A MECHANISTIC MODEL TO EXAMINE MERCURY IN AQUATIC SYSTEMS

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by

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ABSTRACT

Elevated mercury levels have been observed in a wide variety of aquatic systems. A mass balance non-steady state model was developed to examine mercury cycling in lakes and reservoirs. Hg(II), methylmercury, Hg^{o}, dimethylmercury and solid phase HgS cycles were interconnected. Compartments included air, water, sediment, suspended solids, plankton, benthos, and two generic fish categories based on diet.

Bioenergetics equations for individual fish were extended to consider mercury dynamics for entire fish populations. Biota represented large methylmercury fluxes in the water column and were found to be important methylmercury repositories. In a simulation of a generic well-mixed shield lake in Ontario, the fish population contained about 4 times as much methylmercury as water. Uptake of methylmercury by individual walleye and yellow perch was predicted to be dominated by the food pathway (eg. 99% of total uptake).

Based on simulations for the generic shield lake, the watershed has the potential to be an important source of methylmercury in some shield lakes (exceeding in-situ methylation in the generic simulation). Methylation in the water column and sediments were both simulated to be significant. Simulated net production of methylmercury in the generic shield lake was on the order of 0.05 to 0.15 ug methylmercury m^{-2} $year^{-1}$ in the water column, with similar rates in sediments. Simulated rates of net methylation in polluted sytems were higher. Fractions of total dissolved Hg(II) or methylmercury available for methylation and demethylation in aerobic waters were thermodynamically predicted to be small (e.g. <1%).

Dissolved organic carbon and sulphides (if present) were thermodynamically predicted to dominate Hg(II) and methylmercury complexation in freshwaters.

Hg(II) burial and outflows represented about 85-90% of total mercury losses for the generic shield lake (2 year hydraulic retention time). Volatilization of Hg°, produced by demethylation and Hg(II) reduction, represented the remaining 10-15% of losses. Considerable system to system variability is expected for sources and sinks of total mercury and methylmercury in shield lakes. In simulations of two mercury contaminated environments, Lake St. Clair and Clay Lake, Ontario, sediment return of Hg(II) caused the lakes to be net sources of mercury to downstream areas. Sediment return of mercury could partially explain observed two-phase recoveries of fish methylmercury levels in some polluted systems. The time required for Hg(II) and methylmercury concentrations in various compartments to respond to changes in loads was simulated. There was a tendency towards relatively rapid internal cycling of Hg(II) and methylmercury, but slower overall system response times (eg. years to decades to respond to recover from flooding or pollution episodes).

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1.0 INTRODUCTION

The use of mercury dates back at least as far as the 5th century B.C., when it was used by the Greeks as a pigment. Later the Romans used mercury to recover gold from clothing (Kaiser and Tolg, 1980). In recent times it has been used for the production of thermometers, batteries, paints, chlorine and caustic soda. Organic mercury compounds such as methylmercury have been used as fungicides and slimicides to preserve grains and paper products.

Unfortunately, mercury has a history of hazards as well as benefits. In the middle ages, risks to mercury miners were recognized and work hours were modified to increase miner longevity. In the 19th century, the expression "mad as a hatter" appeared when many hat makers were poisoned by using inorganic mercury to make felt for hats. The phrase is regrettably appropriate when one considers symptoms such as psychic disorders, salivating, loose teeth and tremors (Environment Canada, 1984). Health hazards associated with direct emissions of organic methylmercury became apparent after the Minimata Bay case in Japan in the 1950's. More than 140 fatalities (Health and Welfare Canada, 1987) were caused by consumption of fish and shellfish laden with methylmercury emitted from a vinyl chloride plant.

Although the Minimata episode led to the realization that direct methylmercury emissions could be hazardous, less concern was shown during the 1950's and early 1960's regarding "routine" emissions of inorganic mercury. The Wabigoon River system in northern Ontario, for example, received more than 10 tonnes of inorganic mercury between 1962 and 1969 from a single chlor-alkali plant (Government of Canada/Government of Ontario, 1984). Fish mercury concentrations rose in some cases into the 10-20 ug g^{-1} range. These are some of the highest concentrations ever reported in fish, far above the limit of 0.5 ug g^{-1} for commercial sale in Canada. Most of the mercury in the fish was methylmercury, rather than the inorganic variety emitted by industry. A connection was first made between inorganic and organic mercury when Jernelov found in the late 1960's that Hg(II) could be methylated by bacteria (Wollast et al., 1975). Canadian regulations and abatement measures for inorganic mercury followed in the 1970's to curtail atmospheric and aquatic emissions. It became apparent that physical, chemical and biological processes, and more than one form of mercury were involved in methylmercury cycling in the environment. Research intensified into the effects of various natural conditions on aquatic cycling of mercury, but the results often led to more questions than answers.

A common question which remains to be fully answered is: How long does it take a system to recover from mercury pollution? Unfortunately, turning off the anthropogenic mercury "tap" does not necessarily lower mercury levels in the environment quickly. Several well documented cases of locally curtailed mercury emissions have shown persistent elevated concentrations in aquatic systems for years and even decades (e.g. Parks et al., 1986). Furthermore, local actions don't always cure the problem. Long range atmospheric transport

of mercury (and/or substances affecting atmospheric chemistry) is likely implicated in mercury levels in remote areas. Hakanson et al. (1988) estimated on the basis of a survey of 1456 Swedish lakes that mercury concentrations seem to be increasing with time despite reductions of mercury emissions within Sweden. Over 50% of Sweden's lakes may have mercury concentrations in excess of 0.5 ug g^{-1} for a standardized 1 kg pike (Hakanson et al., 1988). Wren et al. (in press) reported a mean concentration of 0.58 ug Hg g^{-1} for standardized 41 cm walleye in a study of 255 lakes in Ontario. It is possible that atmospheric mercury transport and/or changes in watershed or lake chemistry due to human activities could have elevated fish mercury levels in these areas relative to earlier periods.

Studies linking methylmercury production to bacterial activity in the 1970's and 1980's were paralleled by reservoir studies which were turning up high mercury levels in fish following flooding. Notable reservoir studies with pre- and post-impoundment data include the Churchill River diversion in Manitoba (Bodaly et al., 1984) and the mammoth James Bay development in Quebec. The concentration in a standardized 700 mm northern pike in the James Bay LG2 reservoir was 2.99 ug g^{-1} in 1988, considerably higher than an estimated background level of 0.61 ug g^{-1} (Brouard et al., 1990). With mercury concentrations in fish in reservoirs often above the limits for commercial sale, much attention has been focussed on this issue in Canada.

The complete mercury cycle has not yet been unraveled. There may still be unidentified processes which are significant, while some processes known to occur remain to be quantified (eg. methylation rates). The current state of understanding has precluded attempts to develop predictive mechanistic mercury models. There remains a need to assess the importance of processes involved in mercury cycling in various types of aquatic systems, for example drainage and seepage lakes, reservoirs, and waterbodies with direct mercury effluents. Until the late 1980's, studies were hampered by an inability to measure concentrations of total mercury and methylmercury in water, and by an inability to measure bacterial methylation rates at natural rates in aquatic systems. Much progress has been made recently in terms of measuring mercury concentrations in water. Although it is still not possible to measure methylation and demethylation rates at natural levels, Ontario Hydro is funding studies in 1991-92 to make advances in this area. A further shortcoming regarding model development is the present lack of comprehensive datasets with measurements of several mercury forms in one system.

The objective of this study was to develop a model for lakes and reservoirs capable of categorizing mercury cycling processes as important, unimportant, or requiring further research to determine their significance. A mass balance non-steady state model was developed and used to examine the distribution, fluxes, and temporal responses of 5 forms of mercury. Environmental compartments include air, water, sediment (porewater and solid phase), suspended solids, water column plankton, benthos, and two generic fish categories based on diet. Subsequent versions of the model may focus on fewer processes, and will be intended to provide a greater predictive capability and insights regarding the value of mitigative activities.

This thesis includes a review of mercury properties, uses, hazards and cycling in aquatic systems. Previous modelling efforts are briefly outlined, followed by the development of the model used in this study. The model is then applied to various systems and results are synthesized in an overall discussion of mercury cycling in lakes and reservoirs. Finally, recommendations for future activities related to mercury modelling are provided.

2.0 MERCURY FORMS, BASIC PROPERTIES AND HEALTH HAZARDS

2.1 Forms and Basic Properties of Mercury

Mercury is found primarily in two oxidation states, zero and plus two, in the environment. A third oxidation state, +1, is also predicted to occur on a thermodynamic basis, but is stable only over a very narrow range of redox and pH values, and reacts readily with organics (Environment Canada, 1981). The U.S. National Research Council (1978) notes that mercurous mercury (Hg_2^{++}) can exist only at levels above 450 mg L^{-1} of total mercury, which is unlikely in natural waters. Mercurous mercury compounds are assumed in this study not to be important in natural systems in terms of quantity or as a flux mechanism between other oxidation states.

For the purpose of modelling, mercury compounds have been grouped into five general categories, as shown in Table 2.1. Further segregation of the methylmercury and Hg(II) groups is possible in terms of soluble thermodynamic species (eg. $HgCl_2$, $Hg(OH)_2$), and will be discussed later in the document. Basic physical and chemical properties of selected mercury compounds assumed to be representative of the above mercury categories are provided in Table 2.2.

TABLE 2.1
GENERAL FORMS OF MERCURY IN THE ENVIRONMENT

	FORM	NOTE
1-	Elemental Hg (Hg^{o})	This reduced mercury form is volatile and neutral. It is the dominant form in air;
2-	Non-methylated Hg(II)	This category includes all non-methylated complexes of Hg^{++} in solution and adsorbed on solids. Solid phase HgS precipitate is excluded. This is the dominant Hg category found in nature. Complexing and adsorption sites may be organic or inorganic.
3-	Monomethyl Hg (CH_3HgX)	Included are dissolved complexes involving CH_3Hg^{+}, and CH_3Hg^{+} bound to solids. Complexing and adsorption sites may be organic or inorganic. This is the dominant form in fish
4-	Dimethyl Hg ($(CH_3)_2Hg$)	This form is volatile and unstable in air. It may be a product of biological methylation at high pH or degradation of methylmercury in anaerobic conditions.
5-	Solid Mercuric Sulphide	Solid precipitate (HgS) in the presence of sufficient free sulphide and Hg^{++}.

TABLE 2.2
BASIC PROPERTIES OF SELECTED MERCURY COMPOUNDS

Property	Mercury Compound				
	Hg°	$HgCl_2$	CH_3HgCl	$(CH_3)_2Hg$	Solid HgS
Mol. wt. (g/mol)	200.6	271.5	251.0	230.6	232.6
Density (kg/L)	13.53	5.44	4.06	3.07	8.1
Melting point (celsius)	-38.9	277	167	-	subl @583.5 C
Boiling point (Celsius)	357.2	304	subl. @100 C	92.5	-
Vapour pressure (Pa, 25 C)	0.246	0.0167	1.76	8.3E3	-
Solubility ($g\ L^{-1}\ H_2O$, 25 C)	6.4E-5	69 (20 C)	4.72	2.5E-2	1E-5
Henry's Law H (dimensionless)	0.29 (20 C)	6.4E-7	1.9E-5	0.31	-

References: Gamble (1986)
Lindqvist and Rodhe (1985)
Iverfeldt and Persson (1984)
Mackay and Paterson (1983)
Hem (1970)

Elemental mercury is the reduced Hg species commonly found in thermometers. With melting and boiling points of -38.9 Celsius and 357.2 Celsius, it is the only liquid metal over the ordinary range of atmospheric temperatures. It represents about 80-95% of total mercury in air (Kim and Fitzgerald, 1986; Lindqvist and Rodhe, 1985), has a low solubility in water, and is relatively volatile with a Henry's law constant of approximately 0.3 (dimensionless). Iverfeldt (1984) noted that the solvation of elemental mercury in water is due only to London forces. At ordinary temperatures, elemental mercury does not react with CO_2, SO_2, P, or O_2, but does react with ozone, halogens, hydrogen peroxide, and nitric and sulfuric acids (Andren and Nriagu, 1979; Environment Canada, 1984). Gold, silver and other metals readily form amalgams with elemental mercury, a characteristic used to advantage by the mining industry.

Non-methylated Hg(II) (henceforth referred to simply as Hg(II)) is the dominant form of mercury in the biosphere. The Henry's law constant, solubility and vapour pressure for $HgCl_2$ were chosen as representative of the Hg(II) category. Humic complexes with Hg^{++} may be the dominant mercury species in solution in many natural waters but the Henry's law constant and other basic properties of humic/Hg(II) complexes (which are quite variable in composition) are not available.

Iverfeldt (1984) concluded that the solvation of $HgCl_2$ and other Hg(II) halides is governed by hydrogen bonding and London forces. Thus the moderate solubility of $HgCl_2$ (69 g L^{-1} H_2O at 20 °C) is greater than for Hg°, and the Henry's law constant is lower for Hg(II) compounds than Hg°. The Henry's law constant also reflects a lower vapour pressure for $HgCl_2$ than Hg°. It is important to remember that Henry's Law constant reflects partitioning

between air and water, not simply solubility or vapour pressure alone.

Dimethyl mercury is volatile with a Henry's law constant approximately equal to that of elemental mercury (H= 0.3, dimensionless) since the solvation of dimethyl mercury also is governed by London forces (Iverfeldt, 1984). Dimethyl mercury is unstable in the atmosphere and degrades to methylmercury through reactions with OH and Cl radicals (Peterson et. al (1989). Photochemical degradation of dimethyl mercury to elemental mercury and methane in air may also occur (Lindqvist and Rodhe, 1985).

Methylmercury compounds are toxic, and although they make up a small fraction of the global biosphere mercury mass (e.g. a few percent), they form 95-99% of the mercury burden in fish and are consequently a concern to human health. The Henry's law constant, solubility and vapour pressure for CH_3HgCl were chosen as representative of the general methylmercury category for this study. Humic complexes with the CH_3Hg^+ ion may be dominant in solution in many natural waters, but the Henry's Law Constant and other basic properties of such compounds are not available. CH_3HgCl is sparingly soluble in water (4.72 g L^{-1} H_2O at 25 °C), having a solubility greater than that for elemental or dimethyl mercury, due primarily to hydrogen bonds. The solubility of CH_3HgCl is lower than that assumed for compounds in the Hg(II) group. CH_3HgCl is crystalline at room temperature but volatilizes above 100 °C (Environment Canada, 1981).

Solid mercuric sulphide (HgS, cinnabar) is formed geologically at temperatures less than 300 °C and is usually found in mineral veins or fractures, or in rocks near volcanic areas (Hem, 1970). HgS can also be formed in anaerobic waters in the presence of adequate free

sulfide ion and Hg^{++} ($K_{sp}= 10^{-52}$).

2.2 Thermodynamic Equilibria

There are many soluble complexes of Hg(II) and methylmercury in freshwaters. The distributions of these complexes are a function of pH, Eh, the nature of anions and other complexing groups. Mercury speciation may have an important impact on the partitioning of mercury species between water and other compartments such as plankton and suspended solids, and may affect biological methylation rates if some complexes are more easily utilized for methylation and demethylation.

Several Hg(II) speciation diagrams (Eh-pH) were developed in the 1970's. For example, Hem (1970) estimated that in a solution with Hg^{++} and inorganic ligands (10^{-3} M each of chloride and total sulphur, no organics), $HgCl_2$ would dominate in aerobic conditions when the pH is low and the Eh is in the vicinity of +0.5 V. $HgOH_2$ would dominate in more alkaline conditions. Aqueous elemental mercury, and Hg(II) complexes with sulphide would be expected to be important from a thermodynamic standpoint at lower Eh values. More recently, Dyrssen (1989) and Dyrssen and Wedborg (in press) have updated several Hg(II) complexation constants and provided constants for additional complexes, particularly sulphide/mercury complexes. Selected constants were used for thermodynamic components of the model developed in this study, and are discussed in later chapters.

Regarding methylmercury, Zepp (1974) estimated that in the absence of organics, methylmercury complexes with hydroxide and chloride dominate in aerobic conditions. In

certain natural waters, Zepp (1974) estimated that complexes with sulphide (if present) and organics would dominate methylmercury complexation.

Thermodynamic equilibria for methylmercury and Hg(II) in solutions more representative of freshwaters, including organic complexes and considering implications of adsorption of Hg^{++} and CH_3Hg^+ on solids, will be addressed in Sections 7 and 8.

Although thermodynamic equilibria calculations predict elemental mercury (Hg°) to be dominant in some situations, limited field data found in the literature suggest elemental mercury does not follow thermodynamic equilibrium in natural aquatic systems. Iverfeldt (1984) observed volatile mercury concentrations in Swedish coastal surface waters ranging from 0.06 to 0.43 ng L^{-1}, above thermodynamically expected concentrations for surface waters, assuming most volatile mercury is elemental. It is assumed for the purposes of this study that chemical or biological kinetics control elemental mercury concentrations in natural aquatic systems, rather than thermodynamic equilibrium with other inorganic species. Hg(II) species were assumed to exist in thermodynamic equilibrium with one another.

2.3 Health Hazards and Regulatory Guidelines for Mercury

Health hazards due to inorganic mercury exposure have a long history. In the Middle Ages detrimental health effects to mercury miners were well recognized. Therapies for mercurial diseases were developed (Kaiser and Tolg, 1980) and work days were shortened to four hours to increase the longevity of miners (Environment Canada, 1981). Mercury was also prescribed in the past for the treatment of various illnesses, apparently with no success

and/or unacceptable side effects, since this practice ceased in the 19th century (Kaiser and Tolg, 1980). More recently, health problems have been identified with other inorganic mercury related occupations. The term "mad hatter" in Alice in Wonderland is not just a creation from a fairy tale. Many hatters who used mercury nitrate to make felt for hats suffered from mercury poisoning (Environment Canada, 1984). Manifestations of inorganic mercury poisoning include psychic disorders, salivating, loosened teeth, ulcers on lips and cheeks, speech disorders, liver and kidney damage, and tremors in the extremeties (Environment Canada, 1984; Kaiser and Tolg, 1980).

In recent decades, cases of organic mercury poisoning (eg. methylmercury) have been identified in situations involving both long and short term exposure. The best known example of methylmercury poisoning is the Minimata Bay case from the 1950's. By 1975, 899 people were reported as affected, including 143 deaths (Health and Welfare Canada, 1987). Poisoning arose from sustained consumption of fish and shellfish from Minimata Bay. The bay received direct methylmercury effluents from a vinyl chloride plant. A similar situation occurred in Niiagta, Japan, where 520 cases and 44 deaths were observed by 1974 (Health and Welfare Canada, 1987). A larger but less well known case of organic mercury poisoning took place in Iraq in 1971-72 when 450 deaths and more than 6000 hospital admissions were recorded due to the consumption of bread made with seed grain treated with organic mercury (Health and Welfare Canada, 1987). Methylmercury poisoning is associated primarily with the nervous system in adults and serious cases can cause irreparable damage to neuronal cells (Health and Welfare Canada, 1987). Congenital malformations and cerebral palsy in newborns have also been observed (Kaiser and Tolg, 1980).

In Canada, elevated fish mercury levels have been observed in systems with inorganic mercury effluents, reservoirs and even remote lakes with no point sources of pollution. A study of Indian and Inuit communities in northern regions of Ontario, Quebec and Manitoba concluded that although severe methylmercury poisoning has not been found in these peoples in Canada, mild cases may be occurring (Health and Welfare Canada, 1987). Concern was also expressed regarding possible prenatal exposure. Variations in mercury blood levels (as estimated from hair concentrations) were observed between communities. Health and Welfare Canada (1987) uses a standard of 20 ppb in human blood as an acceptable limit. The range of 20 to 100 ppb is classified as "increasing risk", while concentrations in excess of 100 ppb are considered "at risk". Of 655 people tested in Southern Indian Lake, Manitoba, 90% exceeded 20 ppb Hg in blood. In contrast, Norway House, Manitoba, had 25% of samples exceeding 20 ppb, a lower but still very significant percentage.

The Canadian Water Quality Guidelines (Environment Canada, 1987) recommend a maximum concentration for total mercury of 0.1 ug L^{-1} in drinking water and 0.2 ug L^{-1} in water to protect aquatic life. Although the standard for sale of fish in Canada is 0.5 ug Hg g^{-1} for general consumption, such concentrations apparently due not put the fish at risk, only the people who eat them.

3.0 MERCURY USES AND EMISSIONS

3.1 Historical Uses of Mercury

The term "Hg" is derived from the latin term *hydrogyram* which is in turn based on the earlier naming of the substance as quick silver or liquid silver by the Greeks (Environment Canada, 1981). Cinnabar (HgS) was used as a pigment by the Greeks in the 5th century B.C. By the first century B.C., the preparation of elemental Hg by heating HgS and distillation was established. Romans used amalgamation to recover gold from clothing, and by the 16th century amalgamation was used on a large scale to recover silver in South America (Kaiser and Tolg, 1980).

3.2 Modern Uses and Emissions of Mercury

With the onset of the industrial revolution, mercury emissions increased through the burning of fossil fuels, base metal mining, production of chlorine and caustic soda using mercury cathodes, the use of mercury in consumer products such as paints, batteries and thermometers, and the use of organo-mercury compounds as fungicides and slimicides,. Some uses have been curtailed in recent years and mercury is no longer produced within Canada (Environment Canada, 1984). For instance, regulations introduced in the 1970's and 1980's in Canada have almost completely curtailed aquatic and atmospheric emissions of mercury from

chlor-alkali plants. In 1972, the Chlor-Alkali Mercury Liquid Effluent Regulations were established under the Fisheries Act and revised in 1977. In 1978 the Chlor-Alkali Mercury National Emissions Standards Regulations were established to limit atmospheric emissions. Of 15 mercury cell chlor-alkali plants operating in Canada in 1970, four converted to a diaphragm process and six closed (Bissett and McBeath, 1988). Five remain, using control measures such as improved waste handling, mercury recovery, and spill controls to minimize emissions to the environment. Liquid effluents from chlor-alkali plants have been reduced by over 99% from 67 tonnes yr^{-1} in 1970 to less than 0.1 tonne yr^{-1}. The corresponding reduction for air emissions from chlor-alkali plants is 95%, from 24 tonnes yr^{-1} to 1.1 tonnes yr^{-1} (Bissett and McBeath, 1988).

It is important to consider estimates of anthropogenic atmospheric emissions in the context of natural emissions. Unfortunately, considerable uncertainty exists regarding natural mercury emissions to the atmosphere. Earlier studies by Environment Canada (1981), for example, assumed a mean soil flux to the atmosphere of 132 ug Hg m^{-2} yr^{-1} and fluxes for vegetation ranging from 8 ug Hg m^{-2} yr^{-1} (tundra) to more than 700 ug Hg m^{-2} yr^{-1} (coastal mountain forest). Based on more recent studies, such flux rates appear high, perhaps by an order of magnitude. Estimates by Kim and Fitzgerald (1986) and Lindqvist and Rodhe (1985) suggest a total global mercury atmospheric emission rate of 8×10^9 g Hg yr^{-1}, (approximately 16 ug m^{-2} yr^{-1}). Further analysis of data presented in these studies suggests anthropogenic mercury emissions are comparable to natural continental (soil, vegetation and freshwater) emission rates, both being on the order 15-25 ug m^{-2} continent yr^{-1}, or 30-35% of total global emissions (see Table 3.1).

Table 3.2 provides estimates of annual anthropogenic and natural air emissions for Canada, using both older and more recent natural emissions estimates. Based on more recent estimates, anthropogenic emissions may represent 10-20% of natural emissions in Canada. Considerable uncertainty is assigned to natural and anthropogenic estimates, and further research in this area would be useful. It is noteworthy that if an estimate of 650 anthropogenic tonnes of mercury per year in the United States (Peterson et al., 1989) is realistic, then anthropogenic emissions in the U.S. may exceed natural sources by a factor of 3 to 5, assuming 15-25 ug m^{-2} yr^{-1} for natural emissions.

TABLE 3.1

ESTIMATES OF GLOBAL ANTHROPOGENIC AND NATURAL EMISSIONS OF MERCURY TO THE ATMOSPHERE

Units:	Total Global Emissions	Ocean Emissions	Continental Emissions	Anthropogenic Emissions
- 10^9 g Hg yr	8.0	2.9	2.7	2.4
- ug m^{-2} yr^{-1}	16 (m^{-2} globe)	8 (m^{-2} ocean)	18 (m^{-2} continent)	16 (m^{-2} continent) 5 (m^{-2} globe)
- % global total	100	36	34	30

Based on emissions estimates from Kim and Fitzgerald (1986) and Lindqvist and Rodhe (1985)

Global Surface Area: 5.1×10^{14} m^2
Ocean Surface Area: 3.6×10^{14} m^2
Continent Surface Area: 1.5×10^{14} m^2

TABLE 3.2

ESTIMATED ANTHROPOGENIC AND NATURAL MERCURY EMISSIONS TO THE ATMOSPHERE IN CANADA

Natural Emissions in Canada		Anthropogenic Emissions in Canada		
Estimate by Environment Canada (1981) (tonnes yr^{-1})	Estimate Assuming 15 to 25 ug m^{-2} yr^{-1} (tonnes yr^{-1})	From Peterson et al. (1989) (tonnes yr^{-1})	Anthropogenic Emissions as a Percent of Natural Emissions (%)	
			Based on 1981 Estimate of Natural Emissions	Based on Estimate of 15-25 ug m^{-2} yr^{-1} of Natural Emissions
3460	145 to 245	30	1	12-20

4.0 MERCURY CONCENTRATIONS IN AQUATIC SYSTEMS

Due to long range atmospheric transport of mercury and other anthropogenic emissions, current "background" mercury cycling conditions in remote areas probably reflect an anthropogenic influence. The following discussion therefore describes mercury concentrations in the context of "pre-industrial background", "present background" and "elevated relative to present background". Wide variability in mercury concentrations may occur within each category.

Table 4.1 provides estimates of present background concentrations in water, sediments and fish. Table 4.2 shows mercury concentrations measured in biota in remote lakes, reservoirs and industrially polluted systems.

4.1 Pre-Industrial Background Mercury Concentrations

Since direct measurements of mercury concentrations in water, sediments or biota from pre-industrial times do not exist, indirect means must be used to estimate historical trends. Arguments have been made on the basis of estimated anthropogenic emissions, soil cores and sediment mercury cores to suggest that concentrations in sediments and fish before the industrial revolution were significantly lower than today.

Table 4.1

Estimated Background Concentrations of
Total Mercury and Methylmercury in
Water, Fish and Sediments

Water		Sediment		Predatory Fish (Adult)		Prey Fish (Adult)	
MeHg ug m^{-3}	Total ug m^{-3}	MeHg ug g^{-1} dry	Total ug g^{-1} dry	MeHg ug g^{-1} wet	Total ug g^{-1} wet	MeHg ug g^{-1} wet	Total ug g^{-1} wet
0.02 to 5.0[a]	0.5 to 10.0[b]	0.001 to 0.01	0.05 to 0.5	0.2 to 1.5	0.2 to 1.5	0.05 to 0.5	0.05 to 0.5

Notes: a: Usually less than 0.5 ug m^{-3} in aerated lake waters.
b: Usually less than 2 ug m^{-3} in aerated lake waters.

Table 4.2
Selected Measurements of
Total Mercury Concentrations in
Aquatic Biota

1) Predatory Fish (ug g^{-1}):

Lakes in Relatively Remote Areas:	
- 255 Ontario lakes	0.58[1]
- 90 Ontario lakes	0.34[2]
- 91 Ontario lakes	0.26[3]
- 1456 Swedish lakes	0.81[4]
- 93 lakes in south/central Finland	0.53[5]
- 8 Finnish Lakes in north Finland	0.28[6]
- 251 Lakes in Northern Manitoba	0.43[7]
- 115 Lakes in Northern Saskatchewan	0.23[8]
Reservoirs:	
- James Bay LG2	
- Background	0.68[9]
- 9 yrs post-impoundment (1988)	2.80[10]
- 20 Finnish Reservoirs (3-19 yrs post impoundment)	0.89[11]
- Southern Indian Lake (Manitoba)	
- Pre-impoundment (1971-1977)	0.2-0.3[12]
- 5 yrs post-impoundment (1981)	0.95[13]
Mercury Polluted Systems:	
- Clay Lake in Wabigoon River system, Ontario	
- 1971	9.09[14]
- 1982	2.32[15]

Notes:

1 : 41 cm walleye, mean (Wren et al., in press)
2 : 31 cm smallmouth bass, median (McMurtry et al., 1989)
3 : 44 cm lake trout, median (McMurtry et al., 1989)
4 : 1 Kg pike, mean (Hakanson et al., 1988)
5 : 1 Kg pike, mean (Verta et al., 1986)
6 : 1 Kg pike, mean (Verta et al., 1986)
7 : Northern pike, median (Rannie and Punter, 1987)
8 : Northern pike, median (Rannie and Punter, 1987)
9 : 40 cm walleye, mean (Brouard et al., 1990)
10 : 40 cm walleye, mean (Brouard et al., 1990)
11 : Northern pike mean (Verta et al., 1986b)
12 : Northern pike range of means for 1971-1977, commercial catch (Bodaly et al. (1984))
13 : Northern pike, commercial catch mean (Bodaly et al. (1984))
14 : Northern pike, mean value, mean length=50.8 cm (Government of Canada/Government of Ontario, 1984)
15 : Northern pike, mean value, mean length=53.5 cm (Government of Canada/Government of Ontario, 1984)

Table 4.2 (Continued)
Selected Measurements of
Total Mercury Concentrations in
Aquatic Biota

2) Prey Fish (whitefish) (ug g^{-1}):

Reservoirs:	
- James Bay LG2, Quebec	
- Background	0.16[16]
- 5 yrs post-impoundment (1984)	0.57[17]
- Southern Indian Lake, Manitoba	
- Pre-impoundment (1975)	0.06[18]
- 3 yrs post-impoundment (1979)	0.25[19]

3) Benthos (ug g^{-1} wet)

Lakes in Relatively Remote Areas:	
- Zoobenthos, Lake Pihlajavesi, Finland	0.05[20]
- Zoobenthos, Lake Seinajarvi, Finland	0.04[21]
- Crayfish, 13 South-Central Ontario Lakes	0.04-0.30[22]
Reservoirs:	
- Zoobenthos, Kyrkosjarvi Reservoir, Finland (0-3 yrs post-impoundment)	0.20[23]
- Zoobenthos, Kalajarvi Reservoir, Finland (3-7 yrs post-impoundment)	0.08[24]
- Chironomids, Southern Indian Lake, Manitoba (5 yrs post impoundment (1981))	0.11-0.21[25]
- Chironomids, Notigi Reservoir, Manitoba (5 yrs post-impoundment (1981))	0.02[26]
- Oligochaetes, Notigi Reservoir, Manitoba (5 yrs post-impoundment (1981))	0.04-0.34[27]
- Oligochaetes, Southern Indian Lake, Manitoba (5 yrs post-impoundment (1981))	0.7[28]
Mercury Polluted Systems:	
- Clay Lake (Wabigoon River System)	
- Crayfish, 1970	10.5[29] (approx)
- Crayfish, 1983	0.7[30] (approx)

Notes:

16,17 : 40 cm, mean value (Brouard et al., 1990)
18,19 : Mean value, commercial catch, regions 2 and 6, mean lengths 33-34 cm (Bodaly et al., 1984)
20,21 : Mostly trichoptera larvae and dragonfly larvae, lake mean value (Surma-Aho et al., 1986)
22 : Range of lake mean values (Allard and Stokes, 1989)
23,24 : Mostly trichoptera larvae and dragonfly larvae, reservoir mean value (Surma-Aho et al., 1986)
25 : Range (Jackson, 1988a)
26 : Range (Jackson, 1988a)
27 : Range (Jackson, 1988a)
28 : Single sample (Jackson, 1988a)
29,30 : 7.1 cm (Parks and Hamilton, 1987)

Table 4.2 (Continued)
Selected Measurements of
Total Mercury Concentrations in
Aquatic Biota

4) Water Column Plankton (ug g^{-1} dry)

Lakes in Relatively Remote Areas:	
- Granville Lake, Manitoba (1985)	0.06[31]
- Granville Lake, Manitoba (1984)	0.23[32]
- Lake Pihlajavesi, Finland	0.22[33]
- Lake Blacksastjarn, Sweden	0.13-0.27[34]
- 8 small Swedish Forest Lakes	0.1-0.7[35]
Reservoirs:	
- Southern Indian Lake, Manitoba (9 yrs post-impoundment (1985))	0.06[36]
- Southern Indian Lake, Manitoba (8 yrs post-impoundment (1984))	0.16[37]
- Kyrkosjarvi Reservoir, Finland (0-3 yrs post-impoundment)	0.42[38]

Notes:

31 : Net plankton, >53 um net size, July-August 1985, lake mean value (Ramsey and Ramlal, 1987a)
32 : Net Plankton, >53 um net size, June-Sept 1984, lake mean value (Ramsey and Ramlal, 1987b)
33 : Zooplankton, > 400 um net size, lake mean value (Surma-Aho et al., 1986)
34 : Crustacean zooplankton, lake range (Meili, 1988a)
35 : Crustacean zooplankton, range in 8 lakes (Meili and Parkman, 1988)
36 : Net plankton, > 53 um net size, July-August 1985, mean (Ramsey and Ramlal, 1987a)
37 : Net plankton, > 53 um net size, June-Sept 1984, mean (Ramsey and Ramlal, 1987b)
38 : Zooplankton, >400 um net size, reservoir mean value (Surma-Aho et al. (1986))

4.1.1 Pre-Industrial Background Mercury Concentrations in Sediments

Several studies suggest lower mercury concentrations existed in sediments before the industrial period. Meili (1988b) cited studies of Swedish forest lakes which indicate mercury concentrations in older sediments in southern Sweden are one-fifth the concentration of surficial sediments deposited during the 20th century. Rekolainen et al. (1986) also noted that surficial sediments tend to be higher in mercury content than deeper, older sediments (eg. 1.4 to 6.6 times) in sediment samples from southern Finland.

