/g Appendix J. temp. sp. cond. field pH lab pH álk. hardness Hg seston Hg phyto Mg Cl pCl NO2+NO3 PO4 unfil PO4 filt SiO2 Al 8 8 8 9 0 V ch1 **S04**

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Appendix K.	Correlation	coefficients bet	ween fish mercury
concentration and wate	chemistry parameters.		
	walleye	•	small mouth bass
•	mean mercury	standard length mercury	mean mercury
field pH	64	- 64	- 62
lab pH	74	76	- 70
specific conductance	60	61	- 49
alkalinity	57	~,53	27
chloride	56	58	- 58
magnesium	60	60	- 52
calcium	39 (12	- 46
total hardness	43	 55	- 47
sulphate	27	27	~.11
surface sediment H g -	.40	.43	.61
lower sediment Hg	·16	38	_
surface soil Hg	¯ − ₄01	.08	.01
Volower soil Hg	23	15	16

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surface sediment Hg to surface soil Hg

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Appendix L.

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Method of Analysis

The analytical procedures for mercury follow those of Environment Canada's Analytical Methods Manual (Environment Canada 1979). Inorganic forms of mercury are extracted and organic forms are oxidized by strong acids and oxidizers. After oxidation, Hg^{2+} is reduced to elemental mercury by stannous sulphate. The mercury is sparged from the solution with a stream of air and passed through a cell in an atomic absorption spectrophotometer.

Quality Centrol

Detection limits for mercury in waters and extracts varied over the period of the analytical program. When the program commenced, the detection limit was 0.05 μ g/L. With refinements in the technique, this became 0.02 μ g/L. Precision at 0.05 μ g/L was 0.01 μ g/L.

Field and laboratory blanks were tested throughout the study. This included tests on bottle blanks, water blanks and acid/dichromate preservatives, all of which were transported on the field surveys. Laboratory blanks consisted of distilled de-ionized water blanks as well as various chemical blanks which were used to zero the baseline of the auto-analyzer. No contamination of any blanks was detected, as all blank analytical results were found to be at or below the detection limit in effect at the time of the analysis.

All samples were analysed in duplicate, being split at the laboratory, and their results averaged, except for suspended sediment, phytoplankton and zopplankton, which were sampled in duplicate and reported as such. Results were arbitrarily accepted as valid if laboratory splits were within 15% of one another.

An aqueous sample was spiked with mercury on each separate analytical run. The results of the run, in terms of spike recovery, were considered valid if the recovery was between the arbitrarily set limits of 90 and 100%.

Five water subsamples, split from a single sample, had a mean mercury content of 0.078 μ g/L and a standard deviation of 0.0084 or 10.7%. Five sediment samples, split from a single sample, had a mean mercury content of 112 μ g/kg. The standard deviation was 8.4 or 7.5%.