Arguments have also been developed to suggest that mercury profiles in sediments in northern areas of Sweden and Finland may better reflect pre-industrial conditions than sediment cores from more southerly areas. Bjorklund et al. (1984) estimated mean mercury concentrations in surface sediments in northern Sweden to be 0.10 ug g^{-1} dry weight for oligotrophic forest lakes free of local anthropogenic influence. Rekolainen et al. (1986) suggested lower values (eg. 0.05 ug g^{-1} dry weight) for northern Finland in comparison to more southern areas. In addition to the above studies in Scandinavia, Evans (1986) estimated a pre-industrial background concentration of 0.10 ug g^{-1} in deeper sediments of fourteen south-central Ontario lakes.

Arguments for increasing sediment concentrations in recent times generally make two assumptions: (i) total mercury is conservative with time in sediments, and (ii) the tendency towards higher concentrations in surficial sediments is not significantly shaped by variations in sediment characteristics with depth. These assumptions should be carefully examined. It is

possible for example that Hg(II), the dominant form of mercury in sediments, could be reduced chemically to elemental mercury and subsequently migrate upwards, generating a profile which exhibits decreasing total mercury concentration with depth. Strunk et al. (1989) suggested that in Lake Superior sediments, mercury profiles were influenced by anthropogenic loading, but the depth at which "background" concentrations occurred appeared to be related more to the depth of the redox boundary than the age of the sediment.

4.1.2 Pre-Industrial Background Mercury Concentrations in Fish

Verta et al. (1986a) estimated pre-industrial mercury concentrations in standardized 1 kg northern pike in Finland to be 0.05 to 0.2 ug g^{-1} in clear lakes, increasing with water colour up to 0.25 to 0.4 ug g^{-1} in highly coloured waters (eg. 200 mg Pt L^{-1}). Bjorklund et al. (1984) estimated pre-industrial of standardized 1 kg pike (Esox lucius) to be 0.05 to 0.2 ug g^{-1} in Swedish oligitrophic lakes.

Most mercury in fish is methylmercury, which may or may not be conservative with time in tissue. Furthermore, a database of pre-industrial fish does not exist from which mercury samples can be taken. Estimates of pre-industrial mercury concentrations in biota must therefore be qualified with a fair degree of uncertainty. Also, similar to present conditions, one would expect a fair degree a variability in fish mercury concentrations during pre-industrial times as a function of local environmental conditions.

4.2 Present Background Mercury Concentrations

4.2.1 Present Background Mercury Concentrations in Sediments and Soils

Many studies have been undertaken to assess mercury concentrations in recently deposited freshwater sediments. Regional variations are readily apparent, with concentrations usually falling between 0.05 and 0.50 ug g^{-1} dry weight. Data representing the higher end of this range are often explained in terms of natural and/or anthropogenic influences, such as long range atmospheric transport of anthropogenic emissions, weathering of geologic mercury from watersheds rich in mercury containing sulphide ores, or positive correlations with organic content of the sediment.

As mentioned previously, north-south mercury concentration gradients in surficial sediments have also been established in Sweden and Finland, quite possibly reflecting anthropogenic influences in southern areas. Bjorklund et al. (1984) estimated mean mercury concentrations in surface sediments in northern and southern Sweden to be 0.10 and 0.29 ug g^{-1} dry weight respectively, for oligotrophic forest lakes free of local anthropogenic influence. Surface sediments in Finnish lakes ranged from 0.17 to 0.55 ug g^{-1} in southern and western regions, while northern values were lower (eg. 0.05 ug g^{-1}) (Rekolainen et al., 1986). Similar concentration gradients have been found in soils and rainwater, with concentrations being five times higher in southern Sweden relative to northern areas (Meili, 1988b).

Rannie and Punter (1987) calculated a mean of 0.06 ug g^{-1} dry weight for sediments of 1293 lakes in northern Manitoba in the region of the Churchill River diversion (depth of sediment cores unknown). Evans (1986) studied surficial sediments (0-2 cm) in fourteen south-central Ontario lakes and reported mercury concentrations ranging from 0.12 to 0.7 ug g^{-1} dry weight.

The affinity between mercury and organic carbon has often been used to at least partially explain higher mercury levels in surficial sediments. Swedish and Finnish studies of sediment mercury and organic content between lakes in different regions found significant correlations within regions. Different regressions were required for northern and southern areas of the countries however. This was attributed to increased regional loading of mercury (Bjorklund et al., 1984; Rekolainen et al., 1986). Rada et al. (1989) studied sediment samples from a vertical perspective in 11 north-central Wisconsin lakes and generally found poor correlations between organic content and mercury. It was concluded that increased loading of mercury, rather than organic content, was primarily responsible for higher mercury concentrations in newer sediments in the region.

It is assumed for the present study that surficial sediment mercury concentrations in lakes without local anthropogenic pollution typically range from 0.05 to 0.5 ug g^{-1} (see Table 4.1), being higher in regions subject to anthropogenic mercury, and in sediments with higher organic content. Mercury enrichment by a factor of 2 to 5 is assumed typical for surficial sediments relative to deeper sediments. This trend may be related to changes in sediment characteristics with depth, or processes gradually purging mercury from a given sediment layer

with time, or increased mercury loading in recent times. Increased mercury loading to surficial sediments could occur as a result of (i) direct atmospheric deposition on the lake surface, (ii) increased mercury in runoff (which is a combination of mercury originating from the atmosphere and the land surface), and/or (iii) changes in the physical, chemical or biological status of the sediments or overlying waters. Any of these mechanisms could be anthropogenically influenced. The development of a mechanistic model will help evaluate the possible significance of the above mechanisms.

Soil mercury concentrations are on the same order of magnitude as sediment concentrations. Borg and Johansson (1989) cited a range of 0.1 to 0.5 ug g^{-1} mercury and a mean mercury content of 0.24 ug g^{-1} in the mor layer of Swedish forest soils. It was concluded that a significant cause of variability was atmospheric deposition, and that mercury accumulation in soils still exceeds losses. Rannie and Punter (1987) reported mean mercury concentrations of 0.095 and 0.090 ug g^{-1} in the moss/litter/humus and "A" horizons respectively for samples taken in the region of the Churchill River diversion in Manitoba. Higher mercury concentrations may occur in soils above sulphide ore bodies (Rannie and Punter, 1987).

The potential for flooded soils to act as a mercury source to a reservoir is an important question in light of elevated mercury concentrations commonly observed in fish in reservoirs. Bodaly et al. (1987) examined this issue for the Churchill River diversion in Manitoba by studying mercury concentrations in unflooded soils, flooded soils (5 years after flooding), and sediments of established lakes. The overall mean depletion of mercury in paired samples

(flooded versus unflooded) was only 6.7%, and results were qualified with a high degree of variability, ranging from 67% depletion up to 271% mercury enrichment. Total mercury in flooded and unflooded soils both averaged roughly 0.1 ug g^{-1} dry weight. Sediment mercury concentrations were significantly lower, averaging 0.03 ug g^{-1}. These results suggest that impoundments provide some sediment substrates higher in mercury content than tend to occur in natural lake sediments. Given the relatively minor depletion of mercury from flooded soils after 5 years and the variability in depletion/buildup rates between sites, it is difficult to arrive at conclusions regarding the potential for flooded soils to act as a source of mercury, particularly methylmercury, to overlying waters, relative to natural sediments. It is plausible, for example, that upon flooding, Hg(II) could be leached from soils, followed by effective binding of Hg(II) to suspended organic particles which then settle, generating relatively high mercury concentrations in newly forming sediments. Finally, a gradual return to Hg(II) concentrations typical of natural lakes (equal or lower than the original soil mercury content) might occur when the trophic surge ends in the reservoir. Verta et al. (1986b) reported that newly formed sediments in 6 Finnish reservoirs contained significantly more mercury (0.22-0.36 ug g^{-1}) than underlying older sediments (0.05-0.27 ug g^{-1}) or the soils before flooding (0.13-0.16 ug g^{-1}), except for the new Kalajarvi reservoir (0.09-0.1 ug g^{-1} from 0-5 cm) for which no new organic sediments were found. Field experiments to monitor Hg(II) in soils before and after flooding, and in the water column, would be very useful.

4.2.2 Present Background Mercury Concentrations in Fish

The mercury burden in fish is a function of available mercury in the surrounding environment, the physiological interaction of the fish with the mercury to which it has been exposed, and the time of exposure. Fish take up mercury through food and water pathways. Intake via food and across the gills can be estimated on the basis of a bioenergetics approach which considers the mercury concentrations in food and water, the efficiency of extraction of mercury from these sources, and quantities of food and oxygen needed to satisfy energy requirements of the fish (Norstrom et al., 1976). Since the activity level and dietary habits of fish vary with age, species, and the surrounding environment, and since the environment also affects available mercury levels in water and food, it is not surprising to find a range of mercury levels in fish in nature. The following discussion briefly considers variations in fish concentrations due to age, species and surrounding environment.

4.2.2.1 Fish Mercury Concentrations as a Function of Age And Species

Mercury intake is partially offset by excretion, but bioaccumulation generally occurs for steady-state environmental conditions, ie. a fish's mercury concentration increases with age. Weight, length or age is therefore typically used as a normalizing variable to compare fish in different environments.

In comparable environments, fish higher in the food chain (eg. northern pike, walleye) tend to have higher concentrations of mercury than prey species such as yellow perch (Meili 1988a; Wren and MacCrimmon, 1986). Arguments have been put forward that this trend simply reflects a tendency for predatory fish to live longer than prey species. Wren and MacCrimmon (1986) concluded however that predatory species have higher mercury concentrations than prey species of the same age in Tadanac Lake in the Canadian Shield.

Biomagnification of mercury up the food chain has been suggested to occur due to higher mercury concentrations in predators in comparison to their prey. There are also variations in mercury levels (standardized to length or weight) between species with quite similar diets. This may be partially due to different activity levels between species, resulting in varying rates of food consumption and mercury intake. Mathers and Johansen (1985) estimated that in Lake Simcoe, Ontario, walleye had a higher food consumption rate (gram food per gram fish per year) than northern pike. Species specific growth patterns, mercury uptake efficiencies and clearance rates could also result in species to species variations in mercury concentrations at a given age or weight.

4.2.2.2 Fish Mercury Concentration as a Function of Lake Type and Location

A wide range of indicators relating to water quality, sediment quality, lake morphometry, hydrology, and trophic status have been considered in terms of potential interactions with fish mercury levels (McMurtry et al., 1989; Bjornberg et al., 1988; Stokes and Wren, 1987; Wren and McCrimmon, 1983). Attention has focussed on pH, carbon type and quantity,

productivity, dissolved oxygen, Eh, and water temperature, and ratios of watershed area to lake area or volume. These factors will be discussed further in a discussion of mercury cycling in Section 5. Table 4.2 illustrates the variability of mercury concentrations in fish for a variety of natural lakes, reservoirs, and industrially polluted systems.

4.2.3 Present Background Mercury Concentrations in Plankton and Benthos

Measurements of mercury concentrations in phytoplankton and zooplankton in relatively remote lakes suggest total mercury concentrations typically in the range of 0.05-0.5 ug g^{-1} dry weight. Assuming plankton are roughly 75-85 percent water, the above concentrations would translate into about 0.01-0.1 ug g^{-1} wet weight. Ramsey and Ramlal (1987b) reported no significant variation in total mercury concentrations for net plankton samples ranging from 53 to 150 *u*m net size, and noted other studies with similar findings. Measurements of mercury concentrations in benthos (eg. chironomids, oligochaetes, crayfish) in relatively remote lakes suggest total mercury concentrations comparable to or higher than in plankton, typically in the range of 0.05-0.3 ug g^{-1} wet weight (see Table 4.2).

The fraction of total mercury which is methylmercury is variable in plankton and benthos. Surma-Aho et al. (1986) reported a range of 45-100 percent methylmercury in zooplankton in a study of two reservoirs and three lakes in Finland, while in zoobenthos the range was 35-100 percent methylmercury. For this study, Hg(II) and methylmercury were assumed to both represent significant fractions of total mercury in plankton and benthos (eg. 25% to 75%). For methylmercury, these percentages represent an intermediary step between

abiotic compartments which contain only a few percent methylmercury, and fish in which methylmercury is the dominant fraction of total mercury.

4.2.4 Present Background Mercury Concentrations in Water

Methods developed within the last few years (Bloom, 1989; Bloom and Watras, 1989a) to determine total mercury and methylmercury concentrations in natural waters indicate that concentrations are considerably lower than previously reported during the 1970's and most of the 1980's. Fitzgerald and Watras (1989) found total mercury concentrations ranging from 0.9 - 1.9 ng L^{-1} in four rural Wisconsin lakes. Bloom and Watras (1989a) reported up to 11 ng L^{-1} total mercury in the anoxic hypolimnion of an experimentally acidified basin (pH 5.2) of Little Rock Lake, a small seepage lake in Wisconsin. Iverfeldt and Johansson (1987) reported mean total mercury concentrations in runoff waters from 13 catchment areas in Sweden ranging from 1.0 - 6.5 ng L^{-1}

Regarding methylmercury, Bloom (1989) estimated a range of 0.02-0.10 ng L^{-1} in surface waters in lakes. Lee (1987) reported similar methylmercury concentrations in four Swedish lakes, with values ranging from 0.05 - 0.26 ng L^{-1}. Bloom and Watras (1989a) reported a significantly higher concentration, 4 ng L^{-1} of methylmercury, in the oxygen depleted hypolimnion of Little Rock Lake, Wisconsin.

It is assumed for this study that aerobic lake waters typically contain total mercury in the range of 0.5 - 2.0 ng L^{-1} and methylmercury in the range of 0.05 - 0.2 ng L^{-1}. Highly

coloured waters may exceed these ranges. Total mercury and methylmercury concentrations in runoff (the dissolved component) are assumed to range from 1 - 10 ng L^{-1} and 0.1 - 1 ng L^{-1} respectively. Higher values may reflect higher DOC in runoff relative to receiving waters, acting as a complexing agent for Hg(II) and methylmercury. Total mercury and methylmercury concentrations in oxygen depleted hypolimnia are assumed to range from 1 - 10 ng L^{-1} and 0.05 - 4 ng L^{-1} respectively.

4.3 Elevated Mercury Concentrations Relative to Present Background Levels

The following discussions provide examples of elevated mercury concentrations in industrially polluted environments or reservoirs, in sediments, fish and water. Data are provided for total mercury, and where possible, methylmercury.

Extremely high sediment mercury concentrations have been reported in the polluted Wabigoon River system in Ontario (eg. 29 - 31 ug total Hg g^{-1} dry weight in 0-2 cm depth sediments 12 km downstream of Dryden (Government of Canada/Government of Ontario, 1984). These concentrations are about two to three orders of magnitude above "background" sediment concentrations. Approximately 10 tonnes of inorganic mercury were discharged to the river from a chlor-alkali plant at Dryden between 1962 and 1970 (Parks et al., 1989). Even higher sediment concentrations (eg. 25 - 125 ug total Hg g^{-1} dry weight) were reported by Elwood et al. (1987) in East Fork Poplar Creek, Tennessee. This creek passes through the site of a nuclear weapons production plant which used elemental mercury to separate lithium isotopes. Approximately 250 tonnes of inorganic mercury were released into the creek

between 1950 and 1966.

Sediments in reservoirs may be somewhat elevated in mercury content relative to sediments in natural lakes, but not to the extent (i.e. orders of magnitude) reported above for industrially polluted situations. As discussed in Section 4.2.1, flooded and unflooded soils in the region of the Churchill River diversion in Manitoba both averaged roughly 0.1 ug g^{-1} dry weight five years after flooding, about three times higher than natural sediments in the area, which averaged 0.03 ug g^{-1} (Bodaly et al., 1987). Verta et al. (1986b) reported mercury concentrations in newly formed sediments in 6 established Finnish reservoirs ranging from 0.22 - 0.36 ug g^{-1}, except for the new Kalajarvi reservoir (0.09-0.1 ug g^{-1} from 0-5 cm) for which no new organic sediments were found.

Reports of mercury concentrations in water must be examined carefully, since most measurements prior to the late 1980's suffered from overestimation due to analytical errors. Measurements from the late 1970's and 1980's in highly polluted systems such as the Wabigoon River and East Fork Poplar Creek may reflect true values however. Parks and Hamilton (1987) reported total and methylmercury concentrations in water in Clay Lake, Ontario (Wabigoon River system) of 26.5 and 1.4 ng L^{-1} respectively, about an order of magnitude above present background values. Elwood et al. (1987) reported total and methylmercury concentrations in water in New Hope Pond (East Fork Poplar Creek system) of about 3400 and 0.5 ng L^{-1} respectively. It is interesting that although the total mercury concentration in water in this system is elevated about 3 orders of magnitude above present background values, the methylmercury concentration is only about 5 - 10 times higher than

background levels. Measurements of total mercury and methylmercury in reservoir waters are lacking.

Fish mercury concentrations in 50 cm walleye in Clay Lake were reported as high as 15 ug g^{-1} in 1971 (Parks and Hamilton, 1987), about 10-50 times above present background values. Concentrations in walleye in this system have been dropping since abatement measures in the early 1970's, but still remained in the 3-4 ug g^{-1} wet weight range in 1983.

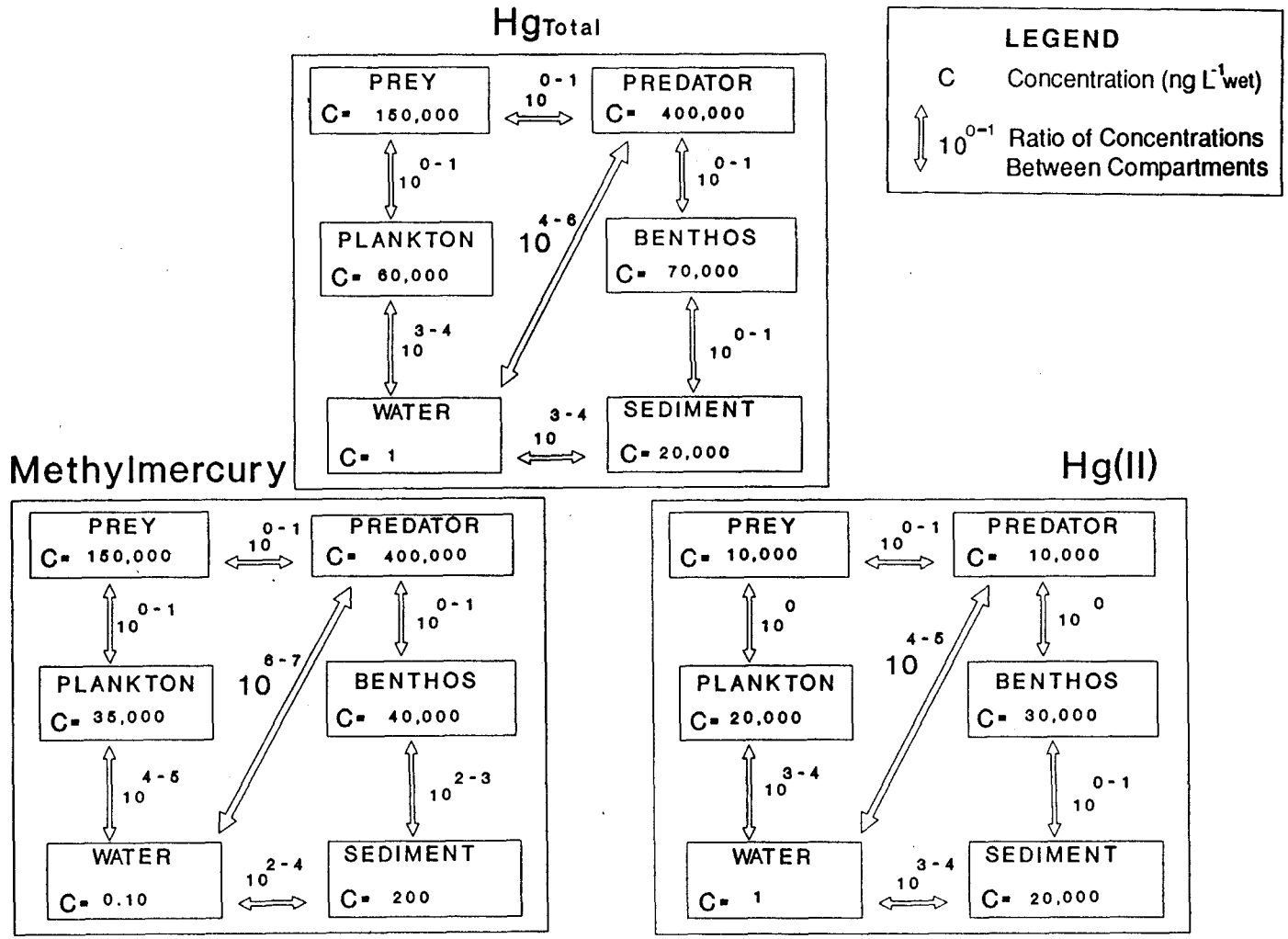
Several reservoirs have experienced elevated fish mercury levels. In the James Bay LG2 reservoir in Quebec, mean mercury concentrations in standardized 40 cm walleye and 70 cm northern pike rose to 2.80 and 2.99 ug g^{-1} wet weight respectively by 1988, nine years after flooding (Brouard et al., 1990).

4.4 Ratios of Mercury Concentrations Between Abiotic and Biotic Compartments

Figure 4.1 illustrates mercury concentrations assumed representative for total mercury, methylmercury and Hg(II) in various biotic and abiotic compartments in lakes. Ratios of concentrations between compartments are also indicated. These values are subjectively chosen based on literature data, and considerable ranges of concentrations and ratios exist in nature (otherwise no model would be necessary!). The ratios do not necessarily represent traditional equilibrium partition coefficients, since many processes in aquatic systems may preclude equilibrium conditions.

Figure 4.1 suggests that fish methylmercury concentrations tend to be 6-7 orders of magnitude greater than their surrounding waters, but only 0-2 orders of magnitude greater than the methylmercury concentrations in their diet. The greatest increase in mercury concentration between compartments tends to occur at the base of the food chain (eg. between plankton and water), particularly for methylmercury. When considering the potential for biomagnification of methylmercury in biota it is important to investigate whether the mercury is taken in primarily from a water pathway (gills) or via the diet. The difference in methylmercury concentration between water and predatory fish, 6-7 orders of magnitude, is quite large. It may be difficult to pass enough water across the gills to extract sufficient mercury from water to create such a concentration differential, implying that food mediated uptake of mercury may be more significant. Modelling food and water based mercury uptake pathways is one of the objectives of this study.

FIGURE 4.1
Generic Estimates of Mercury Partitioning in Freshwater Systems



5.0 MERCURY CYCLING IN AQUATIC SYSTEMS

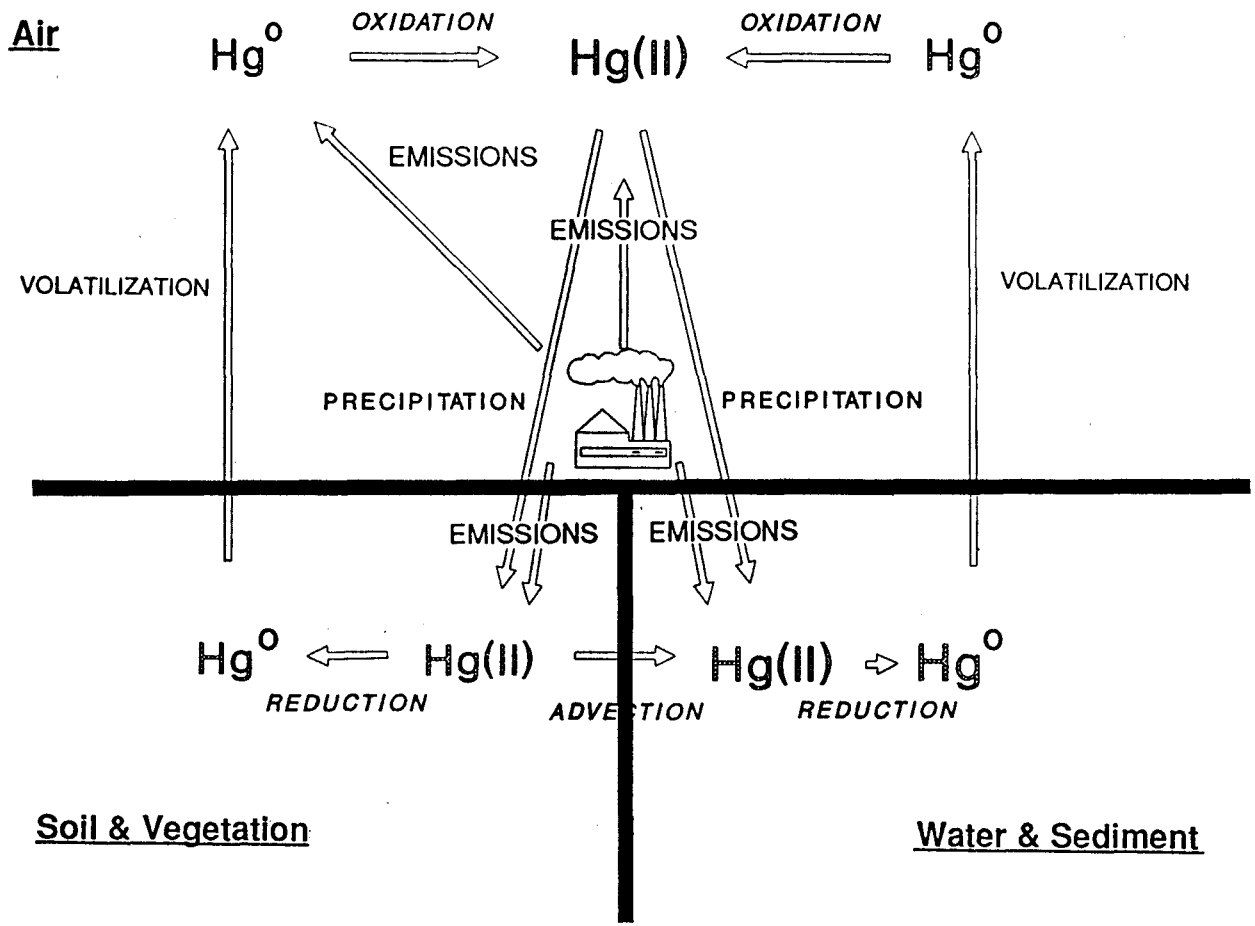
5.1 A Basic Two Species Mercury Cycle in the Environment

Although many forms of mercury exist in natural systems, a simplified mercury cycle based on two mercury species is presented in Figure 5.1. In this representation, a cycle exists between elemental mercury and Hg(II). Elemental mercury is the dominant form in air, while Hg(II) is dominant in water, sediments and soils. Hg(II) is reduced chemically or biologically to elemental mercury in soils, water and sediments, and volatilizes to the atmosphere. Once in the atmosphere, elemental mercury is oxidized to Hg(II) and is deposited back to the surface in wet or dry deposition, completing the basic cycle.

Estimates of the Henry's law constant for elemental and dimethyl mercury (e.g. 0.3 dimensionless), and measurements of volatile mercury concentrations in water and air support the concept of a flux of volatile mercury from water to air (Lindqvist and Rodhe, 1985). Several studies (Lindqvist and Rodhe, 1985; Kim and Fitzgerald, 1986) also suggest significant volatilization of elemental mercury from soils and vegetation (see Section 3).

Lindqvist and Rodhe (1985) estimated the atmospheric residence time of elemental mercury to be on the order of a few months to a year or two, while more soluble mercury (presumably mostly Hg(II)) likely has a shorter atmospheric residence time, on the order of

FIGURE 5.1
Simplified Hg Cycle



days to weeks.

5.2 A Five Species Mercury Cycle for Aquatic Systems

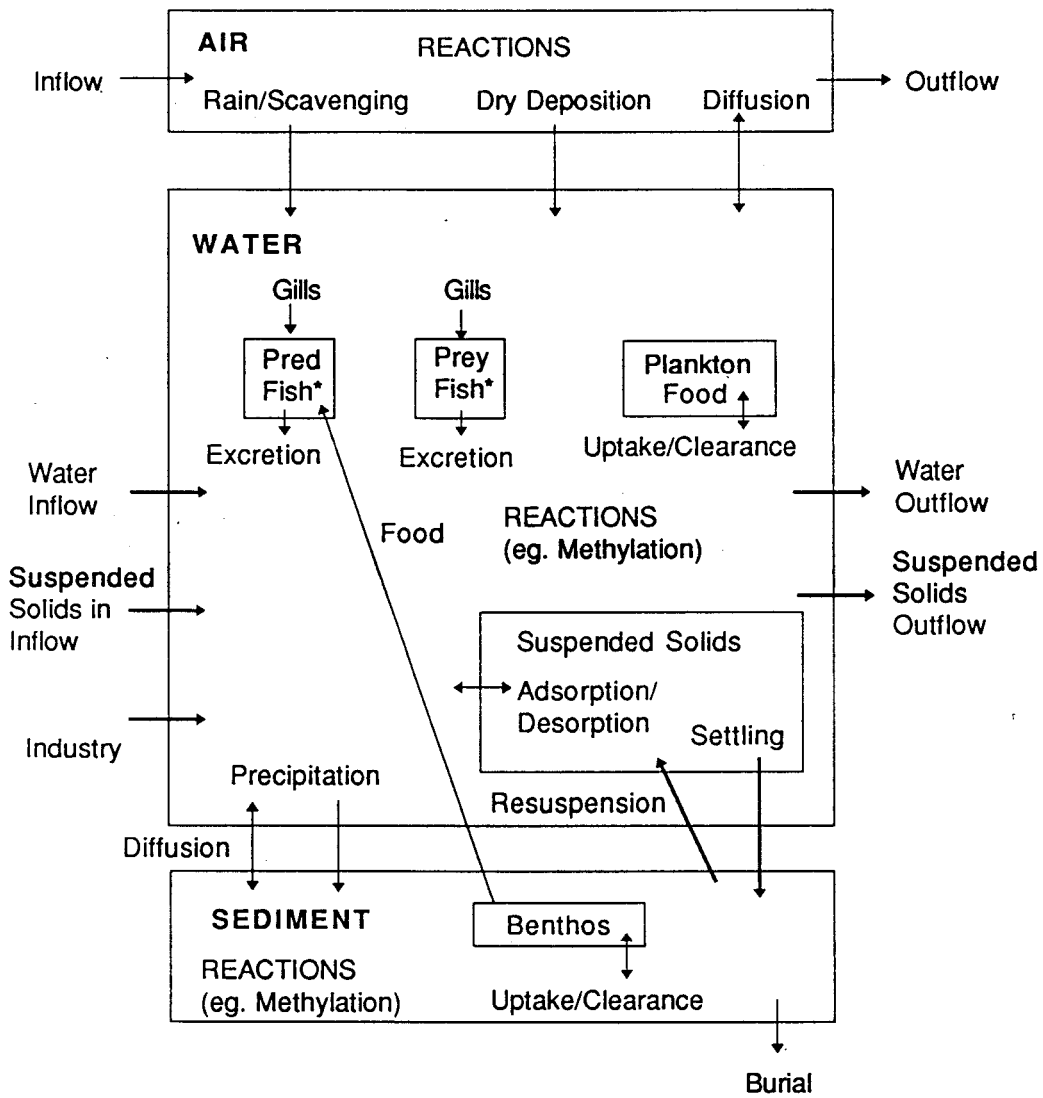
When fish mercury levels are of interest, there is a need to consider methylmercury cycling, since methylmercury is the dominant mercury form in fish. The production of methylmercury in the water column and sediments is thought to be primarily a biological process, although chemical methylation by organics has been observed. In general terms, Hg(II) is methylated to monomethyl mercury by a variety of bacteria (aerobes, facultative anaerobes and strict anaerobes), while other bacteria demethylate methyl mercury first to Hg(II) as an intermediate and finally to Hg°. Other methylmercury fluxes include watershed runoff and outflows from the waterbody (dissolved and on suspended solids), adsorption on solids in the water column and sediments, settling via suspended solids, air/water surface exchange, groundwater exchange (not treated in this study), diffusion between porewater and the water column, wet and dry deposition from the atmosphere, uptake and excretion by biota, and sediment burial. Transformations of methylmercury to dimethyl mercury, and vice versa, are also possible. Conversion of dimethyl mercury to methylmercury and methane may occur in low pH environments. Conversely, methylmercury may be transformed to dimethyl mercury and HgS in the presence of sulphide, or theoretically to dimethylmercury and $Hg(OH)_2$ in the presence of OH^- ions (high pH).

Dimethyl mercury may be produced by bacteria in sediments or the water column (Beijer and Jernelov, 1979) although most methylation measurements tend to identify monomethyl mercury as the primary product of bacterial methylation. Dimethyl mercury is relatively volatile, but is unstable in air and converts into methylmercury through reactions with OH^{-1} and Cl^{-1} radicals (Peterson et al., 1989). Although concentrations of dimethyl mercury may be low in sediments, water and air, it may represent an important intermediate state and flux mechanism in terms of the total mercury cycle.

Hg(II) fluxes within an aquatic system include watershed runoff loading and outflows (dissolved and on suspended solids), adsorption on solids in the water column and sediments, settling via suspended solids, air/water surface exchange, groundwater exchange, diffusion between porewater and the water column, wet and dry deposition from the atmosphere, chemical and biological reduction to elemental mercury, sediment burial, bacterial methylation and demethylation, and uptake and excretion by biota. The latter four processes are more significant for methylmercury than Hg(II). Hg(II) concentrations in water and porewater may also be affected by the formation of solid phase HgS. Anaerobic conditions with sufficient sulphide and Hg^{++} are required for HgS precipitation ($K_{sp}= 10^{-52}$).

Figure 5.2 provides a conceptual illustration of environmental compartments and transport processes which may play a significant role in a mercury cycle which considers Hg(II), elemental mercury, monomethyl mercury, dimethyl mercury and solid phase mercuric sulphide. A more detailed representation of mercury cycling is developed for modelling purposes and discussed in Section 7.

FIGURE 5.2
Compartments and Fluxes Relevant to Mercury Cycling in Aquatic Systems



*Note: Fish Harvesting & mortality may also be significant

5.3 Methylation and Demethylation in Aquatic Systems

In recent years, much research has been devoted to understanding and quantifying mercury methylation and demethylation. Jensen and Jernelov were the first to show in the late 1960's that lake sediments incubated with mercuric chloride could produce methylmercury, and found that this capability was lost when samples were autoclaved (Wollast et al., 1975). Several subsequent studies have also indicated a biological dominance of mercury methylation in aquatic systems (Jackson, 1988b; Xun et al., 1987; Callister and Winfrey, 1986).

In addition to biochemical methylation in the water column or sediments, chemical methylation may occur in the presence of suitable methyl group donors. For example, mercury can be alkylated by tin and lead alkyls. Photochemical methylation may occur at a lake surface (Furitani and Rudd, 1980) and several synthetic methods have been used to produce organomercurials in agriculture and industry for pharmaceuticals, fungicides and bactericides (Carty and Malone, 1979). In sediments, processes involving methyl transfers from methylcobalamin can synthesize both methylmercury and dimethyl mercury in enzymatic and non-enzymatic systems (Wood et al., 1972). Humic substances, particularly fulvic acids have also been identified in terms of their capability to chemically methylate Hg(II) (Weber et al., 1985; Nagase et al., 1982; Lee et al., 1985) although these studies used very high mercury and/or carbon concentrations. The significance of chemical mercury methylation by humics or other substances in the aquatic environment remains to be established, although the predominance of literature suggests a general perception that biochemical mercury methylation is more important than chemical methylation in sediments or the water column.

Methods exist to measure methylation or demethylation rates in natural waters or sediments using radiolabelled mercury, but the necessary spikes overwhelm natural mercury in the samples, precluding estimates of methylation rates at natural levels. Ontario Hydro is funding a two year study to significantly improve the ability of radiolabelled techniques to measure methylation rates at natural levels. Conventional "cold" determinations of net methylation rates are now possible as well, due to advances in the ability to measure methylmercury concentrations in sediments and water.

5.3.1 Specific Methylation

The following discussions focus on microbiological methylation of mercury in aquatic systems. The terms "specific methylation" and "specific demethylation" are used to distinguish one-way processes from net methylation.

There remains a fair degree of uncertainty in terms of the nature of biochemical methylation and the influences of environmental conditions on methylation rates. Uncertainty also remains regarding the relative contributions of methylation in the water column and sediments, and perhaps within fish. All three of these methylating sites have been identified.

Mercury is not required by organisms, and mercury methylation may be a detoxification process or involved in an incorrect synthesis of organic molecules. Biochemical methylation is based on the interference of mercury with a metabolic reaction involving methyl transfer. There are 3 methylating coenzymes which are involved with methyl transfer in biological systems (Wood et al., 1972):

1- S-adenosyl methionine,

2- N^5-methyltetrahydrofolate derivatives and

3- methyl corrinoids (methyl-B_{12}).

Methyl corrinoids are the only biological molecules having a metal-carbon bond and are the only known agent which can methylate inorganic mercury salts into methylmercury. They can transfer methyl groups as carbanions (CH_3^-), carbonium ions (CH_3^+) or radicals ($CH_3\cdot$). S-adenosyl methionine and N^5-methyltetrahydrofolate derivatives transfer CH_3^+ carbonium ions and are unlikely to react with Hg^{++}, a positively charged ion (Wood, 1980).

It should be noted that Landner proposed a mechanism in 1971 of methylation by an isolated fungal species of Neutrospora crassa, which is believed to lack B_{12} enzymes (Beijer and Jernelov, 1979; Bisogni, 1979). The process could involve S-adenosyl methionine. It was proposed that a methyl group could be tranferred to mercury which is bound to homocysteine, resulting in an incorrect synthesis of methionine.

Methyl corrinoids are implicated in methyl transfers in 3 enzyme systems (Wood, 1972):

(i) - methionine synthetase (cobalamin dependant)

(ii) - acetate synthetase

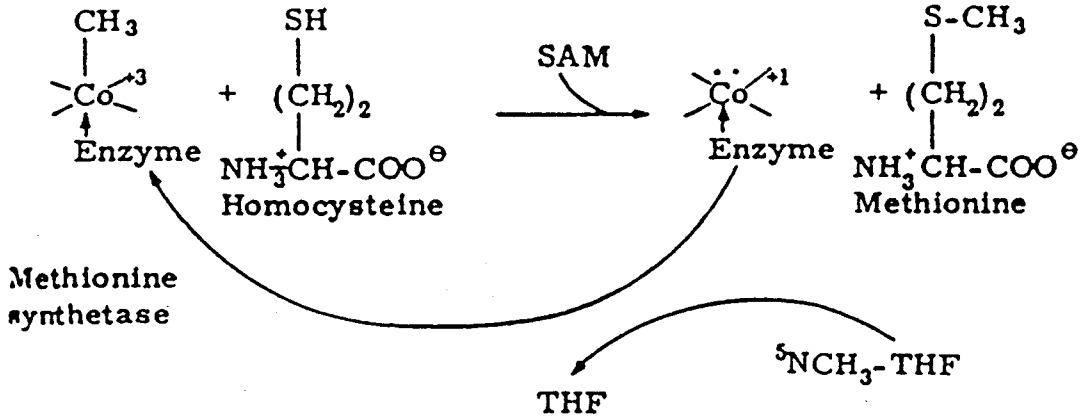
(iii) - methane synthetase

Methionine Synthetase

Several organisms (e.g. E. coli) use the cobalamin dependant methionine synthetase to create the amino acid methionine. This enzyme exists in some aerobes, facultative anaerobes and anaerobes. Without the interference of mercury, the process proceeds as shown in Figure 5.3.

Aerobic micro-organisms and facultative anaerobes which use the cobalamin dependent methionine synthetase may methylate mercury (Wood et al., 1972). The process could proceed as shown in Figure 5.4. Electrophilic attack on the methyl group of the methylcobalamin methionine synthetase generates CH_3Hg^+ and an aquocobalamin enzyme complex.

FIGURE 5.3
Methionine Synthesis With No Mercury Interference

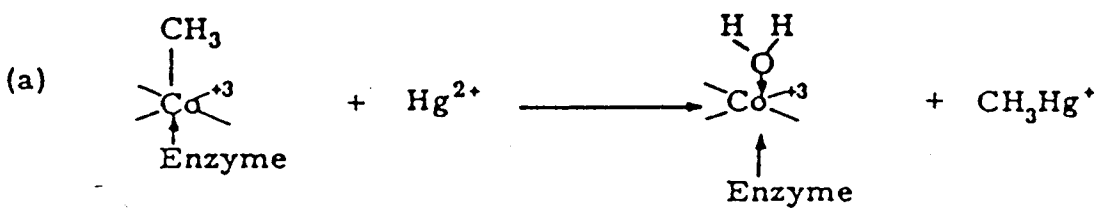


THF = tetrahydrofolate

SAM = catalytic amounts of S-adenosylmethionine

(Source: Wood et al., 1972)

FIGURE 5.4
Possible Methylcobalamin Pathway for Mercury Methylation



(Source: Wood et al., 1972)

Acetate Synthetase

Clostridium thermoaceticium and Cl. sticklandii are anaerobes synthesizing acetic acid from CO_2, using methylcobalamin as a substrate for carbon (Wood et al., 1972). A possible mercury methylation pathway based on acetic acid is shown in Figure 5.5.

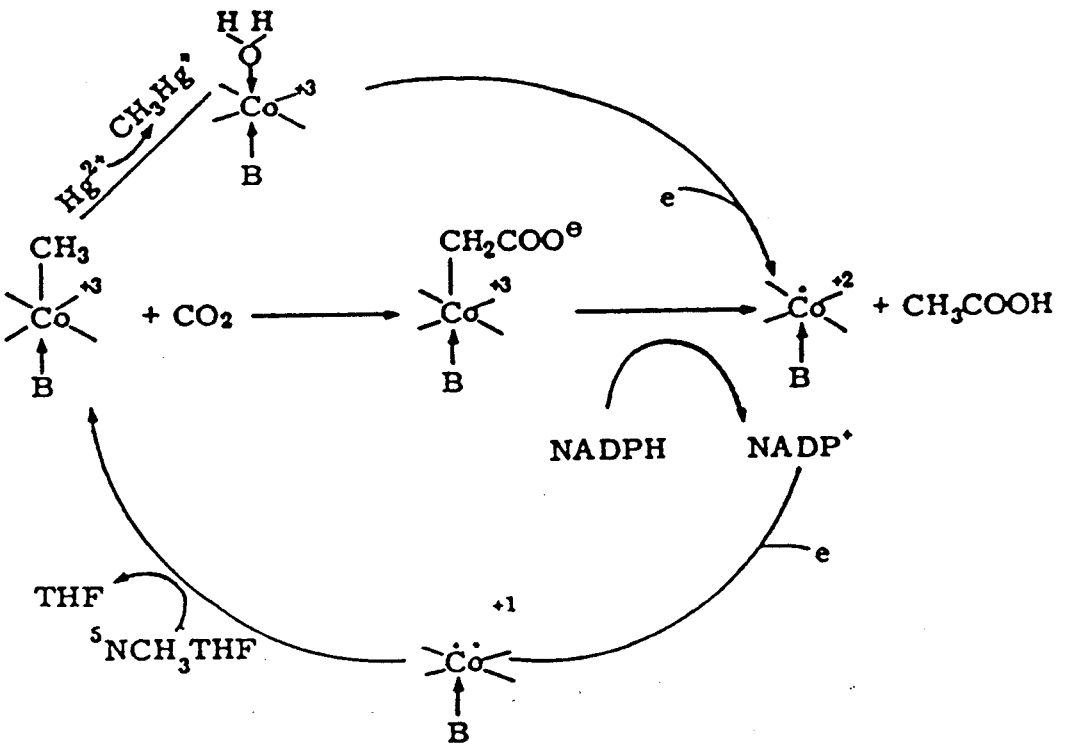
Methane Synthetase

This is a common enzyme system in anaerobic systems, and involves methylcobalamin and other methyl corrinoids as substrates. In anaerobic conditions (Eh less than -400 mV) an inorganic mercury salt could be reduced to elemental mercury and the reaction would proceed as shown in Figure 5.6, generating dimethyl mercury. It is also possible that Hg^{++} could be transported across the cell membrane by anaerobes, then reduced to elemental mercury and methylated to dimethyl mercury which could easily diffuse out of the cell. If the water were acidic the dimethyl mercury could break down to CH_3Hg^+ and methane (Wood et al., 1972).

5.3.2 Specific Demethylation

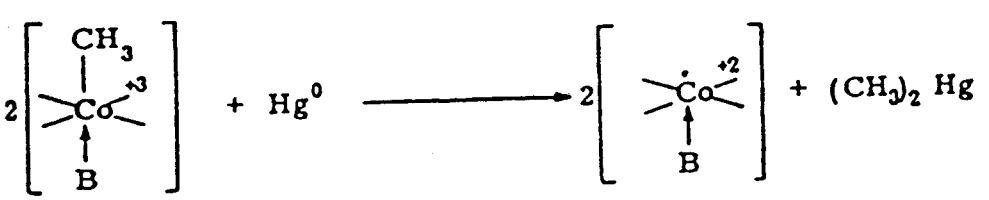
Demethylation is likely a general occurrence in the aquatic environment (Beijer and Jernelov, 1979) and can occur non-enzymatically or enzymatically. Mineralization of methylmercury into elemental mercury and methane has been established in lake and river sediments (Wollast et al., 1975). Bisogni (1979) suggested that photolytic decomposition of

FIGURE 5.5
Possible Acetic Acid Pathway for Mercury Methylation



Source: Wood et al., 1972

FIGURE 5.6
Possible Methane Pathway for Mercury Methylation



Source: Wood et al., 1972

methylmercury seems to be the only significant non-enzymatic demethylation process. In the presence of ultraviolet light, organic mercury degrades into elemental mercury with Hg^{++} as an intermediary product (Jensen and Jernelov, 1972). During biochemical demethylation, the demethylating enzyme system has been shown to contain a hydrolase, which hydrolizes the mercury/carbon bond to produce methane and Hg^{++}, and a reductase which reduces the Hg^{++} to elemental mercury, which volatilizes (US National Research Council, 1978). Large numbers of bacteria have been found able to demethylate mercury in aerobic conditions and some facultative anaerobes degrade methylmercury in oxidizing anaerobic conditions (e.g. Eh= 100 mV) (Wollast et al., 1975).

Several environmental factors have been found to influence demethylation rates and are discussed in Section 5.4.

5.3.3 Net Methylation

Methylation and demethylation may occur at comparable rates in the natural environment. Shifts in favour of one process or the other could be significant in terms of fluxes and mass balances of various mercury forms (Wollast et al. (1975)). Shifts in net methylation rates were found by Xun et al. (1987) to be affected more by changes in the rate of specific methylation than demethylation . Several environmental factors have been found to influence demethylation rates and are discussed in Section 5.4

5.3.4 Methylation in Fish

In addition to methylation in sediments and the water column, the potential for bacterial mercury methylation in fish intestinal contents has been identified (Rudd et al., 1980) using radiolabelled mercury. Species tested were walleye, pike, sauger, cisco, whitefish and sucker, all of which methylated mercury. The lack of methylation in fish noted elsewhere may have been attributable to the fact that other studies used bacterial antibiotics which could eliminate bacteria in the intestines. It is uncertain whether methylating bacteria are indigenous to the intestines or simply pass through with food. This has implications regarding environments in which fish would methylate mercury internally.

In summary, the above processes indicate the potential in the water column and sediments for methylation and demethylation by aerobes, facultative anaerobes and anaerobes. Chemical methylation and methylation in fish are possible but have not been identified as significant in aquatic systems. The mechanisms of biochemical methylation are not fully understood. The most common mechanism proposed is the transfer of a methyl group from methylcobalamin (B_{12}) to Hg^{++}. Demethylation mechanisms on the other hand are better defined, involving a two step process eventually generating methane and elemental mercury. From a modelling perspective, it would be useful to understand the functional purpose underlying methylation and demethylation, particularly if a unified explanation could be applied to both processes. For example, detoxification has been suggested as a possible reason for methylation and demethylation. In this study, both processes are modelled in a similar fashion, i.e. depending on a supply of available mercury (methylmercury or Hg(II)), levels of

bacterial activity, and the methylating/demethylating efficiencies of bacteria. Methylation and demethylation are considered individually since the relative importance of these processes remains to be quantified and may vary significantly in different conditions. Research clarifying the mechanisms and underlying purposes implicated in methylation and demethylation would be useful.

5.4 Factors Affecting Mercury Cycling in Aquatic Systems

Many water quality and trophic variables have been considered to explain mercury cycling and concentrations in fish. These include pH, carbon, water temperature, bacterial activity, colour, oxygen, redox potential, sulphide, selenium, alkalinity, hardness, conductivity, lake productivity, and ratios of watershed area to lake area or volume. Table 5.1 lists selected variables which may affect mercury cycling in aquatic systems.

5.4.1 pH

Increased acidity has often been associated with higher fish mercury content. Thorough reviews of pH implications regarding methylmercury bioavailability and/or content in fish have been presented by others (e.g. Richman et al., 1988). Generally, pH effects can be grouped into two categories, those affecting mercury loading to the waterbody and those affecting in-situ cycling. Several possible pH related interactions with mercury cycling and elevated fish mercury levels are presented in Table 5.2.

TABLE 5.1
SELECTED FACTORS POTENTIALLY RELATED TO MERCURY CYCLING IN AQUATIC SYSTEMS

1- pH associations with (see Table 5.2):

- watershed and atmospheric loading of Hg(II) and/or methylmercury
- available mercury for methylation (H^+ competition, DOC aggregation/settling)
- cobalt availability of methyl cobalamin mediated methylation
- biota biomass, metabolism, and diet
- calcium effects on fish mercury uptake
- microbial activity
- hydrolysis of dimethyl mercury to monomethyl mercury

2- Carbon associations with:

- Watershed loading of Hg(II) and methylmercury
- available mercury for methylation
- microbial activity
- biota biomass, metabolism and diet
- Water column reduction and volatilization of mercury

3- Productivity, Dissolved Oxygen and Eh associations with:

- microbial activity of methylators and demethylators
- available mercury for methylation
- biomass

4- Temperature associations with:

- microbial activity of methylators and demethylators

5- Microbial Adaptation to Elevated Mercury Concentrations

- microbial balance of methylators and demethylators

TABLE 5.2
POSSIBLE INTERACTIONS BETWEEN pH AND MERCURY CYCLING IN AQUATIC SYSTEMS

1.0 Factors increasing the rate of in-situ net methylation:

1.1 Potential for increased available Hg(II) in solution due to pH related shifts in complexation and adsorption at low pH;

1.2 Potential for increased available Hg(II) in solution due to aggregation/settling of humic acids in waterbody at low pH;

1.3 Potential for increased sediment Hg(II) due to aggregation/settling of humic acids from the water column at low pH (Rekolainen et al., 1986);

1.4 Lower rate of surface water reduction and volatilization of Hg(II) by humic acids in acid conditions due to aggregation/settling of humics at low pH (Winfrey and Rudd, in press);

1.5 Lower rate of surface water reduction and volatilization of Hg(II) by H_2O_2 in acid conditions (Brosset, 1987);

1.6 Atmospheric oxidation of elemental mercury by H_2O_2 in acidic atmospheric conditions could lead to increased Hg(II) for methylation in surface waters, due to increased atmospheric deposition of Hg(II);

1.7 Potential for increased methylation by sulfate reducing bacteria in acidic conditions;

1.8 Enhanced methyl cobalamin mediated methylation due to increased cobalt availability at low pH;

1.9 Easier flow of Hg(II) across bacterial cell membranes at lower pH (Xun et al., 1987);

1.10 Decreased rate of demethylation on either side of pH 6.6, perhaps due to suppressed enzymatic activity of demethylators or lower rate of membrane transport of methylmercury (Xun et al., 1987);

1.11 Possible chemical hydrolysis of dimethyl mercury to monomethyl mercury at low pH (Beijer and Jernelov, 1979; Wood, 1980);

2.0 Factors Increasing Loading of Methylmercury to a Waterbody

2.1 Increased methylmercury loading from acid impacted watershed due to increased abiotic methylation at low pH;

2.2 Several of the above factors applicable to in-situ methylation may also apply to the watershed.

TABLE 5.2 (CONTINUED)
POSSIBLE INTERACTIONS BETWEEN pH AND MERCURY CYCLING

3.0 Impacts on Biota

3.1 Lower biomass in acid stressed lakes resulting in higher mercury available per fish;
3.2 More metabolic activity for individual fish to reach given weight in acid stressed waters, resulting in greater uptake of methylmercury (Rodgers et al., 1987);
3.3 Increased methylmercury in food (for a given food supply);
3.4 Increased methylmercury in food (shift in prey species);
3.5 Shifts in the ability of fish to excrete mercury.

4.0 Correlations Between pH and Other Variables

4.1 Correlations with hardness, alkalinity or calcium, which may reflect competition by anions for transport across membranes by fish;
4.2 Relationship between pH and humic content of water, which may reflect watershed Hg(II) or methylmercury loading (Mannio et al., 1986);
4.3 Correlations between anthropogenic acidic deposition and anthropogenic atmospheric mercury loading to a waterbody

5.4.1.1 pH and In-Situ Mercury Cycling

Within the water column and sediments, pH may affect mercury cycling through several mechanisms which are discussed in the following sections.

pH and Specific Methylation and Demethylation Rates

Several studies have suggested that lower pH results in higher net methylation rates and methylmercury concentrations in water and surficial sediments. Xun et al. (1987) found that acidification increased specific methylation and decreased demethylation in water column samples from ELA lakes in Ontario. Net methylation was seven times faster at pH 4.5 than pH 8.5. Demethylation decreased with pH shifts on either side of ambient (pH 6.6). This may have been due to suppressed enzymatic activities of demethylating bacteria or interference with cross-membrane transport of methylmercury (Xun et al., 1987).

Ramlal et al. (1985) found less radiolabelled Hg(II) in porewater at pH 4.0 than pH 7.0. (0.6% versus 4.4%). This result is contrary to what would be expected solely on the basis of H^+ competition for binding sites on solids. Consistent with these results, Hakanson (1974) found that 3% of mercury added to a sediment sample was in solution at pH 5, versus 68% at pH 9, and hypothesized that this may have been due to aggregation and settling out of organics at low pH. In systems with solids and soluble complexes competing for Hg^{++} ions, the amount of Hg(II) in solution and on solids depends on the ratio of the complexation and adsorption constants. Lower pH may alter these constants to varying extents through H^+

competition and DOC precipitation. If the soluble complexing capability is reduced relative to the adsorption strength, the concentration of Hg(II) in solution could drop.

It is important to note that a reduction in total Hg(II) in solution (due to DOC aggregation and settling) would thermodynamically be expected to be paralleled by an *increase* in the fraction of Hg(II) in solution assumed available for methylation (represented by Hg^{++} and other inorganic Hg(II) complexes). It is unclear whether the absolute concentration of Hg(II) available for methylation would increase or decrease due to DOC aggregation and settling. Similar trends are possible for total methylmercury and free CH_3Hg^+ in solution and on solids, although data were not found in the literature to provide insights or direction.

Hydrolysis of Dimethyl Mercury at Low pH

The hypothesis that lower pH increases net methylation is also supported by literature which suggests that methylation may produce mainly monomethyl mercury in neutral and acid conditions, and dimethyl mercury in alkaline conditions (see Figure 5.7) (Fagerstrom and Jernelov, 1972). It is possible that both monomethyl and dimethyl mercury are produced by bacteria in a two step process which adds a second methyl group to monomethyl mercury.

FIGURE 5.7
Effect of pH on formation of Monomethyl and Dimethyl Mercury

Formation of mono- and dimethyl mercury in organic sediments at different pH during 2 weeks with a total mercury concentration of 100 ppm in the substrate.
○ CH_3Hg^+ found in water and sediment. × Volatile CH_3Hg-compound trapped in Hg^{2+} after aeration $(CH_3)_2Hg$.

(Source: Beijer and Jernelov, 1979)

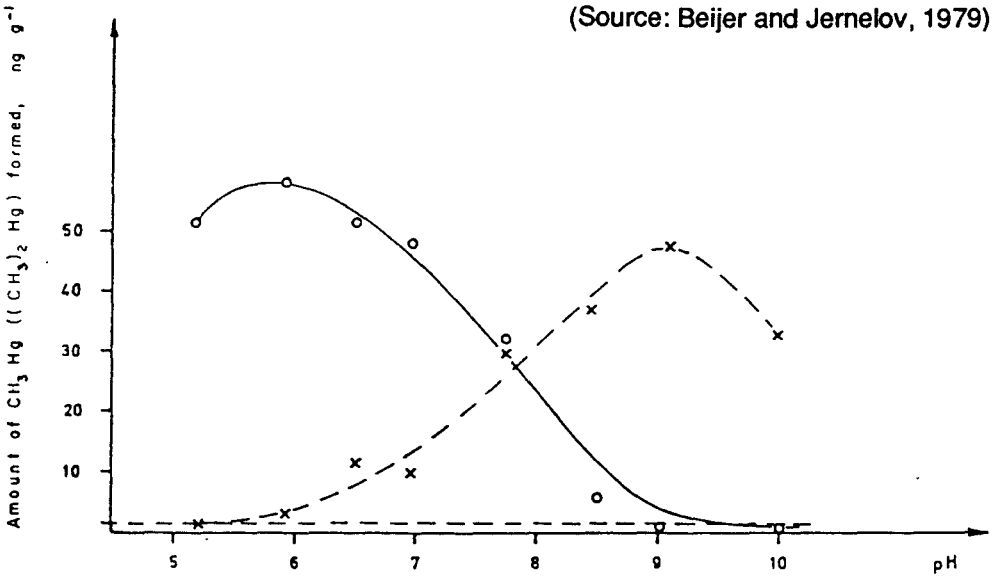
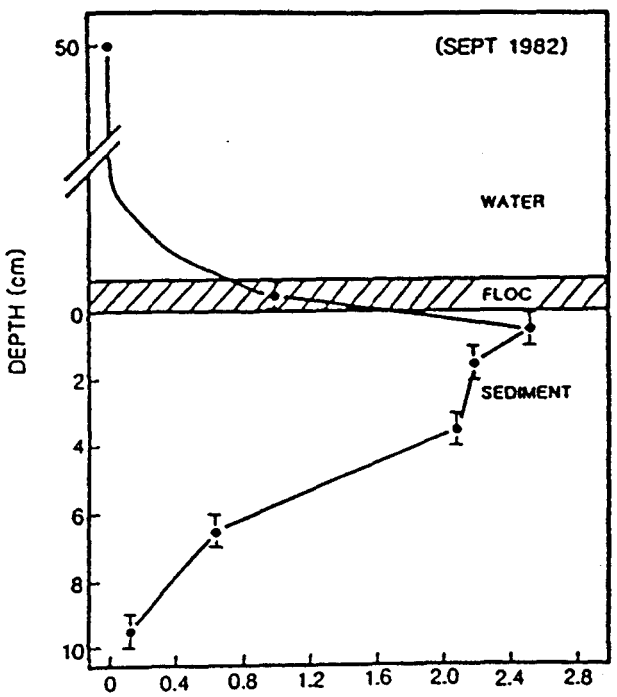


FIGURE 5.8
Depth Distribution of Hg Methylation in Wisconson River Sample.
Error bars represent depth intervals of sediment assayed. Shaded area represents the sediment-water interface.



(Source: Callister and Winfrey, 1986)

Transformation of methylmercury to dimethyl mercury is also theoretically possible via reactions with sulphide and perhaps OH^-. Craig and Moreton (1986) found that samples of sediments from British estuaries volatilized mercury when sufficient sulphide was present (eg. 4 mg g^{-1}), and suggested the followed reaction:

$$2\ CH_3Hg^+ + S^{--} \text{---> } (CH_3Hg)_2S \text{ ---> } (CH_3)_2Hg + HgS$$

In low pH conditions however, dimethyl mercury is unstable and could break down to monomethyl mercury and methane through hydrolysis (Jensen and Jernelov, 1972):

$$(CH_3)_2Hg + H^+ \text{---> } CH_3Hg^+ + CH_4$$

Thus, although sulphide disproportionates methylmercury chemically to dimethyl mercury in anaerobic conditions, dimethyl mercury could be hydrolyzed back to methylmercury in acid conditions (Wood, 1980).

Altered Rate of Hg(II) Reduction by H_2O_2 or Organics at Low pH

Brosset (1987) suggested that in alkaline waters H_2O_2 tends to reduce Hg(II) to elemental mercury which is then volatilized to the atmosphere. The potential therefore exists to return some mercury in precipitation back to the atmosphere before it effectively enters the water column. Acid waters however would not sustain this process and could allow more effective atmospheric loading of mercury in acid lakes. This would increase the availability of

Hg(II) for methylation. Organics may also act as reducing agents for Hg(II), however precipitation of humic acids at low pH could restrain this process.

Influences of Low pH on Individual Fish

On an individual fish basis, factors affecting mercury kinetics include metabolism, growth rates and diet. Rodgers et al. (1987) found that accumulation of mercury in 3 experimental trophic levels was not directly related to pH, but suggested that higher metabolic activity and subsequently more mercury intake may be required for fish to reach a given weight in acid stressed waters. This concept could at least partially explain results obtained by Wren and MacCrimmon (1983), who studied sunfish (Lepomis gibbosus) from 16 Ontario lakes ranging in pH from 5.6 to 8.4. As pH declined, growth rates decreased while average mercury concentrations increased. In contrast however, Wren and MacCrimmon (1986) found that pike in Tadenac Lake, Ontario grew faster and had higher mercury levels than comparable fish from Tadenac Bay. Perhaps acidity has system specific effects on relationships between the following biological factors: growth rates, metabolic rates, food intake required for growth and metabolism, associated mercury intake and possibly mercury clearance. Other environmental factors, such as a shift in diet or a shift in the mercury content of a fish's diet, could also be implicated.

Uptake of mercury via gills could be related to pH by correlation rather than cause. For example, mercury uptake via gills could be reduced if hard waters result in less efficient mercury transport across gills due to calcium competition. Rodgers and Beamish (1983) found

that the efficiency of methylmercury uptake by rainbow trout was roughly three times higher in soft water (8% at 30 mg $CaCO_3$ L^{-1}) than in hard water (25% at 385 mg $CaCO_3$ L^{-1}). This possibility is only significant if mercury intake via gills is significant relative to the food pathway, or if uptake of methylmercury by a fish's prey is influenced by calcium.

5.4.1.2 pH Influences on External Loading of Mercury and DOC

Increased or decreased external loading of Hg(II) or methylmercury could occur due to acidic impacts on atmospheric and terrestrial processes. Several factors are discussed below.

Enhanced atmospheric oxidation of elemental mercury to Hg(II) in acid conditions has been discussed by Brosset (1987). Ozone can react with atmospheric water to generate H_2O_2 which in turn can oxidize elemental mercury in the presence of hydrogen ions. Increased Hg(II) loading could then occur through rainfall, either directly on the water surface or indirectly via runoff.

Since most methylation routes found in the literature involve methylcobalamin, the availability of cobalt may be important in terms of rates of methylcobalamin mediated methylation. Wood (1989) reported Swedish studies indicating acidification may liberate cobalt in soils. This process could elevate methylation rates in soils, runoff waters, or in the waterbody.

DOC precipitation at low pH could lower Hg(II) and methylmercury in solution in runoff waters. Lodenius and Autio (1989) reported less total mercury in leachate from peat at low pH (pH 3.6-5.4) than in distilled water. The net result in terms of Hg(II) loading to the waterbody is uncertain however, since it is the sum of dissolved and particulate mercury in runoff which loads the waterbody. Further research in this area would be instructive for methylmercury and Hg(II).

5.4.2 Carbon Quantity and Type

5.4.2.1 Allocthonous versus Autochthonous Carbon

DOC has been closely examined in association with mercury in fish. Oligotrophic drainage lakes and dystrophic lakes higher in colour and humic acid content often show positive correlations between DOC and fish mercury content. Eutrophic waterbodies often tend however towards lower Hg in fish (Beijer and Jernelov, 1979; Bjornberg et al., 1988). Winfrey and Rudd (in press) discussed studies of yellow perch in seepage lakes which exhibited negative correlations between water DOC and fish mercury content.

The existence of both positive and negative correlations between DOC and fish mercury levels in different environments has been a source of considerable speculation. A partial explanation may lie in a closer examination of the origin of the carbon which makes up the DOC in a lake.

DOC, which represents the largest fraction of total organic carbon in a lake (e.g. 90%), is comprised mainly of humic and fulvic acids. The fraction of non-humic organics (carbohydrates, amino acids, fatty acids, etc.) tends to be low, even in eutrophic conditions (Pennanen et al., 1986). Watershed based DOC tends to be partially degraded prior to reaching the lake and thus has a higher proportion of high molecular weight humic acids. These acids are relatively resistant to degradation and tend to be responsible for much of the colour content of the waters (Wetzel, 1983). Lower molecular weight fulvic acids on the other hand are somewhat more labile and may correlate better with chemical oxygen demand (Pennanen et al., 1986). The distribution between high and low molecular weight organic acids will depend on the origin of the carbon (watershed versus in-situ) and the extent of degradation of the watershed organics prior to reaching the lake.

Borg and Johansson (1989) found that in Swedish podzolic soils, mercury is mainly bound to humic substances. Mercury transport from soils to water was closely related to the flow of humic substances, with mercury bound mostly to the high molecular weight humic acid fraction of soluble humics. Mercury accumulation exceeded losses in upper soil layers, with transport via volatilization, runoff and migration to deeper soil layers being small compared to atmospheric deposition. Borg and Johansson (1989) concluded that mercury is probably accumulating slowly in soils in Sweden and at present, only 0.1% of mor layer mercury is released per year by runoff.

The affinity between mercury and carbon would suggest that lakes receiving a large fraction of their DOC from the watershed are also receiving significant watershed inputs of

Hg(II) and possibly methylmercury. In a study of 91 Ontario Lakes, lake trout were positively correlated with variables indicating dystrophy (e.g. DOC, colour, iron) and watershed area (McMurtry et al., 1989). In 93 Finnish drainage lakes, Verta et al. (1986a) found that allocthonous organic matter correlated positively with pike Hg. These lakes were mostly low in productivity, and ranged from clear to very coloured (e.g. 10-280 Pt mg L^{-1}). Ratios of drainage area to lake volume ratios also correlated positively with fish Hg. It was concluded that the mercury originating from the catchment area represented the main load of mercury in small forest lakes in southern Finland. In 14 shield lakes in Ontario, Suns et al. (1980) established correlations between mercury in yearling yellow perch Hg and the ratio of drainage area to volume, however no correlations were found with TOC or colour. The lack of correlations with TOC may have been partially due to a narrower colour range (5-20 Hazen units) relative to the Finnish datasets, or an overiding influence of pH related effects on fish mercury levels in different waterbodies. Significant correletions were reported with epilimnetic pH and aluminum (pH ranged from 5.1 - 7.5).

Although high humic concentrations in runoff may be associated with mercury loading to a lake, allochthonous DOC *within* the waterbody may tend to remove mercury from the pools available for methylation or demethylation (assuming DOC/mercury complexes are unavailable for these processes). This could offset to varying degrees the effect on methylation of Hg(II) loaded via humics from the watershed. Farrell et al. (in press) studied the effect of chloride and cysteine complexation on rates of methylation. Cysteine additions promoted bacterial activity but reduced production of methylmercury. Cysteine was found to have a strong complexing capability for Hg(II) and it was suggested the Hg(II) availability for

methylation decreased with increasing cysteine concentrations. Furthermore, stimulation of microbial activity by allochthonous carbon may be low in some systems if the DOC has been degraded prior to reaching the watershed. It is plausible then that in some high colour, low productivity lakes, elevated fish mercury levels could be associated with direct methylmercury loading from the watershed or atmosphere, rather than allochthonous Hg(II) loading or in-situ methylation.

The DOC in eutrophic waters with low terrestrial inputs would be primarily autochthonous, and would not reflect high watershed loading of Hg(II) or methylmercury. Furthermore, although the elevated carbon content of such waters would reflect increased bacterial activity, in-situ methylation could be restrained if the DOC effectively removed Hg(II) fro the bioavailable pool. These conditions could contribute to negative correlations between DOC and fish mercury content in some systems (e.g. productive seepage lakes).

New reservoirs may present an environment with a pulse of Hg(II) and/or methylmercury from flooded soils, compounded with a plentiful supply of degradable carbon which may also stimulate in-situ methylation. In such situations, it is plausible that in-situ methylation could dominate external methylmercury loading.

Different types of aquatic systems may have very different driving mechanisms in terms of methylmercury loading and cycling. The above concepts may help reconcile positive and negative correlations between fish mercury levels and DOC. Many other relationships between carbon and fish mercury levels are also possible, including carbon associations with

(i) biomass, metabolism and diet, (ii) water column reduction and volatilization of mercury, and (iii) pH.

5.4.2.2 Carbon, Microbial Activity, and Methylation

General Microbial Activity

Methylation is likely enhanced when general microbial activity is enhanced. Microbial activity is in turn a function of several variables, including the quantity and degradability of organic carbon, temperature, and redox potential. Several studies indicate that the rate of methylation correlates reasonably to general microbial activity. For example, Furitani and Rudd (1980) found that the amount of specific methylation, expressed in radioactive disintegrations ($CH_3{}^{203}Hg^+$), paralleled bacterial growth, expressed as optical density. Jackson (1988b), based on studies in the Churchill River diversion, concluded that elevated methylation rates in flooded terrain resulted primarily from increased bacterial activity due to submerged organic matter. Methylmercury production correlated highly with CO_2 production which in turn correlated with organic carbon in sediment. The increase in available mercury was considered a factor, but of secondary importance. In Wisconsin River sediments, the depth distribution of methylation agreed well with the distribution of general microbial activity and supported the notion of biological methylation (see Figure 5.8) (Callister and Winfrey, 1986).

In the water column, Furutani and Rudd (1980) found that microbial activity was linearly related to methylation, based on a plot of methylation versus oxygen consumption.

5.4.3 Productivity, Dissolved Oxygen and Eh

Productive waters may exert several competing influences on mercury methylation and accumulation in fish. Increased bacterial activity may lead to increased methylation in productive waters. The contribution of sulphate reducing bacteria to mercury methylation under anaerobic conditions is unresolved. These organisms have been suggested as effective methylators in marine and estuarine environments (Winfrey and Rudd, in press).

Several factors could lead to decreased methylation rates in productive waters. Less Hg(II) may be bioavailable in sediments or the water column due to (i) complexation of Hg(II) by elevated DOC or sulphide, (ii) adsorption by increased suspended particulate concentrations, or (iii) precipitation of HgS in systems with sufficient sulphide and Hg^{++}. Relative shifts in the activity of methylating and demethylating bacteria in low Eh conditions in some productive waters could also influence net rates of methylation.

Jackson (1988b) found that sulphides affected methylmercury production but not bacterial activity (CO_2 production), suggesting sulphide was affecting Hg(II) availability. Methylation of HgS can occur, but at a much slower rate (e.g. 3 orders of magnitude slower) than for $HgCl_2$ (Beijer and Jernelov, 1979). It is noteworthy that Clay Lake in the mercury polluted Wabigoon River system in Ontario experienced active methylation in sulfide containing sediment floc samples taken from the anoxic western basin (Furitani and Rudd, 1980). The sulfide was present as amorphous FeS which has a solubility product of about 10^{-}

^{16} to 10^{-17} in comparison to 10^{-52} for HgS. It was suggested that the dissociation of FeS and the sulfide binding of mercuric ion as HgS did not occur quickly enough to severely inhibit methylation, since the activities of the anoxic samples and aerobic samples were similar. Some of the mercury entering the anoxic sediments on particulates may have been methylated before it could be bound as mercuric sulfide. The result was a gradual accumulation of hypolimnetic methylmercury in the presence of sulfide. Bloom and Watras (1989a) reported similar profile shapes for methylmercury in the anoxic hypolimnion of Little Rock Lake, Wisconsin.

The literature contains conflicting information on the effects of dissolved oxygen on net methylation, but the prevalent opinion seems to be that transitional aerobic/anaerobic sediments methylate more mercury than purely aerobic or anaerobic sediments. Wollast et al. (1975) postulated three methylating zones in terms of final electron acceptors:

(i) an aerobic zone with O_2 present and aerobic respiration,

(ii) an oxidizing anaerobic zone with no O_2 or sulphides, but nitrate, manganese and iron respiration and several fermentations occur, and

(iii) a reducing anaerobic zone with sulphides generated through sulphate respiration.

When fields of microbiological activity were considered and combined with the regions where Hg(II) is available, Wollast et al. (1975) concluded methylation is most likely optimized in oxidizing anaerobic conditions. Callister and Winfrey (1986) suggested oxygen may directly inhibit methylation, while Ramlal et al. (1986) noted that demethylation is faster

in the presence of oxygen. Both of these trends would result in higher rates of net methylation in low oxygen environments. Jackson (1988b) found that organic matter promoted net methylation in the presence and absence of oxygen. Rates were higher in the absence of oxygen, providing sulfide levels were low. It was suggested that the oxygen effect may be related to improved demethylation in the presence of oxygen. Craig and Moreton (1986) studied methylmercury and sulphide levels in the sediments of selected British estuaries. As sulphide levels increased, methylmercury concentrations in sediments increased to a maximum and then declined. Net methylation rates were suggested to be greatest in moderately anaerobic conditions, based on correlations between methylmercury levels and sulphide or Eh. Hg(II) complexation in the presence of high sulphide concentrations may have reduced methylation rates.

Xun et al. (1987) concluded that in eutrophic lakes, pH may be more important than having more decomposable organic matter to promote methylation. This hypothesis was based on an examination of a eutrophic lake which had a pH of 8.5 and a low methylation/demethylation ratio during an algal bloom, relative to a similar lake of more neutral pH.

In addition to factors related to methylation in productive waters, fish mercury levels could be influenced by biomass dilution, or increased settling of suspended solids, which would help remove methylmercury from the water column. It is also possible that H_2S could disproportionate monomethyl mercury to dimethyl mercury in anaerobic conditions (Wood, 1989) such that monomethyl mercury concentrations could be lowered in anoxic hypolimnia of

productive lakes. Field evidence to support this concept is lacking however. Productive waters with high pH levels could also result in the chemical conversion of monomethyl mercury to dimethyl mercury through a reaction with OH^-, while the potential for the reverse conversion of dimethyl mercury to monomethyl mercury through a reaction with H^+ (as could occur in lower pH conditions) would be lessened. Field evidence to support the occurence of these processes is lacking as well. Finally, Brosset (1987) noted that H_2O_2 may be a reducing agent for Hg(II) in alkaline waters, leading to volatilization and lower Hg(II) concentrations in the water column. These factors would tend towards lower mercury levels in biota in high pH, productive waters.

5.4.4 Temperature

Callister and Winfrey (1986) reported that lower temperatures reduce methylation. The rate was greatest at 35 degrees C, higher than typical field temperatures, such that an increase in field temperature should increase the production of methylmercury. A temperature increase from 20 to 35 degrees C tripled the methylation rate. Fagerstrom and Jernelov (1972) reported that methylation rates tend to double for an increase in temperature of about 10 degrees C.

Callister and Winfrey (1986) also reported higher methylation rates in summer. Some sites exhibited a seasonal trend in methylation, with lower rates in early summer, higher rates in late summer and a sharp decrease in fall. Samples from different periods were all incubated at 20 degrees C, so the effect was not exclusively due to temperature. Maximum methylation

occurred about 1 month after maximum temperature, minimum O_2 and maximum turbidity. It was postulated that increased organic loading from industry in late summer and low flow could have caused the effect. It should be noted that other physical environments do not necessarily experience the same seasonal trends noted by Callister and Winfrey (1986) in Wisconsin River sediments. For example, Furutani and Rudd (1980) found the methylation rate in a basin in mercury polluted Clay Lake, Ontario, was greatest during the spring freshet in sediments and the water column.

5.4.5 Microbial Adaptation to Elevated Mercury Concentrations

Wollast et al. (1975) noted that the addition or production of mercury (inorganic or organic) could alter the composition of the bacterial community. Microbes able to transform it from the form at higher concentration into another form could be favoured. Experiments using pre-cultures containing varying amounts of methylmercury indicated that cultures pre-treated with more methylmercury showed a greater ability to demethylate, due to selective adaptation of the overall culture. Similar adaptation was found in methylating bacteria. Strains of Neurospora crassa pre-treated with $HgCl_2$ were found to have a methylating capacity 10 times higher than natural strains. Wollast et al. (1975) also suggested that the activity of both methylating and mineralizing organisms could increase simultaneously, eventually reaching a new steady state.

Experiments using radiolabelled mercury have indicated that bacteria can survive and methylate or demethylate mercury at concentrations considerably above ambient freshwater or

sediment concentrations. Xun et al. (1987) found that water column rates of specific methylation increased at a greater than linear rate with the addition of Hg(II) up to 66,000 ng mercury L^{-1}. Water column demethylation increased linearly with the addition of up to 3,730 ng methylmercury L^{-1}. These concentrations are orders of magnitude above ambient freshwater concentrations. In sediments from selected ELA lakes in Ontario collected in 1983, it was found that specific rates of demethylation increased linearly up to 44 ug of methylmercury per gram of sediment and continued to increase up to 140 ug of methylmercury per gram of sediment (Ramlal et al., 1986). These concentrations are also orders of magnitude above ambient sediment concentrations.

Bacterial adaptation favouring improved methylating capability was also discussed by Ramlal et al. (1987) and Ramsey and Ramlal (1987a) for studies carried out in limnocorrals in Southern Indian Lake, Manitoba, from 1981-1983. Annual mercury spikes in limnocorrals resulted in the conclusion that bacterial populations can be altered by mercury additions. Net methylation rates (methylation/demethylation ratios) were higher in subsequent years when bacterial populations were already established favourably for methylation. Ramsey and Ramlal (1987a) suggested these results may indicate that bacterial adaptation in reservoirs may account for a greater increase in methylation rates than would be expected due to an increase in microbial growth rates alone.

In summary, the discussions presented in Section 5 reinforce the complexity of methylmercury cycling. Physical, chemical and biological processes all play important roles. The importance of various processes in the mercury cycle remains to be quantified. Effects of

changing environmental conditions on these processes are also discussed by many authors through a wide range of hypotheses. The present state of knowledge has a definite influence on the development of a mercury model for aquatic systems. A framework needs to be constructed capable of testing the importance of various processes, known or hypothesized. Mathematical representations of processes also need to be constructed with the flexibility to address the effects of changing environmental conditions.

6.0 A REVIEW OF MERCURY MODELLING STUDIES

The mercury models which have emerged over the past twenty years can be divided broadly into three main categories: global budgets models, fate models for aquatic systems, and uptake models for individual fish. A few efforts to develop models representing the kinetics of methylation of Hg(II) have also been undertaken.

6.1 Global Budget Models

Several global budget models for mercury appeared in the 1970's, examining the distribution of mercury in various compartments (soils, air, water, biota, etc.) and mercury fluxes between compartments. A study by Wollast et al. (1975) is representative of early budgets undertaken in the 1970's. Global budgets were presented for total mercury in terms of pre-industrial and present conditions. Sediments were estimated to be the main reservoir of mercury for both the pre-industrial and modern scenarios. Anthropogenic fluxes were considered comparable to those of nature. Andren and Nriagu (1979) updated previous budgets of pre-industrial and present conditions using information available as of 1979. Conclusions included an estimate of a 25-30% increase in atmospheric mercury burden due to man. Unfortunately, as was the case for earlier studies, concentrations assumed for various compartments were erroneously high due to analytical limitations during the 1970's. For example, freshwater total mercury concentrations were assumed to be 60 ng L^{-1}, well above

typical present day values of 0.5 - 5 ng L^{-1}. Thus the conclusions of these, and all global budgets found in the literature, must be re-examined and new global budgets should be constructed.

Although a global budget including fluxes was not within the scope of this study, a preliminary estimate of the global distribution of mercury is shown in Table 6.1. Typical mercury concentrations based on recent analytical techniques were used. Compartment volumes were assigned on the basis of environmentally active depths. Soil and sediment depths of 45 and 10 cm were selected respectively. Table 6.1 (c) indicates that Hg(II) is the major constituent of total mercury in the global biosphere (>90%), and most Hg(II) is in soils and ocean sediments. Methylmercury is estimated to form a small fraction of total mercury in the global biosphere, on the order of a few percent. Soils may also be a major repository for methylmercury, while aquatic biota may contain a smaller but significant quantity (on the order of 20-25% in this estimate).

Table 6.1 (d) indicates that Hg(II) dominates (>90%) in all abiotic compartments except air, where more than 90% of the mercury is elemental. It was assumed that methylmercury dominates in biota. These estimates are preliminary only and a more detailed examination would be worthwhile.

TABLE 6.1
PRELIMINARY ESTIMATE OF
GLOBAL BIOSPHERE MERCURY DISTRIBUTION

	Air	Oceans	Ocean Sed	Ocean Sus Sed (2 ppm)	Fresh Water	Fresh Water Sed	Fresh Water Sus Sed (2 ppm)	Aquatic Biota (1 ppm)	Land Biota	Soils	Total
Area (m2)	5.1E+14	3.6E+14	3.6E+14		2.6E+12	2.6E+12				1.5E+14	-
Depth (m)	6000	3800	0.1		11.5	0.1				0.45	-
Volume (m3)	3.06E+18	1.37E+18	3.61E+13	7.22E+07	2.99E+13	2.60E+11	5.20E+05	1.37E+12	8.30E+11	6.71E+13	-
(a) Mercury Concentrations (ug/m3 wet)											
MeHg	0.00001	0.05	1250	2000	0.07	1000	10000	100000	100000	5000	-
Hg(II)	0.00001	0.5	62500	100000	1.5	87500	300000	20000	20000	150000	-
DiMeHg	0.0001	0.001	0.002	0	0.001	0.002	0	0	0	0.001	-
Elemental Hg	0.002	0.02	0.04	0	0.02	0.04	0	0	0	0.02	-
(b) Mercury mass (tonnes)											
MeHg	30.6	68590	45125	0.1444	2.093	260	0.0052	137180	83000	335250	669437.8
Hg(II)	30.6	685900	2256250	7.22	44.85	22750	0.156	27436	16600	10057500	13066518
DiMeHg	306	1371.8	0.0722	0	0.0299	0.00052	0	0	0	0.06705	1677.969
Elemental Hg	6120	27436	1.444	0	0.598	0.0104	0	0	0	1.341	33559.39
total mass	6487	783298	2301377	7	48	23010	0.16	164616	99600	10392751	13771194
(c) Percent of Global Biosphere Total Mercury											
MeHg	0.0	0.5	0.3	0.0	0.0	0.0	0.0	1.0	0.6	2.4	4.9
Hg(II)	0.0	5.0	16.4	0.0	0.0	0.2	0.0	0.2	0.1	73.0	94.9
DiMeHg	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.01
Elemental Hg	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2
All Hg Forms	0.05	5.69	16.71	0.00	0.00	0.17	0.00	1.20	0.72	75.47	100.00
(d) Within each compartment, percent of compartment's mercury represented by each form											
MeHg	0.5	8.8	2.0	2.0	4.4	1.1	3.2	83.3	83.3	3.2	-
Hg(II)	0.5	87.6	98.0	98.0	94.3	98.9	96.8	16.7	16.7	96.8	-
DiMeHg	4.7	0.2	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	-
Elemental Hg	94.3	3.5	0.0	0.0	1.3	0.0	0.0	0.0	0.0	0.0	-
All Hg Forms	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	-

Note: sediment and soil compartments assumed to have porosity of 50%

6.2 Mercury Fate Models

No comprehensive mechanistic model describing the fate of mercury in the natural environment was found in the literature. A few studies are now underway however to develop mechanistic models which simulate at least some portions of the natural environment.

The Electric Power Research Institute (EPRI) is funding a multidisciplinary project to quantify the behaviour of mercury in remote, lake-watershed-airshed systems and evaluate the mechanisms regulating mercury bioaccumulation (Wisconsin Department of Natural Resources Bureau of Research, 1987). The study is quantifying terrestrial and atmospheric mercury inputs to rural lakes, examining processes affecting in-situ Hg cycling, and developing a freshwater mercury model. Field studies and model development are focussing on Little Rock Lake, a seepage lake in rural Wisconsin.

Brouard et al. (1990) presented results from a preliminary model to predict mercury levels in pike and whitefish in the James Bay reservoirs as a function of decomposition. Total phosphorus was mechanistically predicted in the reservoir and used to estimate mercury levels in fish. Mercury clearance from biota and transfers between prey and predators were also considered. The incremental portion of phosphorus estimated to be due to flooding was assigned a weighting factor. The factor allowed a higher impact on mercury levels in fish to be attributed to the phosphorus component induced by flooding. The University of Sherbrooke, Quebec, in connection with environment impact studies of the James Bay hydroelectric developments, is studying mercury leaching from flooded materials, and mercury

mobilization kinetics and transformations through laboratory experiments. The results will be coupled to an existing dissolved organic carbon model for reservoirs.

The National Swedish Environment Protection Board (SNV) is overseeing a five year effort to study mercury cycling in the environment and options available to reduce unacceptably high mercury levels in fish in many Swedish lakes. The program was completed in 1990 and includes a modelling component regarding mercury concentrations in fish. Related publications are expected in 1991.

BIOMOVS is an international forum for various modelling groups to compare models. This group is primarily concerned with radionuclide modelling, but chose mercury as a substance to test the capabilities of models of varying complexity to predict concentrations of non-radionuclides in the environment. An exercise was carried out using five models, ranging from simple 2 compartment equilibrium models to unsteady state multi-compartment models. Modellers were given site data and asked to predict fish mercury levels for East Fork Poplar Creek, Tennessee, North Fork Holston River, Virginia, and Clay Lake in the Wabigoon River system in Ontario.

The BGA model from Germany was originally intended for assessments of radioactive releases and doses to individuals and collective populations (Swedish National Institute of Radiation Protection, 1990). Total mercury was modelled assuming equilibrium conditions and using partition factors between compartments (eg. fish and water). The CRNL model from Canada is a two compartment (sediment/fish) steady-state model and was used to

simulate total mercury concentrations. Neither model distinguished between predatory or prey fish.

The Japanese JAERI models were deterministic and used bioaccumulation factors to predict total mercury in fish and water. The Swedish STUDSVIK model assumed ratios for methylmercury to total mercury in water, sediments and fish. Prey and predator fish species were considered. The STUDSVIK model was dynamic and used first order differential equations.

The simpler models (BGA and CRNL models) provided equivalent or better predictions than more complex models for East Fork Poplar Creek, which was considered to approximate "equilibrium" conditions. The more complex models (JAERI and STUDSVIK) provided better predictions for more dynamic systems, while the simpler model predictions were not adequate under such circumstances (Swedish National Institute of Radiation Protection, 1990).

Mackay and Paterson (1983) modelled several environmental compartments in order to assess the fate of mercury in the polluted Wabigoon/English River system in Ontario and to predict the effectiveness of a variety of remedial measures. A fugacity approach was used to develop an unsteady state model for a series of interconnected systems along the length of the river system. The model examined air, water, sediment, suspended sediment and fish. Total mercury was modelled rather than specific forms. Despite the above efforts, there remains a a need for a mechanistic mercury model in freshwater systems with adequate predictive

capability and flexibility to address a range of scenarios. All modelling efforts to-date have noted a lack of rate constants for important processes such as methylation and demethylation.

6.3 Mercury Kinetic Uptake/Clearance Models

Models describing mercury uptake in fish began to appear in the early 1970's in Scandinavia (Fagerstrom and Asell, 1973; Fagerstrom et al., 1974). A bioenergetics approach was used to consider the exposure of individual fish in terms of mercury in the diet and contact with mercury in water at the gill surface. Exposure was related to rates of food and oxygen consumption, which were in turn related to the size of the fish and growth rates. Clearance was assumed to be a function of fish's body weight and mercury burden. Fish were treated in their entirety rather than attempting to address particular organs or tissues. A significant benefit of this approach is that it allows a comparison of uptake via the diet and across the gills.

Norstrom et al. (1976) built upon previous Scandinavian efforts and provided a good outline of the principles using bioenergetics to predict concentrations of pollutants in fish. It was assumed that mercury clearance was a function of body weight to the power -0.58, but not a direct function of metabolic rate. This clearance constant meant that depuration per unit mass of fish was less effective in older, heavier fish. Mercury intake through food and water was related to metabolic rate. Based on calculations for yellow perch, it was concluded that water based and food based mercury uptake were comparable in magnitude.

Jensen (1988) applied the concepts used by Norstrom et al. (1976) to examine the effect of acidity on mercury uptake by individual walleye. Data for walleye in circumneutral and acidic Wisconsin Lakes indicated higher walleye mercury levels in acid conditions. Jensen used the Norstrom equations to study the potential for increased mercury, in terms of 5 possible mechanisms: (i) increased uptake efficiency from food or water, (ii) increased methylmercury concentrations in water, (iii) increased methylmercury concentrations in food, (iv) different clearance coefficients, and (v) different growth rates, as affected by the pH. He concluded that an increase in the mercury concentration in water and an increase in the uptake efficiency in water were important. However, this study, as well as Norstrom's, used water concentrations which now appear too high for typical conditions (eg. 4 ng L^{-1} methylmercury). There is a need (addressed later in this study) to re-examine uptake pathways in view of recently reduced estimates of methylmercury in water (eg. 0.05 ng L^{-1}).

The above studies treat mercury accumulation in individual fish. In a larger scale fate model, the bioenergetics approach outlined in this article would need to be adapted to accomodate a spectrum of fish sizes representing an entire population of fish. Such an approach was used in this study, and is discussed in later sections of the report.

6.4 Mercury Methylation Models

A model for net Hg methylation by cell-free extracts was developed in the early 1970's by Wood and DeSimone (Bisogni, 1979) and took the following form:

Methylation rate = rate constant * [methylcobalamin] * [Hg^{++}]

Bisogni (1979) developed a model which assumed that net methylation was a function of available inorganic Hg and either the concentration or production rate of methylcorrinoids, enzymes or metabolic products involved in the methylation process. It was also assumed that at steady state the concentration of methylcorrinoids, enzymes and metabolic products would be constant and a function of the metabolic activity of the organism. Thus at a given growth rate the concentration of methylcorrinoids and enzymes should have particular values. These assumptions were reflected in the model equation:

$$NSMR = Gamma * (Beta * [Hg_{total}])^{n}$$

Where:

NSMR = net specific methylation rate (ug MeHg g VSS^{-1} day^{-1})

Gamma = coefficient based on microbial growth rate

$[Hg_{total}]$ = concentration of total Hg

n = pseudo-order of reaction

VSS = concentration of volatile suspended solids (measure of biomass)

Beta = ratio of free Hg^{++} ions to total Hg

Gamma was assumed to vary linearly with the microbial growth rate. The model was compared to experimental data and found to be reasonable in most cases, although discrepancies did occur in some situations. The order of the reaction (n) ranged from 0.13 -

0.17 in aerobic systems, and 0.25 - 0.32 in anaerobic systems. These reaction orders suggest a decreasing influence of additional mercury at higher mercury concentrations. Monod expressions can also be used to generate such relationships, and were used in the present study. The concentrations of mercury added experimentally were not provided.

The review of mercury modelling studies above confirmed that no comprehensive model exists yet which simulates mercury cycling in aquatic systems. Several sub-models have been undertaken however (e.g. mercury uptake by fish), and the approaches used in these sub-models could in many cases be adapted for use in a more holistic model. With recent analytical improvements, mercury modelling efforts are intensifying internationally. Over the next few years, several models will likely emerge to study mercury in the environment, each model having its own emphasis and intended use (e.g. atmospheric models, lake models, reservoir models). The diagnostic model developed in this study is intended to meet a need not yet met elsewhere: provide a framework to better quantify and understand mercury cycling in aquatic systems. Other such models will undoubtedly appear in the next few years and comparisons of such models would be very useful in the evolution of improved models.

7.0 MODEL DEVELOPMENT

In this chapter, the purpose of the model is described in Section 7.1. An outline of the model and its basic principles are presented in Section 7.2. Mathematical representations of specific processes are discussed in Sections 7.3 through 7.7.

7.1 Model Purpose

Elevated fish mercury levels in have been observed in recent years around the world in reservoirs, industrially polluted systems, and even remote lakes with no local anthropogenic activity. There is a strong incentive to understand mercury cycling in aquatic systems in order to develop insights regarding the causes of elevated fish mercury levels in existing systems and possible remedial actions. One tool to help develop insights into mercury cycling is a comprehensive mechanistic model regarding the fate of mercury in abiotic and biotic compartments in freshwater systems. Although previous mercury models have been constructed at scales ranging from global perspectives to uptake by individual fish, there remains a need for a comprehensive model of aquatic systems.

Despite recent improvements in analytical methods, several gaps still exist in the understanding of mercury cycling. For example, it is not yet possible to measure actual methylation and demethylation rates in the field on an absolute basis, nor does a clear

understanding exist of the effects on methylation of variables such as pH or humic acid concentrations. The version of the model used in this study is therefore intended to assemble and test hypotheses regarding the influence of various physical, chemical, and biological factors on the fate of mercury in aquatic systems. The results of this study are also intended to provide direction regarding necessary research towards a predictive modelling capability.

7.2 Basic Approach and Model Outline

A mass balance, multi-compartment, multi-species, unsteady state mercury model for freshwater systems was developed (see Figures 7.1 and 7.2). An unsteady state approach was used to examine temporal trends, particularly in reservoirs and industrially polluted systems. Although the model time step can be selected to examine short term trends (a time step of one day was typically used), the primary intent in this study was to examine trends on a larger time scale (e.g. years). Seasonal dynamics such as temperature and suspended solids variations were combined into mean annual values.

Mercury Forms in the Model

It was concluded that a mechanistic model concerned with fish concentrations would be overly simplified if it considered only total mercury. Many mercury species exist in aquatic systems. Various conversions between these species take place in water and sediments, and each compound has unique physical and chemical properties. For

FIGURE 7.1
Mercury Model
In Freshwater Systems

- UNSTEADY STATE

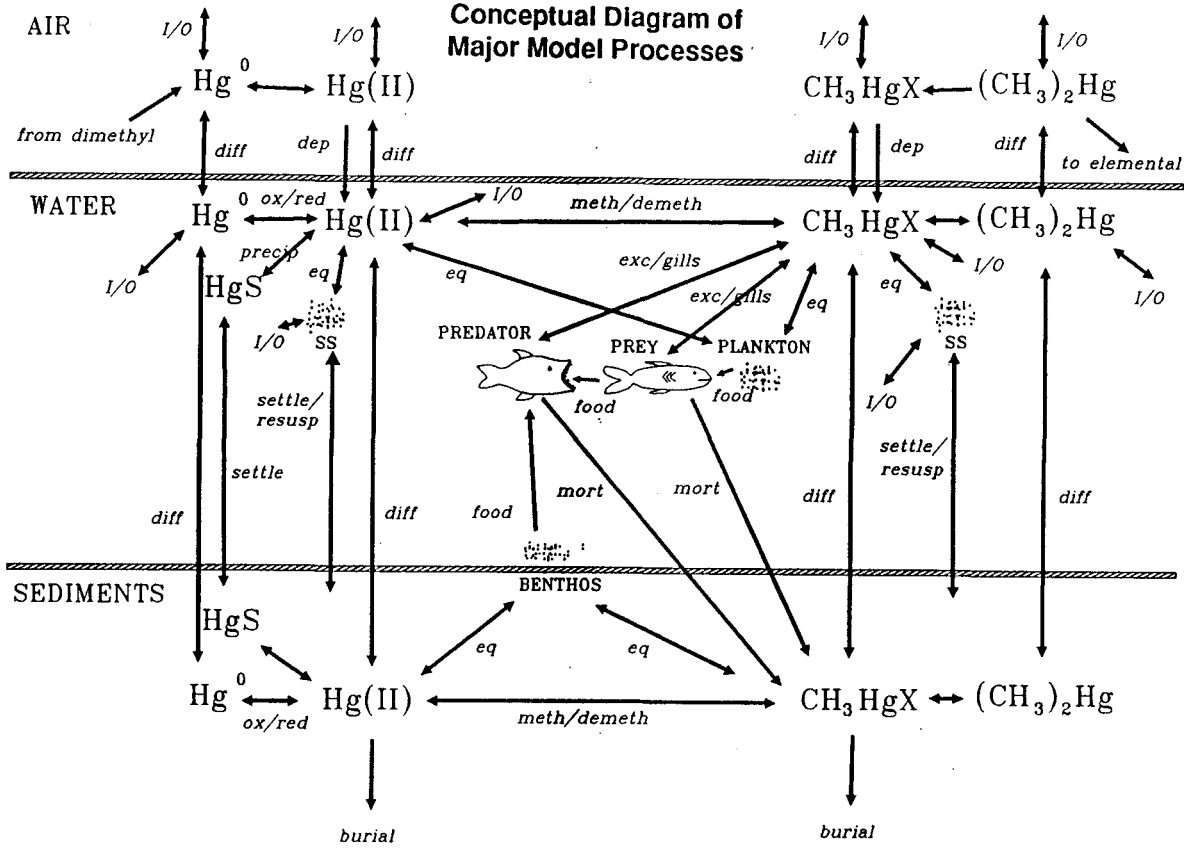
- ENVIRONMENTAL COMPARTMENTS:

1) AIR
2) WATER
3) SUSPENDED SOLIDS:
   - 3a) EXCHANGEABLE
   - 3b) FIXED
4) SEDIMENT:
   - 4a) POREWATER
   - 4b) EXCHANGEABLE SOLIDS
   - 4c) FIXED SOLIDS
5) WATER COLUMN PLANKTON
6) BENTHOS
7) PREY FISH
8) PREDATORY FISH

- Hg FORMS:

1) MONOMETHYL Hg
2) Hg(II)
3) DIMETHYL Hg
4) ELEMENTAL Hg
5) Solid HgS

FIGURE 7.2
Conceptual Diagram of Major Model Processes



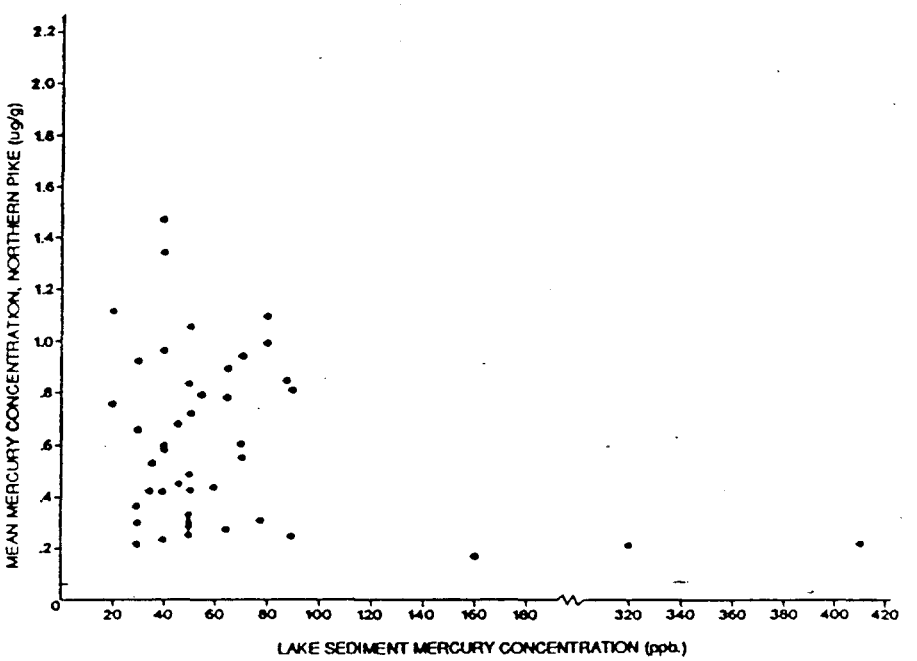
LEGEND

Diff -	Diffusion	precip -	Precipitation	mort -	Mortality
I/O -	Input/Output	meth/demeth -	Methylation/Demethylation	SS -	Suspended Solids
dep -	Deposition	exc/gills -	Excretion/Gills	settle/ resusp -	Settling/ Resuspension
ox/red -	Oxidation/Reduction	eq -	Equilibrium		

example, $HgCl_2$ has a solubilility about 6 orders of magnitude higher than Hg° in water, and a Henry's law constant about 7 orders of magnitude lower than Hg°. Thus to consider processes such as wet deposition and volatilization, one would have to consider the fraction of total mercury in air, water and rain, which are represented by Hg(II) and Hg° (e.g. assume 5% of total mercury is volatile and use the Henry's Law constant for elemental mercury). If these fractions were essentially constant over a range of environmental conditions, then a total mercury approach might function satisfactorily to predict total mercury in water or sediments. Insufficient data exist at this time however regarding mercury speciation in a range of environmental conditions to assess the credibility of such an approach.

A further complication arises if only total mercury is considered. Ratios of fish mercury concentrations to total mercury concentrations in water or sediment can be quite variable between aquatic systems, and are unreliable as a predictive tool for fish mercury content. For example, Verta et al. (1986a) reported that total mercury concentrations in fish and sediment did not correlate significantly in a study of 93 Finnish lakes. Rannie and Punter (1987) studied lakes in the region of the Churchill River Diversion and concluded that lake sediment concentrations, by themselves, provided little indication of fish mercury levels. Some regions with greatly elevated total mercury concentrations in sediment due to mine tailings had low fish mercury levels, while reservoirs with sediments at or very slightly above background concentrations, contained fish with significantly elevated fish levels (see Figure 7.3). East Fork Poplar Creek in Tennessee is polluted with mercury which was used for production of nuclear weapons. Water concentrations of total mercury in this system are on

FIGURE 7.3
Mean Mercury Concentrations in Northern Pike Versus Lake Sediment in the Region of the Churchill River Diversion, Manitoba



(Source: Rannie and Punter,1987)

the order of 1000 ug m^{-3} in the creek (Elwood et al., 1987), i.e. above levels in unpolluted waters by a factor of about 1000. Mercury concentrations in the stream in Redbreast Sunfish are not above background levels by similar amounts however, being in the range of 0.5 - 2.0 ug g^{-1} wet weight (Swedish National Institute of Radiation Protection, 1990). These examples and others indicate that total mercury is not necessarily a reliable predictor of fish mercury levels.

Rather than use basic partitioning between total mercury in fish and sediments, Coquery and Stokes (1989) examined the merits of normalizing sediment mercury content to organic matter content in the sediment. Eight sites in Bentshoe Lake, a remote softwater lake in Ontario were studied, with organic matter in sediments ranging from 1.5% - 50%. Mercury in sediment was highly correlated with organic matter ($r=0.943$; $P<0.001$). Mercury content in the roots of an aquatic macrophyte *Eriocaulon septangulare* only correlated weakly however with mercury content in these sediments, even when the sediment mercury content was adjusted for organic content. These results support the concept that total mercury concentrations alone or sediment mercury concentrations adjusted for organic carbon content, are not necessarily representative of mercury available for uptake in the food chain.

In lieu of an extensive dataset examining ratios of fish mercury to total mercury in water, it is assumed that such ratios would not serve well for modelling purposes. It is also assumed that using kinetic rates of fish uptake and excretion of *total* mercury rather than simple partitioning into fish would not result in adequate predictions.

An assessment of the fraction of total mercury available for uptake and retention by fish was a necessary addition to the model. Most mercury in fish is in the form of methylmercury (e.g. 95- 99%). An assessment of available methylmercury in water and food for fish was considered a logical refinement to the model. If the ratios of methylmercury to total mercury in water and in sediment were relatively constant in a variety of environments, one could use an empirical fraction of total mercury to represent methylmercury. Although such ratios may be relatively constant for given conditions in a given system (e.g. Parks et al., 1989), a wide range of ratios may exist between different aquatic systems. Methylmercury is often in the range of 1-10% of total mercury in water and on the order of 1-5% of total mercury in sediment in unpolluted systems, however wide ranges of ratios exist. Bloom and Watras (1989a) reported methylmercury in the range of 40% of total mercury in water in the anoxic hypolimnion of Little Rock Lake in Wisconsin, while data from the polluted East Fork Poplar Creek in Tennessee indicate very low ratios of methylmercury to total mercury in water (e.g. 0.03%, approximate value based on graph, Elwood et al., 1987). It was therefore assumed that representing methylmercury as an empirical fraction of total mercury would not provide suitable system to system predictive flexibility.

Based on the above factors, the model was refined to consider cycling of monomethyl mercury, Hg(II), dimethyl mercury, elemental mercury and solid phase HgS. Hg(II) is dominant in water and sediment, methylmercury is the main form in fish, and elemental mercury is the primary atmospheric species. Dimethyl mercury may be important as a mercury flux pathway despite low concentrations in the environment. Solid HgS may be significant in anaerobic environments by limiting the bioavailibility of mercury.

Environmental Compartments in Model

For this study, environmental compartments within and external to the aquatic system were included. Conditions outside the aquatic system, i.e. terrestrial and atmospheric conditions, were treated as boundary conditions which could change with time, but were effectively unaltered by conditions within the aquatic system. This was done to maintain a reasonable scope of study. Groundwater interactions were not considered since the focus was on lakes and reservoirs whose mercury inputs are controlled by surface water inputs and/or atmospheric inputs.

Four biotic compartments were incorporated within the model: benthos, plankton, prey fish and predatory fish. This allowed an examination of biomagnification and the influence of changing diets. "Plankton" represented phytoplankton and zooplankton, and were assumed to the be the sole diet for prey species. Benthos represented a mix of bottom based organisms (zoobenthos, macro invertebrates, crustaceans, etc.) serving as a portion or all of the diet for predatory species, which could also eat prey fish.

Abiotic compartments within the aquatic system included water, suspended sediment, sediment porewater and sediment solids. It was assumed that particulate mercury on suspended solids and sediment solids could be represented by an irreversibly fixed component and a reversibly exchangeable fraction which is in equilibrium with the dissolved species according to a partitioning coefficient (discussed later in this section). The same approach was used for particulate methylmercury, although no analogous experiments were found in the

literature to directly support this assumption.

Suspended solids, sediment solids, air particulates and biota were assumed to contain only methylmercury and Hg(II). Plankton were assumed to typically contain 50% methylmercury and 50% Hg(II). Benthos were assumed to be 25-75% methylmercury and 25-75% Hg(II). Water, porewater and air contained Hg(II), methylmercury, dimethyl mercury and elemental mercury. Solid HgS could occur in water and sediments in the presence of sufficient sulphide and Hg^{++}. All of the mercury in plankton and benthos was assumed to be exchangeable.

Overview of Processes in the Model

The model simulated inflows and outflows involving air, water and suspended solids, sediment burial, suspended solids settling, volatilization, atmospheric deposition, methylation and demethylation in the water column and sediments, and industrial point sources. In addition to these mass transport and kinetic processes, thermodynamic concepts were utilized. In the water column, Hg^{++} was distributed on the basis of soluble complexation, adsorption/desorption between water and an exchangeable fraction of suspended solids binding sites, and plankton (which were treated as solids with a partition coefficient). These compartments were assumed to be in instantaneous equilibrium. In sediments, equilibrium partitioning of Hg^{++} was assumed to occur between porewater, an exchangeable fraction of binding sites on sediment solids, and benthos, which were also treated as solids with a partition coefficient as a first approximation. Methylmercury adsorption and complexation was

treated in the same manner as Hg(II).

The above equilibrium concepts were used to calculate concentrations of available Hg(II) and methylmercury for methylation and demethylation in the water column and in porewater. It was assumed that thermodynamic equilibrium applied to 9 dissolved Hg(II) complexes (and solid phase HgS if applicable), and to 5 dissolved methylmercury complexes. Sulphide or humic mercury complexes (and solid HgS) were considered, and assumed to be unavailable for biological transformations. The assumption that humic complexes with mercury were unavailable for transformations was primarily based on Farrel et al. (in press), who reported that additions of cysteine, an amino acid, resulted in less methylation despite increased microbial activity, implying cysteine/Hg(II) complexes may not be bioavailable for methylation.

It was assumed that chemical or biological kinetics control the formation and degradation of elemental Hg in natural aquatic systems, rather than thermodynamic equilibrium with other inorganic species (see Section 2.2 for discussion). Thus Hg(II), methylmercury, dimethylmercury and elemental mercury were not in thermodynamic equilibrium with each other.

Bioenergetics approaches traditionally used for chemical uptake (through food and gills) and excretion by individual fish were extended to year classes based on estimated numbers of fish within each year class. This approach to mercury content in fish was used rather than a simpler fish/water or fish/sediment equilibrium partitioning approach to allow an

examination of the temporal response to environmental changes such as reservoir creation, and to allow estimates of fluxes between fish populations and their surrounding environment.

The remainder of Section 7 provides more detail regarding the approach used to model specific processes.

7.3 Assumed Equilibria

7.3.1 Inorganic Hg Speciation in Surface Waters, Suspended Solids and Plankton

It was assumed that 9 soluble Hg(II) complexes and solid HgS (under specific anaerobic conditions only) were in thermodynamic equilibrium with the Hg^{++} ion in fresh water (see Table 7.1). Further information regarding complexation constants, solubility products, and references is provided in Appendix A.

Water column plankton and an exchangeable fraction of suspended solids were also assumed to be in instantaneous equilibrium with Hg^{++} in solution (see Figure 7.4). Appendix B outlines the derivation of the equations used in the model to calculate concentrations of individual Hg(II) species in surface waters, suspended solids and plankton. The assumption that plankton are in equilibrium with the water column is based on studies by Ramsey and Ramlal (1986a, 1986b) in which no significant variation in total mercury concentrations was observed for net plankton samples ranging from 53 to 150 μm net size.

TABLE 7.1

Hg(II) Complexes in Surface Waters

Hg(II) soluble complexes:

1) $HgCl_2$

2) HgCl+

3) HgOHCl

4) $Hg(OH)_2$

5) $HgHS_2^-$

6) $Hg(HS)_2$

7) HgS_2^{--}

8) HgS (soluble)

9) Hg/humic soluble complexes

Mercuric sulphide (solid):

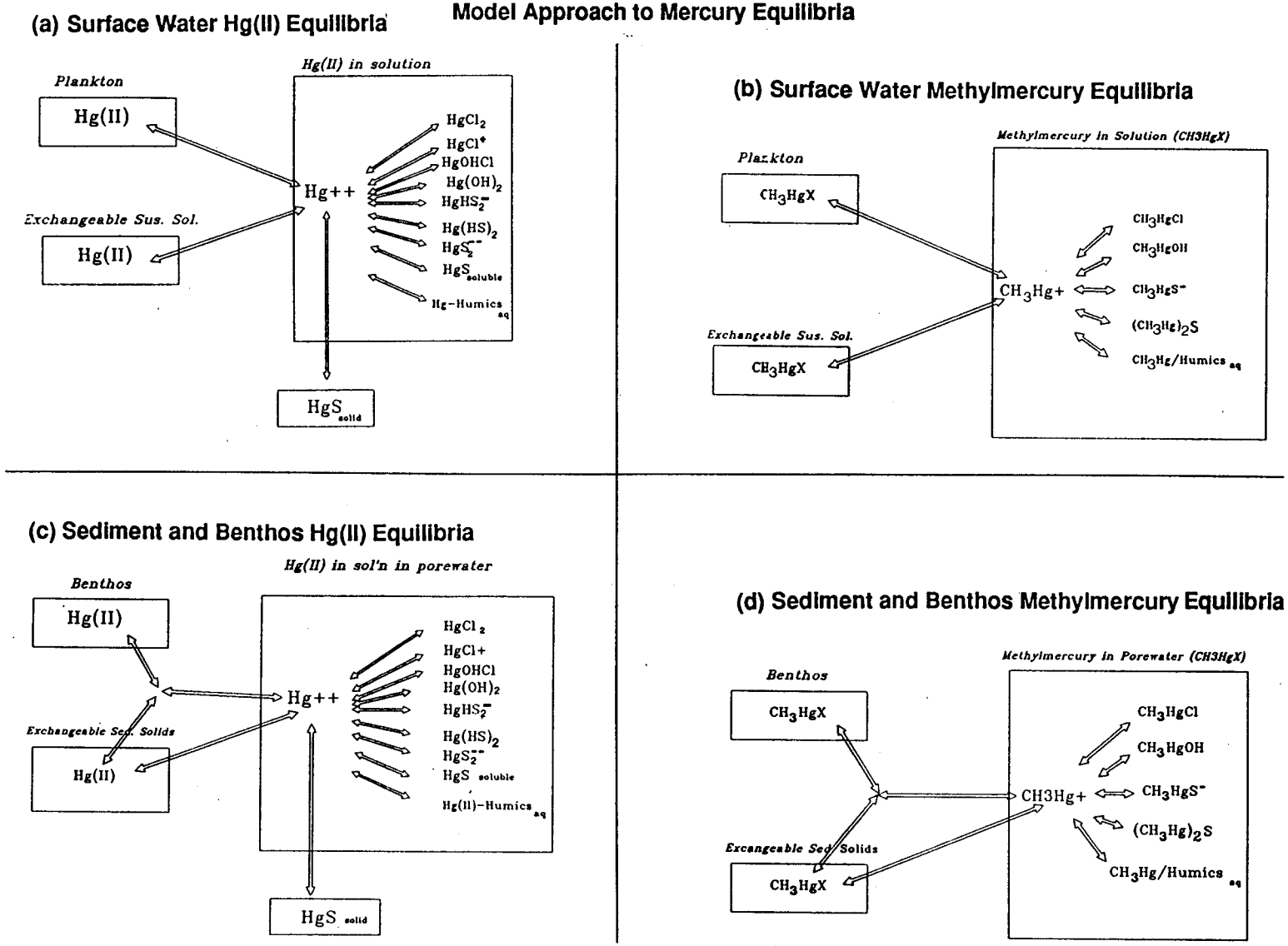
10) HgS

Water may be more important than food as an intake pathway for mercury in zooplankton, due perhaps to a greater surface area to volume ratio than is found in larger organisms such as fish.

Complexation equations for complexes 1 through 8 in Table 7.1 can all be represented with conventional complexation constants. Unfortunately the humic/Hg^{++} complexation constant will vary according to the nature of the humic matter involved, since humics in fact represent a mix of substances with a range of molecular weights. The situation is further complicated by the tendency of high molecular weight humic matter to act in a colloidal fashion, making practical determinations of complexation constants for "soluble" humics subject to operational definitions (e.g. 0.45 μm filtering or centrifugation). To account for the fact that humic substances exist in soluble, colloidal and particulate forms, this model segregates humic matter into two groups: particulate humics which would form part of the suspended solids mass, and soluble humics. Suspended solids partition coefficients incorporate the bonding strength of particulate humics. Complexation constants are used to determine mercury partitioning into soluble humics.

Soluble humics may be important complexing agents for Hg(II), based on positive correlations between mercury concentrations and humic content of natural waters (see Section 5.4.2.1). Based on the affinity of Hg(II) for sulphydryl groups, and studies of methylmercury complexation by Zepp et al. (1974) which concluded that thiol groups were the important methylmercury complexing agent in soluble organics, thiol groups were also assumed to be the dominant complexing agent for Hg(II) in soluble humics. A 1:1 complexation constant of

FIGURE 7.4
Model Approach to Mercury Equilibria



$10^{22.1}$ (Dyrssen and Wedborg, in press) was used for Hg(II) complexes with RS^- (see Appendix A).

The possibility of 1:2 Hg^{++}/RS^- complexation has been discussed by Dyrssen and Wedborg (in press), who estimated a complexation constant of $10^{41.6}$. If RS^- ions were as readily available for 1:2 Hg^{++}/RS^- complexation as for 1:1 complexation, the 1:2 complexes would dominate 1:1 complexes for the levels of RS^- above $10^{-19.5}$ M. For RS^- activities assumed in this study (e.g. 10^{-11} to 10^{-12} M), 1:2 RS^-/Hg^{++} complexes would exceed the 1:1 complexes by many orders of magnitude. It is possible however that the nature of 1:2 Hg^{++} complexes results in a considerably lower probability of two RS^- ions bonding with Hg^{++} than 1:1 bonds. It is feasible that RS^- groups could often be constrained within large molecules. It may be more difficult for two RS^- groups to interact with a single Hg^{++} ion than for a 1:1 interaction. Given this uncertainty, only the 1:1 complexation constant for RS^- was used. This approach is consistent with the objectives of the present study to examine trends. Further examinination of DOC/Hg(II) complexation is recommended to better quantify the effects of DOC complexation on Hg(II) cycling, particularly with regards to bioavailability for methylation.

Sulphide may also be important regarding Hg(II) speciation. It can form a precipitate (HgS) and forms soluble complexes, for example soluble HgS, $HgHS_2^-$, $Hg(HS)_2$ or HgS_2^{--}. These complexes were therefore also included in the model.

In addition to a thermodynamic treatment of soluble mercury complexes, a framework was required to estimate partitioning between Hg(II) on solids and Hg^{++} in solution. An approach to solids partitioning which is often applied to organic chemicals is the use of octanol/water partition coefficients. Southwood et al. (1989) used a relationship where the solids/water partition coefficient was estimated on the basis of an experimentally determined octanol/water partition coefficient as follows:

$$K_p = K_{oc} * phi$$

$$= (0.411 * K_{ow}) * phi$$

where: K_p = solids/water partition coefficient (L/Kg)

K_{oc} = organic carbon partition coefficient (L/Kg)

K_{ow} = octanol/water partition coefficient (L/Kg)

phi = organic carbon fraction of solids

Results of several experiments indicate however that Hg(II) and methylmercury do not show any particular tendency to partition into octanol rather than water. Octanol/water partition coefficients for methylmercury are reported in the range of 2.0 - 2.5 (actual values, not logs) (Halbach, 1985; Lakowicz and Anderson, 1980; Medeiros et al., 1980), while the value for $HgCl_2$ is less than 1.0 (Halbach, 1985). Since field measurements suggest Hg(II) and methylmercury concentrations on sediment solids are orders of magnitude above water concentrations, the above experimental data indicate octanol/water partitioning is not a suitable

measure of the patitioning behaviour of Hg(II) or methylmercury. In lieu of a better available approach at present, partition coefficients were therefore based on field measurements of concentrations in water (porewater if possible) and solids.

To allow for the effects of pH on dissolved complexation constants, protonation constants were used. Protonation of adsorption sites could be addressed in the model through the adjustment of partition coefficients.

7.3.2 Methylmercury Speciation in Surface Waters, Suspended Solids and Plankton

Based on data presented by Zepp et al. (1974), five soluble methylmercury complexes were considered in fresh waters, in addition to the free CH_3Hg^+ ion (see Table 7.2). Chloride and hydroxide complexes with methylmercury were considered, as were three sulphur containing complexes (2 sulphide complexes and the thiol component of humic substances). Zepp et al. (1974) concluded that sulphur was an important MeHg complexing agent. A detailed description of the complexation constants, solubility products and references relevant to methylmercury is shown in Appendix C.

Suspended solids and water column plankton were also assumed to be in equilibrium with water column CH_3Hg^+ (see Figure 7.4). An approach analagous to that outlined for Hg(II) in Appendix B was used to estimate activities of individual methylmercury species in surface waters, and methylmercury concentrations in suspended solids and plankton. The

TABLE 7.2

Methylmercury Complexes in Surface Waters

Methylmercury soluble complexes (in addition to free CH_3Hg^+ ions):

1) CH_3HgCl	Methylmercuric Chloride
2) CH_3HgOH	Methylmercuric Hydroxide
3) CH_3HgS^-	Methylmercuric sulphide
4) $(CH_3Hg)_2S$	Dimethylmercuric sulphide
5) CH_3HgRS	Methylmercury/organic thiol complexes (humics)

Methylmercury Solid Phase complexes:

MeHgOH : Not significant for methylmercury concentrations typical of fresh waters.

assumption that plankton can be considered essentially as solids with a partition coefficient for methylmercury is based on data reported by Ramsey and Ramlal (1986a, 1986b) suggesting that no significant variation in total mercury concentrations was observed for net plankton samples of various mesh sizes (see similar assumption for Hg(II)). Since methylmercury is a significant fraction (e.g. 50%) of total mercury in plankton, these results suggest that methylmercury may effectively equilibrate with water rather than be controlled by metabolic factors.

Complexation of complexes 1 through 4 in Table 7.2 can all be represented with conventional equilibria for specific reagents. However, as is the case for Hg(II), constants for methylmercury complexation with humic substances will vary depending on the nature of the humic matter. In this study, thiol groups are assumed to be the important methylmercury complexation sites in soluble humics. Zepp et al. (1974) indicated that the phenolic component of humics was relatively unimportant when compared to the thiol component, in terms of complexing methylmercury. For this study, a fraction of the humic substances was assumed to be thiol groups (e.g. 0.0001 * 10^{-5} M total humics = 10^{-9} M thiols). Dyrssen and Wedborg (in press) reported a CH_3Hg^+/RS^- complexation constant of $10^{16.12}$, which was adopted for this study.

7.3.3 Hg(II) and Methylmercury Speciation in Porewater, Sediment Solids and Benthos

Porewater Hg(II) and methylmercury were assumed to contain the same individual species and follow the same thermodynamic criteria as in surface waters. Porewater Hg^{++} was in equilibrium with Hg(II) in an exchangeable fraction of sediment solids. Benthos Hg(II) was assumed to be in equilibrium with all exchangeable Hg^{++} in sediments (i.e. porewater and exchangeable sediment solids (see Figure 7.4). The same model structure was used for CH_3Hg^+ (see Figure 7.4). Appendix B outlines the equations used in the computer program to calculate activities of Hg(II) and methylmercury species in porewaters, and Hg(II) and methylmercury concentrations in exchangeable sediment solids and benthos.

Mercury exchange between benthos and solids was intended to accomodate the potential for mercury uptake through ingestion of solid particles during feeding. The degree to which the digestive process liberates Hg(II) and methylmercury from solids would be a valuable subject of research. It was assumed in this study that benthos reach a rapid pseudo-equilibrium with Hg^{++} and CH_3Hg^+ in the surrounding environment.

7.3.4 Exchangeable and Fixed Mercury on Solids

As discussed previously, suspended solids and sediment solids were assumed to have two types of sorption sites for Hg(II) and methylmercury: fixed and exchangeable. This

assumption was based on experiments carried out by Rogers et al. (1981) suggested that Hg(II) adsorption onto solids is very fast, while desorption tends to exhibit two distinct phases, one fast and one very slow. Desorption half-lives were on the order of 5 to 25 years, meaning that some desorption may be slow enough to be considered irreversible as a first approximation.

Although Hg(II) partitioning between solids and water is typically on the order of 10^4 to 10^5 L kg^{-1}, Ramlal et al. (1987) reported considerably lower partitioning coefficients of 345 L kg^{-1} (13:1 water to solids ratio in sample) and 145 L kg^{-1} (25:1 water to solids ratio in sample) in terms of added radio-labelled mercury in sediment samples. This could indicate that the ^{203}Hg additions saturated binding sites. However, Rogers et al. (1981) reported Hg(II) sorption maxima from 17,000 - 24,000 ug g^{-1} sediment, well above the concentrations used for the radio-labelled methylation technique. The lower partition constants observed by Ramlal et al. (1987) could also be explained if only a fraction (e.g. 0.1 - 1 percent) of the mercury in solids were exchangeable. For preliminary purposes, it is assumed that saturation of binding sites does not occur when using radio-labelled techniques for methylation in sediments, and that a small fraction of Hg(II) bound to sediment solids is readily exchangeable.

The mathematical treatment of fixed mercury in the model was relatively simplistic. A mass balance for fixed mercury was calculated for the water column and sediments in a manner analagous to a mass balance for overall solids, i.e. involving inflow, settling, resuspension and burial. As a result, at steady state the concentration of fixed mercury in suspended solids and sediment solids would equal the inflowing concentration of fixed mercury on suspended solids. There were no fluxes of mercury simulated between fixed and

exchangeable compartments. As will be discussed in later sections, this approach was probably overly simplistic and led to some unforeseen problems. Future versions of the model will be modified to provide better realism in terms of "fixed" mercury cycling. It is quite possible, for example, that mercury could be taken up from water by plankton and subsequently "fixed". Settling of dead plankton could then transfer a significant amount of fixed mercury to sediments.

7.4 Mass Transfer Processes Crossing System Boundaries:

7.4.1 Inflows and Outflows

To maintain a manageable scope of study, concentrations in the air compartment were maintained at a steady state. This was done by ensuring that atmospheric inflows and outflows of mercury were far larger than mercury fluxes across the air/water interface. Large advective inflows and outflows for the air compartment were specified as input conditions.

In the water column, all five mercury forms simulated could be loaded to the waterbody in inflows and exported in outflows. Inflows and outflows included dissolved and particulate mercury components. A suspended solids budget was applied to the waterbody, based on inflows, outflows, settling and resuspension.

7.4.2 Burial

Burial of Hg(II) and methylmercury was included, as was burial of solid HgS if sufficiently anaerobic conditions existed. Elemental mercury and dimethyl mercury were assumed not to exist in the solid sediment phase, and porewater burial of these species was considered insignificant relative to volatilization. Sediment burial rates are variable in nature and depend on several factors including suspended solids concentrations, sediment porosity, settling velocities of suspended solids and resuspension rates. Mass balances of solids were used between the water column and sediments to determine burial velocities. Settling and resuspension velocities were set to levels which resulted in net deposition rather than erosion (e.g. resuspension might be 20-80% of deposition). Once the net loading of solids to sediments was established, a burial rate could be calculated for a given sediment porosity, using a mass balance for solids. Sediment porosity was allowed to vary between the top and bottom of the sediment compartment to allow for compaction with depth.

7.4.3 Point Sources

To examine effects of industrial point sources, any of the five mercury forms considered in this model could be loaded into the water column continuously or as a step function which could be turned on and off at set times.

7.5 Mass Transport Processes within the Model System Boundaries

7.5.1 Diffusion

It was assumed that all soluble mercury forms could diffuse between sediment porewater and overlying water. Fick's law was applied to single phase diffusion as described below:

$$Diffusion_{(wat)} = Area * MTC_o * (C_{pw} - C_{wat})$$

where:

$Diffusion_{(wat)}$ = mercury flux between water column and porewater (ug Hg day^{-1})

Area = sediment/water interface area (m^2)

MTC_o = overall mass transfer coefficient between water/porewater (m day^{-1})

= $\{(MTC_{wat})^{-1} + (MTC_{wat})^{-4/3}\}^{-1}$

MTC_{wat} = Mass transfer coefficient for water phase

C_{pw} = Hg concentration in porewater (ug m^{-3})

C_{wat} = Hg concentration in water column (ug m^{-3})

Values for MTC_{wat} in the literature are quite variable. O'Connor et al. (1987) discussed variations in diffusivity as a function of molecular weight to the power -0.67, i.e. larger

molecules have lower diffusivities. Assuming the molecular weights of elemental mercury and Hg(II) and methylmercury compounds in solution are in the range of 200 to 1500, the diffusivities would range from about 10^{-6} to 10^{-5} cm^2 s^{-1}, with corresponding water phase mass transfer velocities being on the order of 0.04 to 0.2 m day^{-1} and overall water/porewater values of MTC_o ranging from 0.01 to 0.08 m day^{-1}. Mackay (1989) assumed a sediment exchange coefficient of 0.01 m day^{-1} for a fugacity analysis of PCBs in Lake Ontario. This value was selected in this study to represent MTC_o between porewater and the water column in simulations of a "generic shield lake". Further discussion and definition of the generic shield lake used in simulations is provided in Section 8.

7.5.2 Volatilization

Volatilization was calculated using two-phase film resistance theory. The approach uses a piston velocity based on resistance in air and water, and the deviation of the air/water concentration ratio from equilibrium partitioning, to estimate the air/water flux:

$$Volat_{(wat)} = Area * k_o * [(C_{air} * (H)^{-1}) - C_{wat)}]$$

where:

$Volat_{(wat)}$	=	mercury flux to water from air (ug Hg day^{-1})
Area	=	air/water interface area (m^2)
k_o	=	overall piston velocity (m day^{-1})
	=	$\{(MTC_{wat})^{-1} + (MTC_{air}*H)^{-1}\}^{-1}$

C_{air}	=	Hg concentration in air (ug m^{-3})
C_{wat}	=	Hg concentration in water (ug m^{-3})
H	=	Henry's Law constant (dimensionless)

Since most simulations covered time spans on the order of years, the fraction of the year during which ice cover existed needed to be addressed. Seasonal variations in elemental mercury concentrations in water could occur due to accumulation under ice, followed by a springtime increase in volatilization. For the purposes of this study however, annual fluxes to the atmosphere were assumed not to be significantly affected by ice. This assumption should be addressed in future studies, since ice cover of 5 months or more is common in central and northern regions in Canada.

Significant uncertainty remains regarding air/water exchange of Hg(II) and methylmercury. Specific Henry's Law constants have been reported in the literature for inorganic compounds such and $HgCl_2$ and CH_3HgCl. Organic complexes of Hg(II) and methylmercury probably dominate in aerated freshwaters however, and could have quite different Henry's Law constants, vapour pressures and/or solubilities in water. Although the model has the capability to consider volatilization for elemental mercury, dimethyl mercury, Hg(II) and methylmercury, the latter two mercury forms were assumed to have negligible air/water diffusive exchange. The values for mass transfer coefficients in water near the surface may be higher than the value of MTC_{wat} at the sediment water interface, due to increased surface mixing. Halfon et al. (1990) used the following formulation to estimate the water side mass transfer coefficient for calculations of volatilization of several organics from

Lake St. Clair:

$$MTC_{wat} = k_{O2} * (32/MW)^{0.5} / 1.024^{(20-T)}$$

where:

k_{O2} = mass transfer coefficient for oxygen (m hr^{-1}), based on the wind speed (u) at 10 m over the water surface

= $1.51 * 10^{-2} * u^{0.5}$ for $u < 5.5$ m s^{-1}

= $1.15 * 10^{-3} * u^{2}$ for $u > 5.5$ m s^{-1}

MW = molecular weight (32 for oxygen)

T = Temperature (Celsius)

Using this approach MTC_{wat} at the water surface was estimated to be in the range of 0.25 to 0.5 m day^{-1} for a generic shield lake. An air phase mass transfer coefficient of 100 m day^{-1} was estimated for Hg° and dimethyl mercury. Thus the overall piston velocity between water and air was calculated to be approximately 0.5 m day^{-1}, with the resistance to transfer being almost completely in the water phase.

7.5.3 Atmospheric Deposition

Lake loading of mercury via wet deposition was modelled by combining annual precipitation rates with specified mercury concentrations in wet deposition (including scavenged mercury). Equilibrium between the air phase and rain was not used. Ontario's mean annual precipitation value of 724 mm $year^{-1}$ (Government of Ontario, 1984) was used as

a typical rate. Bloom and Watras (1989b) estimated that Hg(II) concentrations in rain might typically range between 2-20 ug m^{-3}. A value of 10 ug m^{-3} was chosen for this study. Bloom and Watras (1989b) also suggested a washout effect may have occurred for total mercury during a rainstorm in Sequim, Washington. Samples during the early stages of precipitation tended to have higher particulate content and higher mercury concentrations than samples later during the event. Few measurements of methylmercury in rain have been made, but based on studies by Bloom and Watras (1989b), a value of 0.15 ug m^{-3} was selected as typical for relatively remote areas. Lee and Iverfeldt (1990) reported concentrations of methylmercury in Swedish rainwater ranging from 0.05 to 0.30 ug m^{-3}. Bloom and Watras (1989b) did not observe a methylmercury washout trend in the Sequim, Washington, measurements.

Elemental and dimethyl mercury concentrations in rain were assumed to be negligible. Bloom and Watras (1989b) found no dimethylmercury in any rain samples, while the equilibrium rain concentration of elemental mercury in equilibrium with a gas phase concentration of 2-3 ng/m3 would be far less than observed values of total mercury in rain.

The following equation was used to represent dry deposition:

$$Flux_{dry} = v_{dry} * area * volfrac * C_{air} * K_{dry}$$

Where:

$Flux_{dry}$ = Hg flux to waterbody due to dry deposition (ug day^{-1})

v_{dry}	=	Settling velocity of dry particles (m day^{-1})
area	=	Surface area of waterbody (m^2)
volfrac	=	Volume fraction of particles in air
C_{air}	=	Hg concentration in air (ug m^{-3})
K_{dry}	=	Partition coefficient for Hg between air and particle (dimensionless)

Dry deposition of Hg(II) and methylmercury were both modelled, while dry deposition of dimethyl and elemental mercury were considered insignificant. A dry particle settling velocity of 860 m day^{-1} (Southwood et al., 1989) and particulate volume fraction of 10^{-10} in air were assumed. Few determinations of Hg(II) or methylmercury concentrations in air (gas phase) have been made, nor were partition coefficients for Hg(II) or methylmercury between air and air particles found in the literature. If Hg(II) and methylmercury in air were in equilibrium with concentrations in rain, which is by no means certain, gas phase concentrations of these species would each be in the ranges of 0.001 to 0.01 ng/m3. For the purposes of this study, the concentration of Hg(II) in air was intentionally set to a value of 0.075 ng m^{-3} and K_{dry} was set to a value of $1.5 * 10^9$ (dimensionless) to arrive at a predetermined dry deposition rate of 3.5 ug Hg(II) m^{-2} $year^{-1}$. Fitzgerald et al. (in press) estimated a total mercury dry deposition rate of 3.5 ±3 ug Hg m^{-2} $year^{-1}$ for mid-continental regions.

Bloom and Watras (1989b) cited observed concentrations of gaseous methylmercury in air ranging from 0.05 to 1.5 ng/m3, but attached some uncertainty to the estimates. Due to this uncertainty and the overall lack of information regarding the presence of methylmercury in

dry deposition, this process was considered negligible in the present version of the model. Further research in this area would be useful.

7.6 A Bioenergetic Approach to Uptake and Excretion of Mercury by Fish Individuals and Populations

Bioenergetics approaches traditionally used for chemical uptake have been reviewed in Section 6.3. These approaches estimate growth rates and weight as a function of time for a given species. Based on the energy requirements of the fish, exposure to mercury was estimated using food and oxygen requirements, mercury concentrations in food and water, and an efficiency of mercury uptake via these pathways. Fish were treated in their entirety rather than attempting to address particular organs or tissues. A significant benefit of this approach was that it allowed an analysis of the relative importance of mercury in the diet versus water concentrations of mercury, and allowed estimates of fluxes of methylmercury between fish populations and the surrounding environment.

The overall equation used in this study for methylmercury accumulation in an individual fish is given by Norstrom et al. (1976):

$$\frac{dP}{dt} = \frac{e_{pw}*C_{pw}}{e_{ox}*C_{ox}*q_{ox}} * (a_{lr}*W^{xx} + Beta*\frac{dW}{dt})$$

$$+ \frac{e_{pf}*C_{pf}}{e_f} * [a_{lr}*W^{xx} + (Beta + 1)*\frac{dW}{dt}]$$

$$- k_{el}*P*W^{yy}$$

Where

$\frac{dP}{dt}$ = Change of mercury burden in fish with time (g d^{-1})

$\frac{dW}{dt}$ = Growth rate (g day^{-1})

e_{ox} = Efficiency of oxygen uptake from water

e_{pw} = Efficiency of methylmercury uptake from water

e_{pf} = Efficiency of extraction of methylmercury from food

e_f = Efficiency of food utilization

C_{pw} = Concentration of methylmercury in water (g g^{-1})

C_{ox} = Oxygen concentration in water (g g^{-1})

C_{pf} = Concentration of methylmercury in food (g g^{-1})

a_{lr} = Low routine metabolism (Kcal day^{-1} g^{-1})

W = Weight (g)

P = methylmercury burden in fish (g)

xx = Exponent relating metabolism to weight

yy = Exponent relating clearance to weight

Beta = Coefficient relating growth to energy required for growth (dimensionless)

k_{cl} = Clearance constant (day^{-1} g^{-yy})

q_{ox} = Caloric equivalent of oxygen (Kcal g^{-1})

The equation used for fish weight (W) was:

$$W = W_{max} * (1 - e^{(-kgrowth * (t + to))})^{xxy}$$

where:

W_{max}	=	Asymptotic fish weight (g)
k_{growth}	=	growth rate constant (day^{-1})
t	=	time (days)
t_o	=	constant (days)
xxy	=	Exponent relating weight to length (no units)

Prey fish were assumed to always eat plankton. The diet of each predator year class was based on the assumption that until a specified age is reached (e.g. 1-2 years old), the diet was comprised of benthos. Once the threshold age was reached the diet could expand if desired to consume prey species or smaller members of the same species.

Due to the high methylmercury concentration in fish relative to surrounding waters (e.g. higher by 6-7 orders of magnitude), it was necessary to consider the possibility that fish significantly influence methylmercury cycling in their surrounding environment. Bioenergetics approaches for individual fish were therefore extended to consider entire populations as well as individual fish. Prey and predatory fish populations were divided into year classes and the

mass of fish in each year class was estimated on the basis of total population biomass and a probability distribution for the mass in each year class. The equations used to develop probability distributions for masses in year classes were based on Ricker (1975). The number of fish surviving in a year class at any time "t" after the class hatched was given by:

$$N = N_o * e^{(-z*t)} \qquad \text{(Ricker 1975)}$$

where:

N_o	=	Number of fish in year class at time = 0
z	=	Overall instantaneous mortality decay constant ($year^{-1}$)
t	=	Time (years)

In a steady state population, the number of fish in any year class in the population can be estimated by:

$$N_{inc} = R * A * S^{(t-1)} / z \qquad \text{(Ricker 1975)}$$

where:

N_{inc}	=	Number of fish in year class
R	=	Recruitment (fish per year)
A	=	annual mortality fraction ($1-e^{-z}$) ($year^{-1}$)
S	=	annual survival fraction (e^{-z}) ($year^{-1}$)

Since the mass probability distribution does not depend on the absolute size of the population, a population of arbitrary size was used to develop probability distributions for a hypothetical population. The distributions were then applied to specified biomasses in the model.

The bioenergetics growth equations developed above were used to estimate a mean fish weight for each year class, which was then multiplied by the number of fish in the class (N_{inc}) to provide a biomass for the class. This information was subsequently used to develop the mass probability distributions.

Once the biomass of each year class was estimated, bioenergetics equations for methylmercury uptake and excretion were applied to representative fish of mean weight for the year class and multiplied by the number of fish in the increment to estimate methylmercury fluxes for the class. Fluxes and mean methylmercury concentrations for entire populations could then be estimated.

To provide a level of modelling realism required for predictive purposes, one should probably follow concentrations in each year class with time, i.e. after one year, the fish in year class 1 become the fish in year class 2, and so on. This would allow a temporal examination of each year class. To maintain a level of scope suited to examining trends, a simpler approach which was lower in realism was used and fish from each year class did not advance

to subsequent classes with time. For this reason, concentrations in each year class were not calculated directly. Since clearance is related to mercury burden, an estimate of mercury concentration in each class was necessary. This was carried out using estimated ratios of concentrations in each year class to the mean concentration for the entire population (i.e. young classes would have a ratio less than 1, while older classes would have a ratio greater than 1).

A further simplification involved the assumption that the mass of Hg(II) in fish is small relative to the mass of Hg(II) in water. Assuming the fish biomass density is in the range 0.1 to 2.0 ppm, Hg(II) concentrations would have to be about five orders of magnitude higher (or more) in fish than in water, to place the above assumption in doubt. However, water concentrations of Hg(II) are on the order of 1 ng L^{-1}, while Hg(II) concentrations are usually 10^4 ng L^{-1} or less in fish, assuming 5% or less of total mercury in fish is Hg(II). Hence the above assumption should be reasonable.

Even though concentrations of Hg(II) in fish are low, it is still necessary to consider the possibility that fish uptake and excrete Hg(II) in significant quantities. Assuming a lake with a volume of 10^7 m^3 and 1 ppm of fish (10 m^3), a rough bioenergetics calculation was done to arrive at a total intake of about 1.5 - 2.0 g Hg(II) per year via food. If the fish population's mean total Hg content was about 0.1 to 0.3 ug g^{-1} and 2% of this was Hg(II), then the fish population would contain about 0.2 to 0.5 g of Hg(II), and the turnover rate of Hg(II) in fish would be on the order of 3-10 times per year. In terms of the Hg(II) pool in water however, a loss of 1.5 to 2.0 g of Hg(II) per year would likely represent a small

component of the overall Hg(II) losses, perhaps on the order of 1 to 5%, as will be discussed later in the report. This would justify the assumption that Hg(II) fluxes in fish are sufficiently minor that they can be omitted from the model.

7.7 Transformations Between Mercury Forms

7.7.1 Oxidation and Reduction

Biological and chemical reduction of Hg(II) to Hg° in the water column and sediments have been discussed in several studies. Winfrey and Rudd (in press) noted that humic and fulvic acids can chemically reduce Hg(II) in surface waters. Brosset (1987) suggested that H_2O_2 could chemically reduce Hg(II) in surface waters in alkaline conditions. Turner et al. (1989) studied the reduction and volatilization of radio-labelled spikes of ^{203}Hg from water and sediment suspension samples. In water samples, both abiotic and biotic conversion of ^{203}Hg to volatile mercury were observed. The abiotic component ranged from 10 - 70% of the total in water samples, being higher in warmer conditions. Very low rates of volatilization were observed in sediment samples, and sorption of Hg(II) to solids was suggested as a rate limiting factor. The rates of reduction of Hg(II) reported by Turner et al. (1989) for samples from contaminated and uncontaminated samples were on the order of 10 to 60% per day, being higher in contaminated samples. These rates were based on radiolabelled additions and do not necessarily reflect in-situ rates for real systems.

Given the above information, it was concluded that reduction of Hg(II) to Hg° needed

to be included in the model. A somewhat arbitary range of reduction rates in the water column (5-10% per year) was initially selected to represent a generic uncontaminated system. Simulation results later in the report examine this range of values in terms of concentrations of elemental mercury in the water column in relation to observed values. For the purposes of this study, a single kinetic expression was used to represent biological and chemical reduction of Hg(II) to Hg^{o}. The process was first order with respect to Hg(II).

Information on rates of oxidation of elemental mercury to Hg(II) is lacking in the literature. Accordingly, this process is not included explicitly in the model. Given the uncertainty associated with rates of reduction of Hg(II) to elemental mercury, oxidation can be indirectly addressed in the model in terms of lowering the rate of reduction of Hg(II), i.e. considering the reduction rate to be net rather than absolute. Further information regarding oxidation and reduction of mercury in aquatic systems would be very useful.

7.7.2 Methylation and Demethylation

Methylation and demethylation of mercury were considered separately in this study. The equations proposed were intended to address trends towards increased or decreased net methylation rates in a variety of environmental conditions. The model used the following equations to simulate bacterial methylation and demethylation in the water column and sediments.

In water, the equations were:

$$M = r^*[TOC]^*Const_m * \{[Hg(II)]_{av} * (Monod_m + [Hg(II)]_{av})^{-1}\}$$

$$D = r^*[TOC]^*Const_d * \{[CH_3HgX]_{av} * (Monod_d + [CH_3HgX]_{av})^{-1}\}$$

In sediments, the equations were:

$$M= r^*[TOC]^*porsed^{-1}*Const_m*\{[Hg(II)]_{av}*(Monod_m+[Hg(II)]_{av})^{-1}\}$$

$$D= r^*[TOC]^*porsed^{-1}*Const_d*\{[CH_3HgX]_{av}*(Monod_d+[CH_3HgX]_{av})^{-1}\}$$

where:

M = ug methylmercury produced * day^{-1} * m^{-3} (m^3 surface water or porewater)

D = ug Hg(II) produced * day^{-1} * m^{-3} (m^3 surface water or porewater)

r = TOC consumption rate (day^{-1})

[TOC] = TOC concentration (ug TOC m^{-3}) (m^3 surface water or total sediment)

Const = constant (ug Hg * ug TOC^{-1})

Porsed = sediment porosity (fraction)

$Hg(II)_{av}$ = bioavailable Hg(II) (ug Hg * m^{-3}) (m^3 surface water or porewater)

CH_3HgX_{av} = bioavailable methylmercury (ug Hg * m^{-3}) (m^3 surface water or porewater)

Monod = half saturation constant (ug Hg * m^{-3}) (m^3 surface water or porewater)

Methylation, Demethylation and TOC

Specific methylation and demethylation of mercury were assumed to be first-order with respect to TOC. Total organic carbon was intended as a measure of the potential to support bacterial communities. The biodegradability of carbon and the rate of bacterial methylation, were reflected through "r", the decay rate constant for carbon. Temperature may affect this constant as well. Various studies support first order variation of specific methylation and demethylation as a function of TOC. Section 5.4.2.2 discusses literature relating microbial activity to methylation, and supports the concept of a positive relationship, possibly linear, between microbial activity and methylation. The value of "Const" was used to reflect variations in the methylating and demethylating effectiveness of various microbes (e.g. if anaerobes were more efficient methylators than aerobes, or to reflect microbial adaptation to high mercury environments).

Methylation, Demethylation and Mercury Concentrations

Several studies have examined the influence of mercury concentrations on methylation rates. Using data for water column samples from Ontario ELA lakes, Xun, et al. (1987) found the rate of specific methylation increased at a greater than linear rate with the addition of Hg(II) up to 66,000 ng mercury L^{-1}, orders of magnitude above ambient freshwater Hg(II) concentrations. For example, adding 2.6 times the Hg^{++} increased methylation by 5.6x. A possible cause of the non-linearity was that as mercury was added, binding sites became saturated and the proportion of available mercury increased at higher Hg^{++} levels. Xun et al.

(1987) also noted that the literature indicates specific methylation in sediments (as opposed to the water column) increases linearly with the addition of Hg^{++}.

Xun et al. (1987) found that demethylation in water column samples increased linearly with the addition of up to 3,730 ng methylmercury L^{-1}, above which the rate of increase declined . These concentrations are about 4-5 orders of magnitude higher than typical freshwater methylmercury concentrations. In terms of specific demethylation in sediments, Ramlal et al. (1986) found that specific rates of demethylation also increased linearly up to 44 ug of methylmercury per gram of sediment and continued to increase up to 140 ug of methylmercury per gram of sediment. The different rates at which specific methylation and demethylation responded to increases in mercury concentration in the water column suggested that increases in mercury in the water column may favour an increase in net methylation (Xun et al., 1987).

The above results support a relationship, possibly linear, between mercury concentrations and methylation/demethylation rates in sediments and the water column. At very high mercury concentrations, methylation increases at a less than linear rate, supporting the model use of a monod kinetic expression. The monod expression for the dependency of the reaction rate on available Hg(II) or available methylmercury results in no limiting effect at high mercury concentrations (the value of the expression tends to 1), while at low Hg concentrations the expression is equivalent to a first-order dependency on available mercury. The influence of mercury concentrations at lower, natural levels, on methylation and demethylation rates remains to be clarified.

It is more appropriate to describe methylation and demethylation rates as a function of available rather than total mercury. In this study it was assumed that sulphide and DOC complexes of Hg(II) and methylmercury were not available for methylation or demethylation, while Hg^{++}, CH_3Hg^+, and complexes with hydroxyl and chloride ions would be available to bacteria. Boudou et al. (1983) studied Hg(II) and methylmercury transport across membrane models composed of phospholipid bilayers in water, and concluded that neutral Hg(II) and methylmercury species, particularly $HgCl_2$ and CH_3HgCl, were more rapidly transported across membranes than charged species. It was noted however that ionized mercury forms could in theory be transported via ion pairing in the membrane. Organic complexes were not considered in their study. The results of Boudou et al. (1983) also suggested that low pH environments, which would favour $HgCl_2$ rather than $Hg(OH)_2$, and CH_3HgCl rather than CH_3HgOH, could result in faster membrane transport of Hg(II) and methylmercury at low pH. Considering the low lipid solubility of CH_3HgCl, Boudou et al. (1983) concluded that rapid diffusion across membranes rather than an affinity for lipids is likely responsible for CH_3HgCl transport into cells.

Calibration of Rate Constants for Methylation and Demethylation

No methods presently exist to accurately ascertain methylation and demethylation rates at natural levels in aquatic systems. Initial estimates of values for parameters related to methylation and demethylation coefficients (r, monod, const) were developed on the basis of several previous studies, particularly those using radio-labelled analytical techniques, and are discussed in Appendix D. These coefficients were re-examined during simulations.

8.0 CALIBRATION OF SELECTED MODEL COMPONENTS

Available field data are presently limited to adequately calibrate the complete model developed in this study. Calibration of selected components of the model is feasible however. Sections 8, 9 and 10 are presented in an order which first addresses particular aspects of the model, then discusses application of the entire model. Section 8 first discusses the use of thermodynamics to estimate the bioavailable fractions of methylmercury and Hg(II) for methylation and demethylation. The remainder of Section 8 focusses on bioenergetic estimates of uptake and depuration of mercury by individual fish (yellow perch and walleye), using field data for methylmercury concentrations of fish, their food and water.

8.1 Thermodynamic Equilibria

The model used the complexation constants and solubility products for Hg(II) and methylmercury described in Appendices A and C to estimate the bioavailable fraction of Hg(II) and methylmercury in surface waters and porewater. Of particular interest were the roles of dissolved organics, sulphide, chloride and hydroxyl groups regarding Hg(II) and methylmercury bioavailability for methylation and demethylation.

8.1.1 The Role of Dissolved Organics in Mercury Complexation

The Role of Dissolved Organics in Hg(II) Complexation

As discussed previously, one of the difficulties using complexation constants for dissolved organics is that the value of the constant may change significantly depending on the nature of the organics in any given system. A value for the 1:1 RS^-/Hg^{++} complexation constant of $10^{22.1}$ was presented by Dyrssen and Wedborg (in press) and was used in this study. At neutral pH in oxic waters (assuming negligible sulphide), 0.2 mM chloride, and assuming total thiols represent 0.0001 of humics, the 1:1 RS^- complexes with Hg^{++} would dominate once total thiols exceeded about 10^{-14} M, or 10^{-10} M in terms of total dissolved organics. Although there is a sizeable degree of uncertainty involved in these calculations, it seems likely that DOC/Hg(II) complexes are dominant in most oxic fresh waters. Using the above assumptions, a DOC level of 10^{-5} M (eg. 1 to 10 mg L^{-1}, depending on the molecular weight of the organic molecules), about 99% of soluble Hg(II) would be complexed with DOC rather than inorganic ligands.

Table 8.1 shows representative calculations for Hg(II) speciation in oxic, fresh, surface waters and porewater. Table 8.1 also provides estimates for the fractions of Hg(II) bioavailable for methylation in oxic waters. Approximately 0.1% to 0.2% of Hg(II) in solution is estimated to be available for methylation in surface waters, with less, perhaps 0.05% to 0.1% being available for methylation in oxic porewater. These numbers are important in terms

Table 8.1
Representative Calculations of Hg(II) Speciation in
Oxic, Fresh Surface Waters and Porewater

1) Surface Water:

(0.2 mM chloride, 10^{-5} M DOC, pH 7, negligible sulphide, $5 * 10^{-12}$ M Hg(II) in solution)

	Complex	Complex Activity	% of Total Activity
1)	Free Hg^{++}	$8.7 * 10^{-23}$	$1.7 * 10^{-9}$
2)	$HgCl_2$	$3.2 * 10^{-16}$	0.006
3)	$HgCl^+$	$3.5 * 10^{-19}$	$7.0 * 10^{-6}$
4)	HgOHCl	$2.0 * 10^{-15}$	0.04
5)	$Hg(OH)_2$	$6.0 * 10^{-15}$	0.12
6)	$HgRS^-$	$4.98 * 10^{-12}$	99.8

Percent assumed available for methylation: 0.17%
(Free ion plus complexes with inorganic ligands)

2) Porewater:

(0.5 mM chloride, $5 * 10^{-5}$ M DOC, pH 6.5, negligible sulphide, $5 * 10^{-12}$ M Hg(II) in solution)

	Complex	Complex Activity	% of Total Activity
1)	Free Hg^{++}	$1.0 * 10^{-22}$	$2.1 * 10^{-9}$
2)	$HgCl_2$	$2.4 * 10^{-15}$	0.05
3)	$HgCl^+$	$1.0 * 10^{-18}$	$2.0 * 10^{-5}$
4)	HgOHCl	$1.0 * 10^{-15}$	0.02
5)	$Hg(OH)_2$	$2.0 * 10^{-16}$	0.004
6)	$HgRS^-$	$4.98 * 10^{-12}$	99.9

Percent assumed available for methylation: 0.07%
(Free ion plus complexes with inorganic ligands)

of methylmercury cycling, but are unfortunately also very approximate. As discussed previously, the basis for estimating the fraction of Hg(II) in solution available for methylation was the assumption that organic complexes were unavailable while inorganic complexes (with the possible exception of sulphide complexes) were available.

The Role of Dissolved Organics in Methylmercury Complexation

Based on the complexation constants used in this study, methylmercury complexation in oxic freshwaters is also dominated by organic ligands. Although there is significant uncertainty involved in these calculations, it seems likely that DOC/CH_3Hg^+ complexes are dominant in most oxic fresh waters. At neutral pH in oxic waters, with 0.2 mM chloride and assuming total thiols represent 0.0001 of humics, the 1:1 RS^- complexes with CH_3Hg^+ would dominate once total thiols exceeded about 10^{-12} M, or in terms of total dissolved organics, about 10^{-8} M. Using a DOC level of 10^{-5} M, approximately 99% of soluble methylmercury would be complexed to DOC rather than inorganic ligands.

Table 8.2 shows representative calculations for methylmercury speciation in oxic, fresh, surface waters and porewater. The table illustrates the potential for DOC to dominate complexation of methylmercury for the assumed conditions. Estimates of bioavailable fractions of methylmercury for demethylation in oxic waters are also shown. Approximately 0.1% to 1.0% of Hg(II) in solution is estimated to be available for demethylation in surface waters, with less, perhaps 0.1% to 0.5% being available for demethylation in oxic porewater. As discussed previously for Hg(II), the basis for estimating the fraction of methylmercury in

Table 8.2
Representative Calculations of Methylmercury Speciation in
Oxic, Fresh Surface Waters and Porewater

1) Surface Water:

(0.2 mM chloride, 10^{-5} M DOC, pH 7, negligible sulphide, $2.5 * 10^{-13}$ M methylmercury in solution)

	Complex	Complex Activity	% of Total Activity
1)	Free CH_3Hg^+	$4.4 * 10^{-18}$	0.002
2)	CH_3HgCl	$1.5 * 10^{-16}$	0.06
3)	CH_3HgOH	$1.0 * 10^{-15}$	0.40
4)	CH_3HgRS	$2.49 * 10^{-13}$	99.53

Percent assumed available for demethylation: 0.47%
(Free ion plus complexes with inorganic ligands)

2) Porewater:

(0.5 mM chloride, $5 * 10^{-5}$ M DOC, pH 6.5, negligible sulphide, $2.5 * 10^{-13}$ M methylmercury in solution)

	Complex	Complex Activity	% of Total Activity
1)	Free CH_3Hg^+	$5.0 * 10^{-18}$	0.002
2)	CH_3HgCl	$4.6 * 10^{-16}$	0.18
3)	CH_3HgOH	$2.0 * 10^{-16}$	0.08
4)	CH_3HgRS	$2.49 * 10^{-13}$	99.73

Percent assumed available for demethylation: 0.27%
(Free ion plus complexes with inorganic ligands)

solution available for demethylation was the assumption that organic complexes were unavailable while inorganic complexes (except possibly sulphide complexes) were available.

8.1.2 The Role of Sulphide in Mercury Complexation and Precipitation

The Role of Sulphide in Hg(II) Complexation and Precipitation

Sulphide has a strong affinity for Hg(II). Several sulphide complexes with Hg(II) are identified in the literature (see Section 7.3). Thermodynamic calculations were carried out for a range of sulphide levels at pH 7. Results are presented for surface waters and porewater in Figures 8.1 and 8.2. These figures also were developed considering competition for Hg(II) by solid adsorption sites, and assuming 1:1 DOC/Hg(II) complexation. It is apparent from the figures that any appreciable sulphide would result in most Hg(II) being bound to soluble HgS, or at higher sulfide activities, polysulfide/Hg(II) complexes. Theoretically, sulfide/Hg(II) complexes would dominate at S^{--} activities above about 10^{-30} M. This estimate does not consider 1:2 complexes of Hg/RS^-. At the levels of Hg(II) typically found in unpolluted freshwaters (eg. 1 ng L^{-1}), soluble sulphide complexes with Hg(II) would preclude precipitation of solid phase HgS and maintain the Hg(II) in solution. The total amount of Hg(II) in solution increases noticeably at higher sulphide activities in Figure 8.2 due to successful competition for Hg(II) with solid adsorption sites.

FIGURE 8.1
Simulated Surface Water Hg(II) Speciation as a Function of Free Sulphide Activity

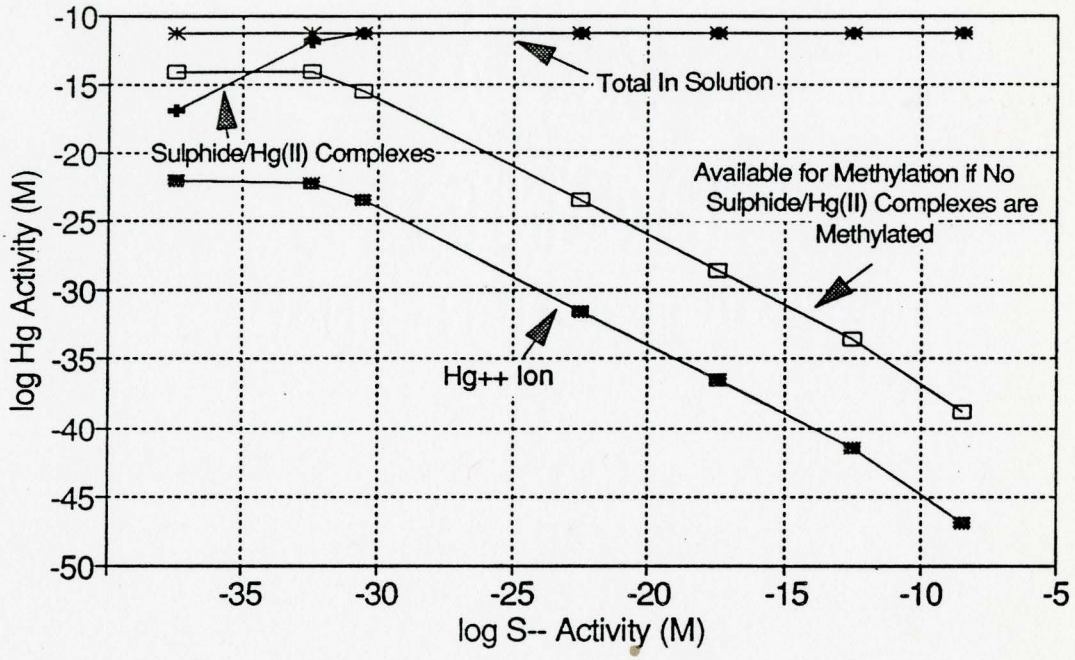
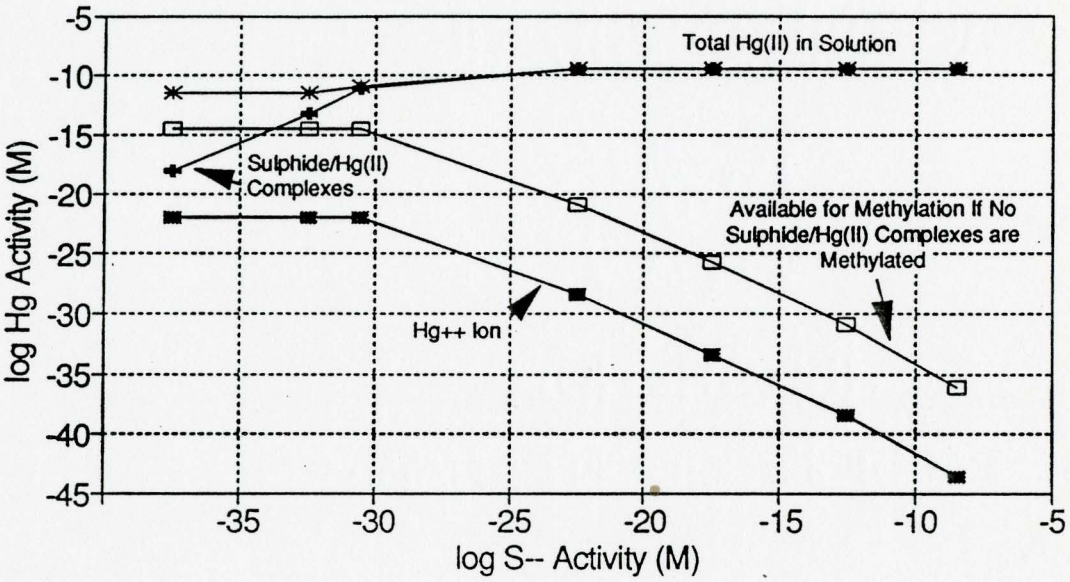


FIGURE 8.2
Simulated Porewater Hg(II) Speciation
as a Function of Free Sulphide Activity



Figures 8.1 and 8.2 show a decrease in bioavailable Hg(II) as S^- activity increases, *assuming* sulphide/Hg(II) complexes are not available for methylation. It should be noted however that methylation has been observed in the presence of sulphide (see Section 5.4.3). Beijer and Jernelov (1979) reported that methylation in the presence of HgS (presumably solid phase) can occur, but at a rate orders of magnitude slower than for $HgCl_2$. Thus it is presently difficult to predict the net impact of sulphide complexation of Hg(II) on biovailability for methylation. Further research would be instructive. Insights regarding the quantities of sulphide in aerobic waters would also be valuable. As mentioned above, even trace quantities of sulphide in aerobic waters could result in significant Hg(II) complexation by sulphides. For the purposes of this study it is initially assumed that sulphide/Hg(II) complexation is not significant in oxic waters.

At this point it is important to develop a perspective on the physical relevance of extremely low theoretical activities. For example, how low would a concentration of 10^{-20} or 10^{-30} be in terms of sulphide mass in water? Considering Avogadro's number, an activity of 10^{-23} M represents on the order of one active sulphide ion per litre. The same ion in the entire volume of Lake Ontario (about 1.6 * 10^{12} m3) would be on the order of 10^{-38} molar. It is postulated that at such low activities as 10^{-20} or less for sulphide and/or mercury, the statistical improbability of immediate and complete molecular interactions would prevent instantaneous equilibrium such that thermodynamic calculations may bear little resemblance to actual concentrations. In addition, at such low activity levels, it is possible that Hg^{++} activity in solution is influenced by coprecipitation with, for example, iron sulphides, rather than by solid HgS formation only.

FIGURE 8.3
Simulated Surface Water Methylmercury Speciation as a Function of Free Sulphide Activity

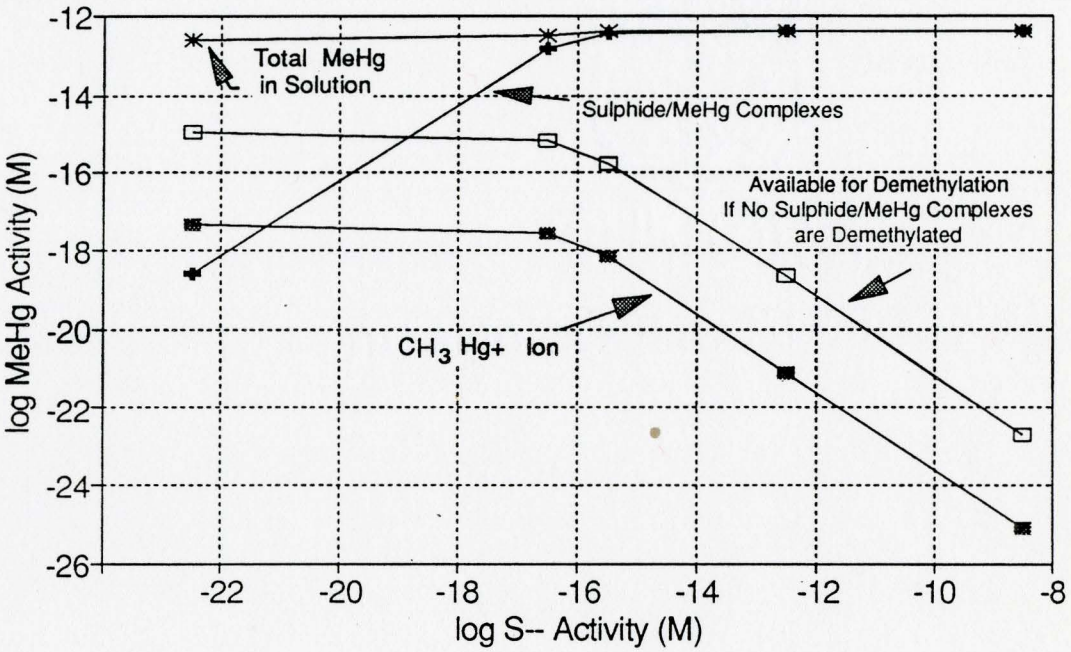
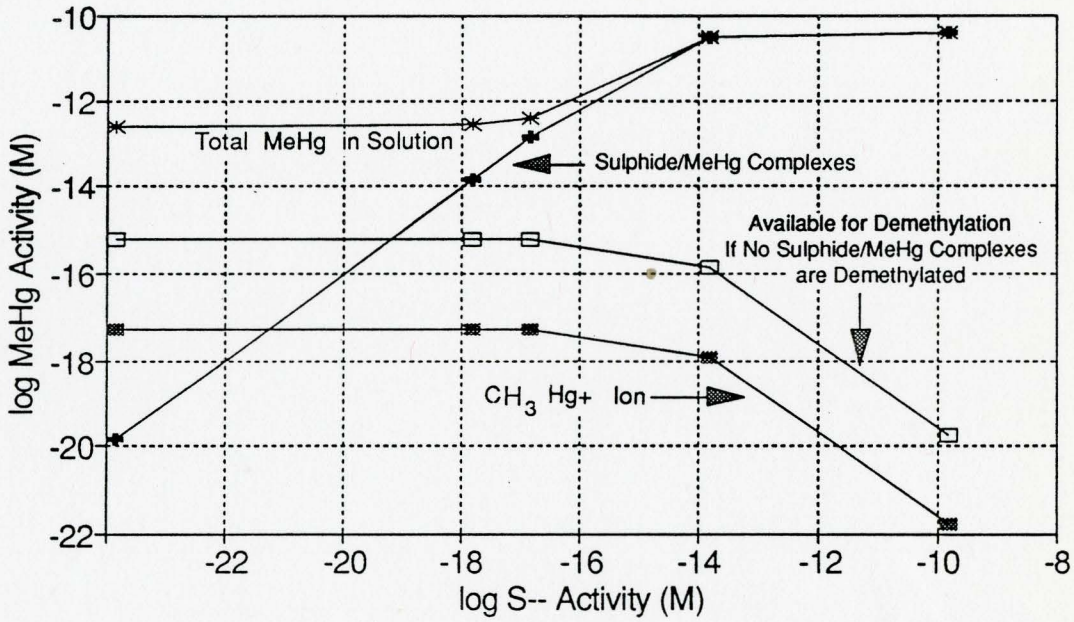


FIGURE 8.4
Simulated Porewater Methylmercury Speciation as a Function of Free Sulphide Activity



The Role of Sulphide in Methylmercury Complexation

Sulphide also has a strong affinity for methylmercury. Several sulphide complexes with methylmercury are identified in the literature (see Section 7.3). Thermodynamic calculations were carried out for a range of sulphide levels at pH 7. Results are presented for surface waters and porewater in Figures 8.3 and 8.4. These figures were developed considering competition for methylmercury by solids. Theoretically, sulfide/MeHg complexes would dominate at S^- activities above about 10^{-16} M. For the purposes of this study it is initially assumed that sulphide/MeHg complexation is not significant in oxic waters.

Analagous to sulphide complexation with Hg(II), sulfides have the potential to compete successfully for methlmercury on solids, as shown in Figure 8.4. In the figure, sulphide levels above approximately 10^{-16} M tend to compete successfully with solid adsorption sites, and increase the total amount of methylmercury in solution. This trend was not as apparent in calculations for surface waters. Figures 8.3 and 8.4 also show a decrease in available methylmercury as S^- activity increases, *assuming* sulphide/methylmercury complexes are not available for demethylation.

8.2 Methylmercury Dynamics for Individual Fish and Fish Populations

The bioenergetics equations described previously were applied to individual walleye and yellow perch. Previous calibrations were also examined in light of more recent estimates of methylmercury concentrations in food and water.

Yellow Perch (*Perca flavescens*)

Norstrom et al. (1976) suggested coefficients to fit a bioenergetics model to data for yellow perch in the Ottawa River (see Figure 8.5). A methylmercury concentration in water of 4 ug m^{-3} was assumed, which is about 2 orders of magnitude above levels now considered representative of background levels for oxic systems not locally contaminated. Figure 8.5 also shows a simulation using Norstrom's coefficients and inputs, but assuming a methylmercury concentrations in water of 0.05 ug m^{-3}.

Figure 8.6 shows the percentage of methylmercury uptake in yellow perch via food, for the above concentrations of methylmercury in water. The simulations represented in these figures suggest that water is a significant source of methylmercury when the water concentration is 4 ug m^{-3} (eg. 65-70%), but the water pathway is essentially insignificant (1% or less) when the water concentration is 0.05 ug m^{-3}.

At a water methylmercury concentration of 0.05 ug m^{-3}, the bioenergetics coefficients originally suggested by Norstrom would significantly underestimate fish methylmercury concentrations relative to observed values. The methylmercury concentration used by Norstrom for food seems reasonable (0.033 ug g^{-1} wet), suggesting that the model coefficients need to be changed to increase methylmercury uptake and/or decrease depuration.

To increase methylmercury uptake, two pathways were considered: gills and food. If the efficiency of uptake of methylmercury from water is increased from the value of 0.12 used

FIGURE 8.5
Observed and Simulated MeHg Concentration Versus Weight for Yellow Perch in Ottawa River

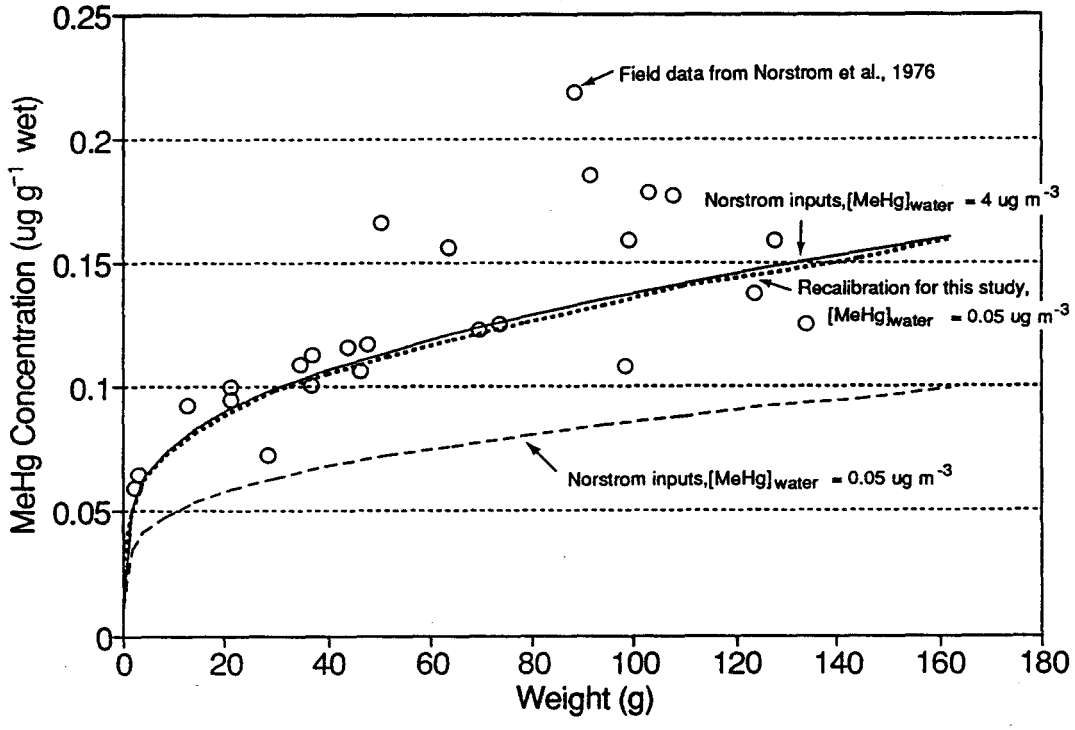
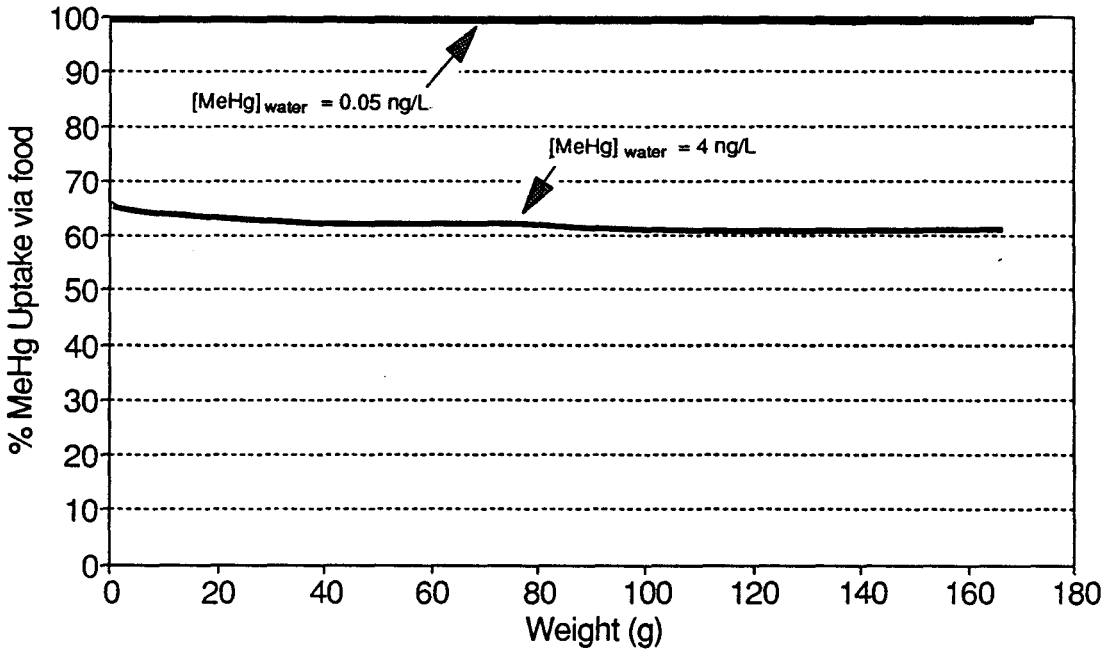


FIGURE 8.6
Simulated Percentage of MeHg Uptake via Food for Yellow Perch



by Norstrom et al. (1976) to 1.0, approximately 93% of uptake would still be via food. A preliminary examination of other coefficients and inputs which could increase methylmercury uptake from water (efficiency of oxygen uptake, oxygen concentration in water, energy content of oxygen, and possibly the efficiency of energy assimilation and conversion to tissue) did not highlight a need for changes in these values. It is therefore assumed that methylmercury uptake via food is the dominant pathway, representing 90% or more of total uptake under typical oxic conditions. A more detailed examination of the bionergetics coefficients for both food and water uptake of methylmercury would be useful to confirm this hypothesis.

To improve the fit of the bioenergetics model to the Ottawa River data, attention was given to depuration and uptake via food. It was found that a 75% decrease in the clearance constant k_{cl} from 0.029 to 0.0075 day^{-1} g^{-58} would be required to generate a simulation similar to that of Norstrom et al. (1976), ie. to give a similar concentration of 0.15 ug g^{-1} in a five year old fish. The approach to simulating clearance by yellow perch used by Norstrom was based on experiments using goldfish and northern pike, and was not directly a function of metabolism. Instead, the effective clearance rate decreases is a function of weight to an exponent (-0.58). Changing the value of this exponent to -0.85 would also reduce clearance and produce a simulation similar to that of Norstrom et al. (1976).

The feasibility of these clearance related values is unclear. Norstrom et al. (1976) speculated that the value of the exponent relating clearance to weight was in the range of -0.2 to -0.8. Rodgers and Beamish (1982) performed experiments with fingerling rainbow trout and determined k_{cl} values between 0.0178 and 0.0242 $g^{0.58}$ day^{-1}, while Norstrom et al. (1976)

cited studies reporting k_{cl} values equivalent to 0.047 to 0.072 $g^{0.58}$ day^{-1} for *Esox lucius* transplanted from a contaminated to uncontaminated lake (whole body fractional clearance of 30% per year).

An increase in simulated perch mercury concentrations could also be obtained by changing variables related to food uptake. For example, lowering the efficiency of food utilization from 0.82 to 0.5 would produce a similar concentration in a 5 year old yellow perch as simulated by Norstrom et al. (1976). No literature data were found to support such a value, however an assumption in the Norstrom simulations was a food energy content of 1 Kcal g^{-1} wet weight. A value of 0.75 Kcal g^{-1} was suggested by Fagerstrom and Asell (1973) for chironomids. A value of 0.9 Kcal g^{-1} was adopted for this study to represent the energy content of the diet of yellow perch. The effect of this value is that more food would have to be eaten by the fish to meet energy requirements, resulting in more methylmercury intake.

The efficiency of uptake of methylmercury from food could be increased slightly, but Norstrom et al. (1976) used a value of 0.8 and literature values ranged from 0.15 to 0.94 (Rodgers and Beamish, 1982; Norstrom et al., 1976; Fagerstrom and Asell, 1973), suggesting little opportunity to raise the value of this parameter dramatically. Other uptake related variables examined include the low routine metabolic rate, the exponent relating metabolism to weight, and a factor relating the energy required to add tissue weight. Significant uncertainty is associated with the values of these parameters as well.

It was concluded that a comprehensive recalibration is beyond the scope of this study. No single parameter was clearly unreasonable, and major alterations would be required for any one parameter to provide a better fit to observations. Several parameter values were therefore adjusted moderately to arrive at a calibration close to the simulation used by Norstrom et al. (1976) for yellow perch in the Ottawa River, assuming a water methylmercury concentration of 0.05 ug m^{-3} (see Figure 8.5). The greatest adjustments were made to the clearance related coefficients since both the methodology (eg. not relating clearance to metabolism) and the coefficients show a fair degree of uncertainty in the literature. Values used in this study are shown in Table 8.3. The values are assumed representative for fish in a typical oligotrophic shield lake.

Table 8.3
Selected Bioenergetic Inputs for a Generic Shield Lake

Process	Rate	
Parameters Related to Individual Fish Bioenergetics	Walleye	Yellow Perch
- Efficiency of Oxygen Uptake	0.75	0.75
- Efficiency of Food Use	0.82	0.8
- Energy Content of Food (kcal g^{-1} wet weight)	1.1	0.9
- Efficiency of MeHg Uptake from Water	0.12	0.12
- Efficiency of MeHg Uptake from Food	0.70	0.80
- MeHg Clearance Constant (g^{-1} day^{-1})	0.03	0.02
- Clearance Exponent Relating Clearance to Weight	-0.65	-0.65
- Ultimate Weight (g)	3700	789
- Growth rate Constant (day^{-1})	0.00066	0.00045
- Exponent relating metabolism to weight	0.77	0.81
- Coefficient relating growth to energy associated with growth	1.0	1.0
- Low Routine Metabolism (Kcal day^{-1} g^{-1})	0.034	0.0178
- Exponent Relating Weight to Length	3.0	3.0
- Age Constant (Provides mass at birth) (days)	60	182
Parameters Related to Fish Populations:		
- Instantaneous mortality rate ($year^{-1}$)	0.45	0.7
- Fish Biomass (ppm by volume)	0.25	1.5

Based on the recalibration, Figure 8.7 shows simulated methylmercury concentrations in yellow perch as a function of age, for different concentrations of methylmercury in food. An increase in food methylmercury levels would result in a corresponding linear increase in the concentration in perch, for steady state conditions in the same system. For example, a 5 year old yellow perch with a diet methylmercury content of 0.03 ug g^{-1} would have a methylmercury concentration of 0.14 ug g^{-1} while the same fish with a diet containing 0.3 ug g^{-1} would have a concentration of 1.4 ug g^{-1}. Furthermore, above the age of 1 year, the increase in methylmercury concentration with age is roughly linear in these yellow perch simulations. Figure 8.8 indicates that such linearities are also simulated to exist as a function of weight for yellow perch above a weight of about 75 - 100 g. Although these results might suggest that relatively simple linear regressions could be used to estimate the methylmercury concentration of adult yellow perch in a steady state environment, the slope and intercept of the regression would vary from lake to lake as a function of fish growth rates, habits, energy requirements and methylmercury content of the diet. Bioenergetics offer the advantage of accounting for such system to system variability, can accommodate unsteady state conditions, and can predict methylmercury fluxes between entire fish populations and their surroundings, as will be discussed later.

FIGURE 8.7
Simulated MeHg Concentration as a Function of Age and Diet for Yellow Perch

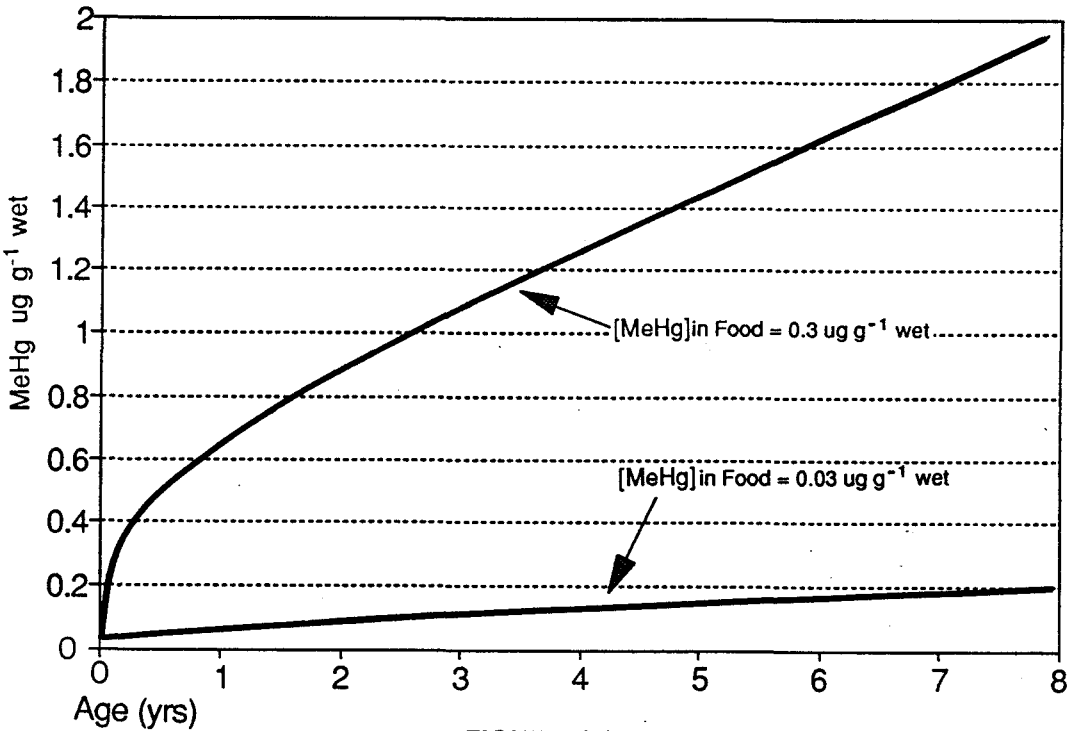
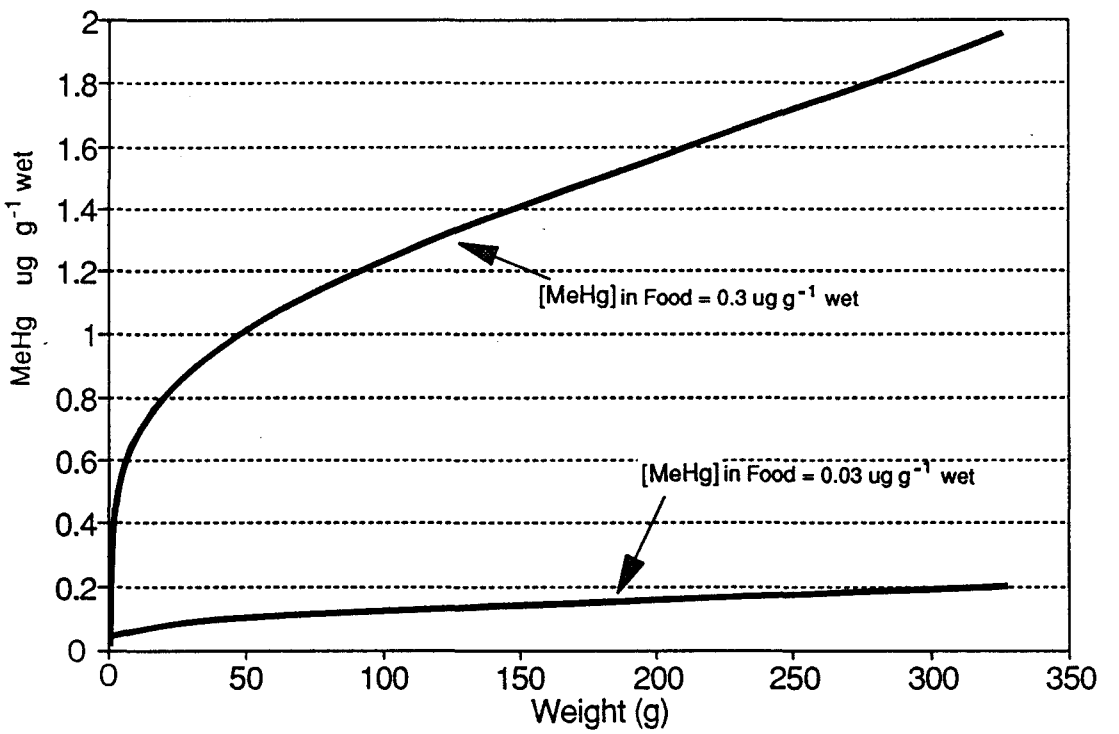


FIGURE 8.8
Simulated MeHg Concentration as a Function of Weight and Diet for Yellow Perch



Walleye (*Stizostedion vitreum*)

Walleye are common in Ontario and were chosen as a representative higher trophic level predatory species for simulations. To calibrate the walleye bioenergetics equations, a study of Lake Simcoe, Ontario, by Mathers and Johansen (1985) was used. The study reported on weight, age, diet and methylmercury concentrations in walleye. Methylmercury contents in the diets of various year classes were also presented. No methylmercury concentrations in water were available. Lake Simcoe has an area of 725 km^2 and a mean depth of 17.2 m (Mathers and Johansen, 1985). The methylmercury content in the diet of age 1+ walleye (primarily mayfly nymphs and crayfish) averaged 0.047 ug g^{-1} wet weight, while the diet of older specimens averaged 0.174 ug g^{-1} wet weight, consisting primarily of smelt.

To apply the bioenergetics equations, growth related aspects of the model were calibrated, followed by a calibration of parameters related exclusively to methylmercury. Figure 8.9 shows the observed and predicted weights for 16 year classes, and the values of growth related parameters used in the calibration. There are many combinations of variables which can be perturbed to change the predicted growth curve, and the values chosen were based on a visual fit to the observations. Most of the selected values are comparable to those used by Jensen (1988), who applied the bioenergetics concepts developed by Norstrom et al. (1976) to walleye for a group a Wisconsin lakes. Possible causes for elevated mercury levels in fish in acidified lakes were examined. The asymptotic weight chosen by Jensen (3687 g) is clearly exceeded in Lake Simcoe and required adjustment upwards.

FIGURE 8.9
Observed and Simulated Weight Versus Age for Lake Simcoe Walleye

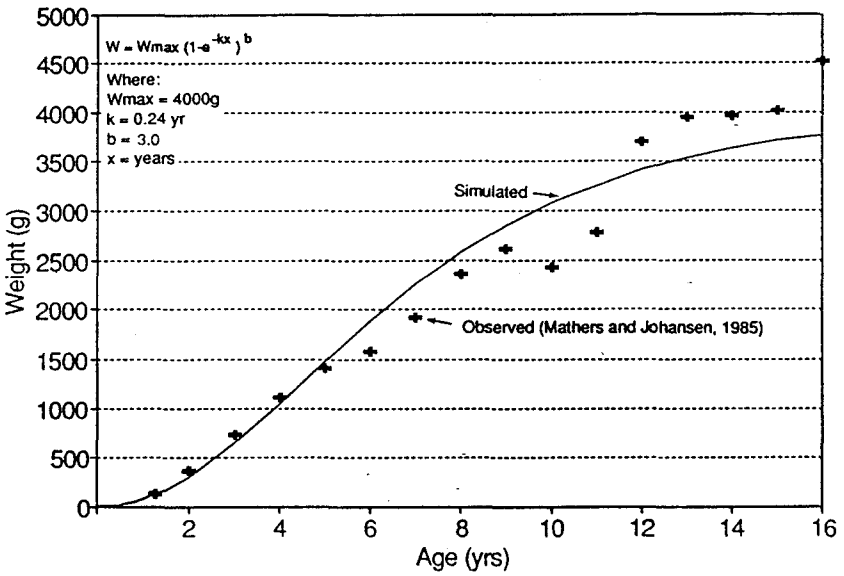
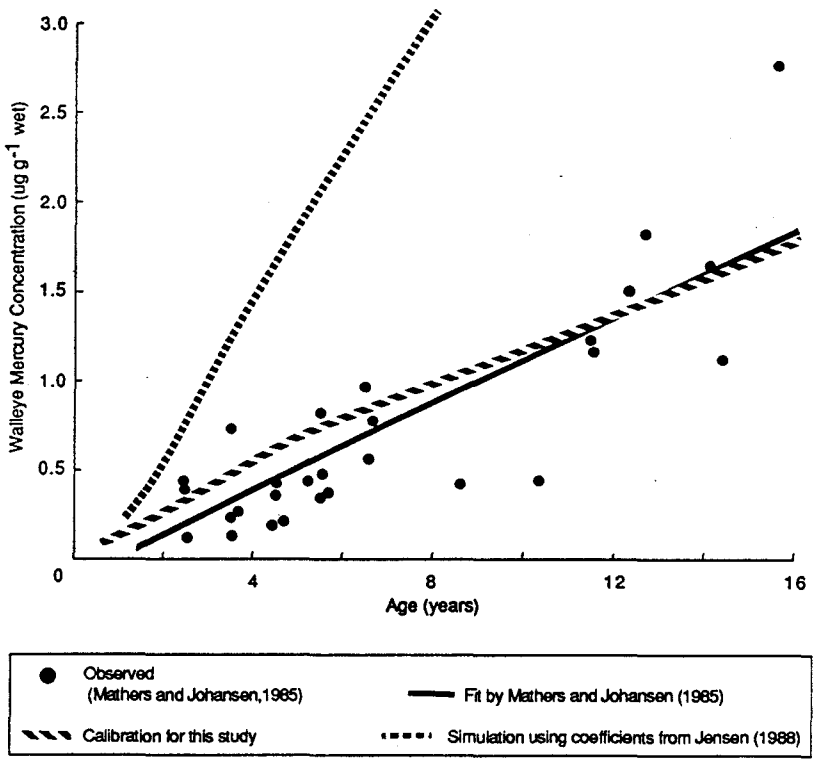


FIGURE 8.10
Observed and Simulated Methylmercury Concentrations in Lake Simcoe Walleye



Once growth related parameters were estimated for walleye in Lake Simcoe, methylmercury uptake and excretion parameters were calibrated. As a starting point, the growth parameters determined above were combined with Jensen's methylmercury related parameter values. The concentration of methylmercury in water was assumed to be 0.05 ug m^{-3} while the dietary habits and methylmercury contents reported by Mathers and Johansen (1985), discussed above, were used. Figure 8.10 shows that this simulation overestimated walleye methylmercury concentrations. A simulation using Jensen's growth related parameter values in lieu of those above resulted in very similar results. As was the case for yellow perch simulations, more than 99% of methylmercury uptake was via food at all ages. Thus mechanisms to increase excretion or decrease uptake via food were considered to improve the fit between observed and predicted concentrations.

An order of magnitude increase in the clearance constant k_{cl} from 0.029 to approximately 0.3 day^{-1} $g^{.58}$ would be required to lower predicted concentrations into the range of observed data. Changing the value of the exponent relating clearance to weight to -0.25 would also produce a better match between observed and predicted concentrations. The feasibility of these values is unclear, however when translated into overall rate constants for clearance (units: $time^{-1}$) these values would result in a 1 kg fish having a clearance rate of 2 to 3 per year. Such a high rate would seem inconsistent with limited estimates on the order of 0.3 per year for fish in this weight range (Norstrom et al., 1976; Fagerstrom and Asell, 1973). It was therefore concluded that the calibration should directed towards uptake via food.

The energy content of the walleye diet is a factor in the uptake of mercury. Higher energy density in the fish diet would mean less food consumption is needed to meet energy requirements. This would result in less mercury uptake. Rodgers and Qadri (1982) reported energy contents for yellow perch equivalent to 0.88 to 1.31 Kcal g^{-1} wet weight. If walleye eat mostly perch or other fish of similar energy content for most of their lives, it seems reasonable to assume an energy content for the walleye diet slightly greater than the 1 Kcal g^{-1} used by Jensen. A value of 1.1 Kcal g^{-1} wet weight was selected for this study.

To reduce predicted concentrations into the range of observations for Lake Simcoe data, the efficiency of food utilization could be increased or the efficiency of uptake of methylmercury from food could be decreased. The efficiency of food utilization used by Jensen, 0.82, was consistent with the literature, and did not present a great deal of opportunity for increases. The efficiency of uptake of methylmercury from food needed to be decreased to a value of approximately 0.2 to produce a reasonable fit between observed and simulated concentrations. Norstrom et al. (1976) and Jensen (1988) used a value of 0.8, and literature values typically were in the range 0.7 to 0.9 (Rodgers and Beamish, 1982). A few studies have reported lower values however. Philips and Gregory (1979) estimated methylmercury uptake efficiencies on the order of 0.15 to 0.2. Fagerstrom and Asell (1973)) used a value of 0.15 for simulations of pike and roach. Ribeyre et al. (1980) observed a temperature dependence for the efficiency of uptake of methylmercury from food in *Salmo gairdneri* in experimental conditions, with values ranging from 0.69 at 10 degrees Celsius to 0.32 at 26 degrees Celsius. The latter study did not clarify whether increased metabolic activity at higher temperatures may have improved clearance. Based on the above studies, a value of

0.7 was selected to represent the efficiency of uptake of methylmercury of food. This value helped to lower simulated mercury concentrations and improve the fit with observed data, and was in the range of literature values.

Other food uptake related variables examined include the low routine metabolic rate, the exponent relating metabolism to weight, and a factor relating the energy required to add tissue weight. Uncertainty is associated with these parameters as well and it was concluded that, as was the case for yellow perch, a comprehensive recalibration is beyond the scope of this study. Since no single parameter estimate was clearly unreasonable and major alterations would be required for any one parameter to provide a reasonable fit with observations, several parameter values were adjusted moderately to arrive at a final calibration for the Lake Simcoe data. The values selected for walleye are shown in Table 8.3. Figure 8.10 shows the Lake Simcoe observations, a linear regression carried out by Mathers and Johansen (1985) and the calibrated simulation. The simulation assumed a water concentration of 0.05 ug m^{-3} in conjunction with the diet previously discussed.

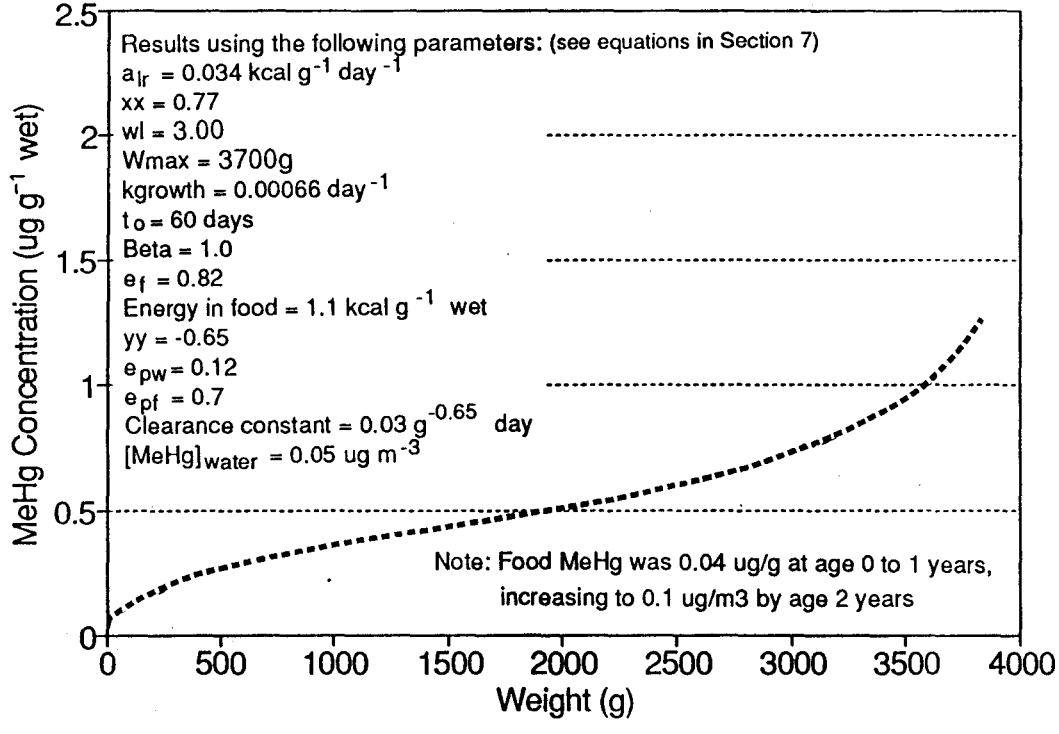
The calibration was based on a visual fit. The greatest adjustments were made to coefficients related to food uptake. The exponent relating mercury uptake to body weight was lowered from 0.92 (used by Jensen, 1988) to 0.77, significantly reducing uptake. This value is in the range of other reported values such as 0.8 used by Norstrom et al. (1976) for yellow perch.

Initially, the calibration shown in Figure 8.10 was obtained using a food concentration of 0.174 ug g^{-1} and a methylmercury assimilation efficiency of 0.6. This efficiency is low but in the range of literature values. With the exclusion of one particularly high set of values, methylmercury concentrations in walleye prey were typically in the range of 0.15 ug g^{-1}. The use of this value allowed a corresponding increase in the efficiency of methylmercury uptake from food from 0.6 to 0.7. The reason for this adjustment was to bring the methylmercury assimilation efficiency more in line with typical literature values. Further studies regarding the above bionergetics coefficients would be very useful.

Using the walleye bioenergetics calibration, a simulation was carried out using a water concentration of 0.05 ug m^{-3} and a diet methylmercury concentration starting at 0.04 ug g^{-1} and increasing between age 1-2 years to a value of 0.1 ug g^{-1}. These diet methylmercury concentrations were comparable but lower than the Lake Simcoe data, and are considered representative of a typical oligotrophic lake in the Canadian Shield. The values were based on a subjective examination of the literature (see Section 4). Considerable variation is possible from system to system. The results of the simulation are shown in Figure 8.11. The simulation suggests a methylmercury concentration in the range of 0.40-0.45 ug g^{-1} for a 1 kg walleye, rising steadily with age to more than 1 ug g^{-1} in older (eg. 3.5-4.0 kg) fish.

The food pathway would totally dominate methylmercury uptake (>99%) based on this simulation. To conservatively examine the potential for water to be a significant pathway, a simulation was performed using a water concentration of 4 ug m^{-3}, which could represent seasonal conditions in anoxic hypolimnia in some lakes, but holding the food concentrations at

FIGURE 8.11
Simulated MeHg Concentration as a Function of Weight for Walleye in a Generic Oligotrophic Shield Lake



the above values. Such conditions are probably unlikely. One would expect the methylmercury content of the walleye diet to increase if the methylmercury concentrations rose in water. An investigation the response time of various levels of the food chain to seasonal changes in water methylmercury concentrations would help address this issue. Under these hypothetical conditions, food uptake would still represent 65 to 80% of total methylmercury uptake.

Based on the calibration, Figure 8.12 shows simulated methylmercury concentrations in walleye as a function of age, for different concentrations of methylmercury in food. An increase in food methylmercury levels would result in a corresponding linear increase in the walleye mercury concentration, for steady-state conditions. For example, a 3 year old walleye eating food with a methylmercury content of 0.3 ug g^{-1} would have a methylmercury concentration ten times higher than if its diet had been 0.03 ug/g. Due to changing diet with age, a linear relationship between mercury concentration and age does not establish itself for walleye until about age 3 in this simulation. This is about a year after the methylmercury in diet is assumed to reach a constant value. If valid, this non-linearity at younger ages for walleye would complicate attempts to carry out linear regressions of mercury concentration versus age for younger walleye. Figure 8.13 indicates that the mercury concentration versus weight relationship is not linear for walleye. Although these results might suggest that relatively simple linear regressions could be used to estimate the methylmercury concentration of older walleye of a given age in a steady state environment, the slope and intercept of the regression would vary from lake to lake as a function of fish growth rates, age at which the switch to a fish diet occurs, energy requirements for routine metabolism, food acquisition and

FIGURE 8.12
Simulated MeHg Concentration as a Function of Age and Diet for Walleye

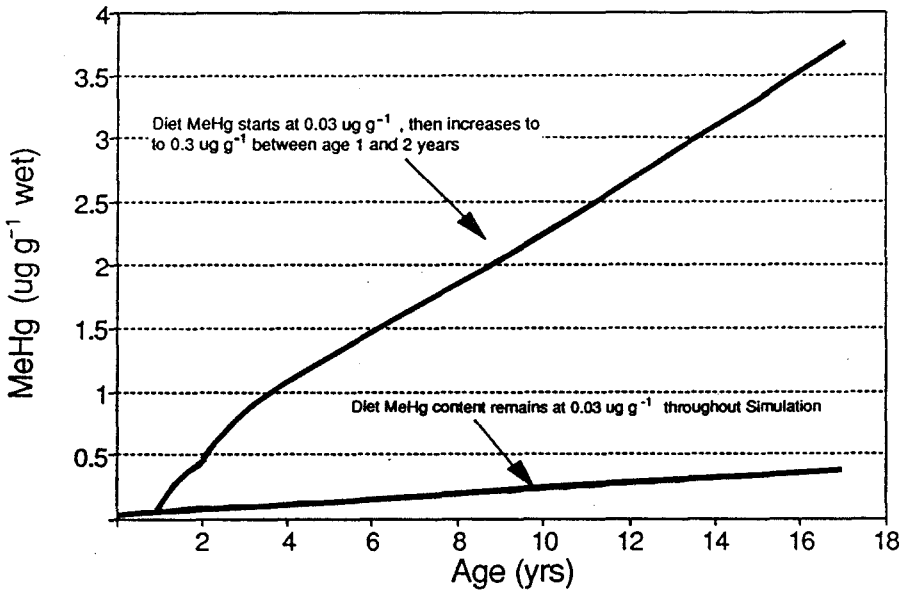
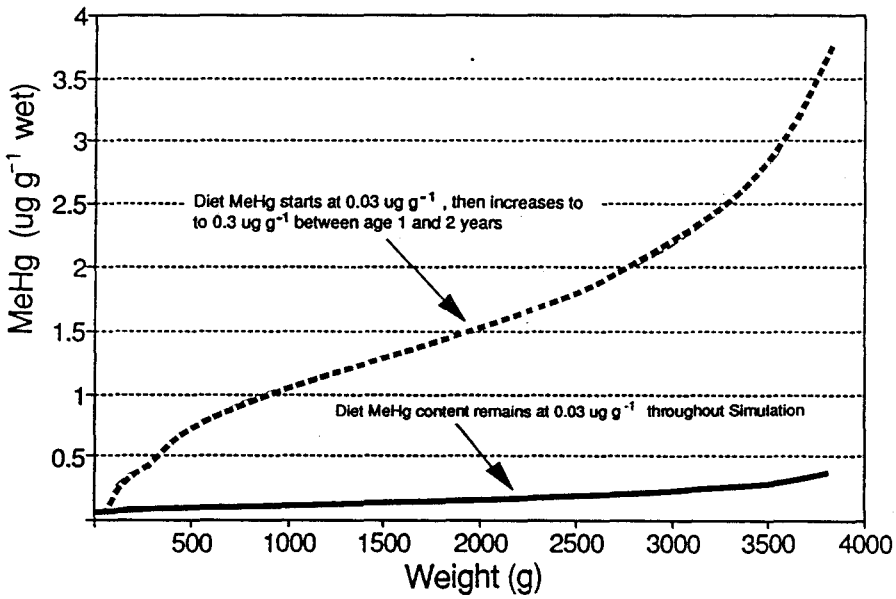


FIGURE 8.13
Simulated MeHg Concentration as a Function of Weight and Diet for Walleye



growth, and methylmercury content of the diet. Bioenergetics offer the advantage of mechanistically accounting for such system to system variability, can accomodate unsteady state conditions, and can predict methylmercury fluxes between entire fish populations and their surroundings, as will be discussed later.

Application of Bioenergetics to Mercury Dynamics for Fish Populations

With the above calibrations for individual prey and predator fish carried out, mercury fluxes and mean concentrations were estimated for entire populations of yellow perch and walleye, using the approach outlined in Section 7.6.

Figure 8.14 shows the mass probability distributions assumed for walleye and yellow perch in a generic oligotrophic to mesotrophic shield lake. Instantaneous mortality rate constants of 0.45 and 0.7 $year^{-1}$ were used for walleye and yellow perch respectively to generate the distributions shown in the figure. These instantaneous rates result in annual mortality rates of 33% and 50% for walleye and yellow perch respectively. Vetter (1988) reviewed instantaneous natural mortality rates in fish stocks, with most estimates being in the range 0.1 to 2.0 $year^{-1}$. Values from 0.36 to 0.56 $year^{-1}$ were reported for sauger in Lake Nipigon. A value in the middle of this range was selected for walleye, and a slightly higher value was chosen for yellow perch, on the assumption that walleye outlive perch. Vetter (1988) noted that mortality is an important but poorly quantified variable in fish population models. Based on Figure 8.14, most of the walleye biomass would be in the 3-6 year old classes, while most of the yellow perch biomass would be in the 2-4 year old classes.

FIGURE 8.14
Mass Probability Distribution for
Walleye and Yellow Perch in a Generic Shield Lake

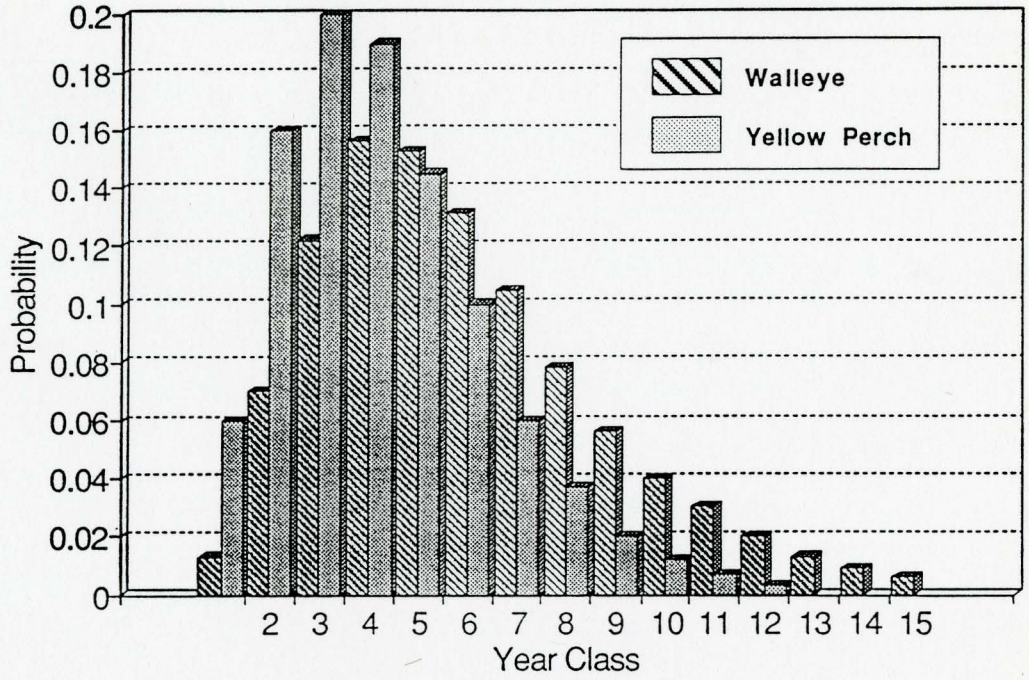


FIGURE 8.15
Numbers of Fish in Each Year Class for
Walleye and Yellow Perch in a Generic Shield Lake

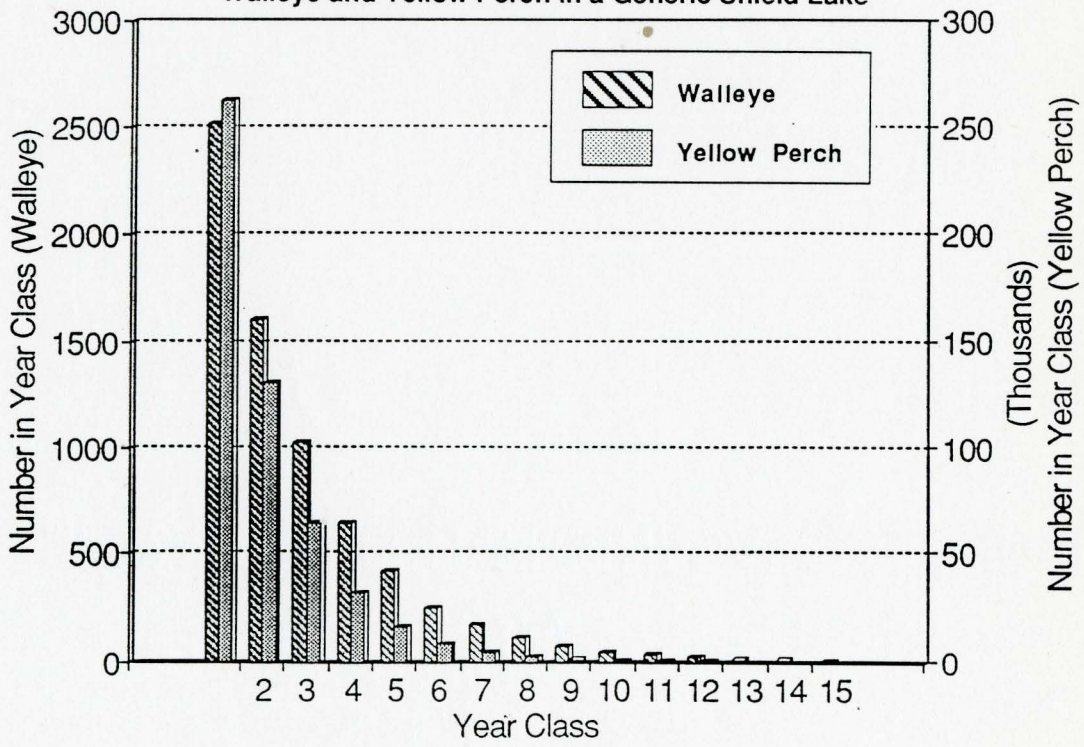


Figure 8.15 shows the number of fish simulated in a generic shield lake (volume 10^7 m^3) in each year class for walleye and yellow perch, and reflects an exponential decline in numbers with time. The numbers require estimates of fish biomass in the lake. Wetzel (1983) presented productivity to biomass (P/B) ratios and productivity values for several freshwater systems. A wide range of values was reported, with productivity typically in range of 10 to 200 kg ha^{-1} $year^{-1}$ for temperate lakes, and P/B ratios in the range of 0.5 to 1.2 $year^{-1}$. A productivity of 100 kg ha^{-1} $year^{-1}$ and a P/B range of 0.5-1.0 $year^{-1}$ were chosen as representative for oligotrophic/mesotrophic shield lakes. These values would result in a total lake fish biomass of 100-200 kg ha^{-1}. In the generic shield lake in this study (mean depth 10 m), the corresponding volumetric concentration would be 1-2 ppm.

In the model, lake productivity was determined using the growth terms from the bioenergetics equations in conjunction with a specified total fish biomass. The segregation between prey and predator biomass was determined by assuming most adult walleye diet (eg. 70% or more) was yellow perch and by assuming most of the yellow perch mortality was as a result of being eaten by walleye. The ratio of walleye to yellow perch biomass could be set such that the productivity of yellow perch properly supplied the walleye diet. The required ratios of yellow perch to walleye biomasses were typically in the range of 3:1-10:1. Similar techniques were used to assign a fraction of walleye diet represented by cannibalism.

As a result of the above analyses, biomass concentrations of 1.5 ppm for yellow perch and 0.25 ppm for walleye were chosen for the generic shield lake. The resulting lake productivity was approximately 115 kg ha^{-1} $year^{-1}$, well within the range discussed by Wetzel

(1983), while the walleye diet was 90% yellow perch, 9% benthos and 1% cannibalism.

Using the values discussed above, about 90-95% of yellow perch mortality would occur through predation, with a corresponding value for walleye of only 8%. The fate of the mercury represented by other mortality mechanisms (disease, old age, fishing) is pursued in later discussions involving applications of the entire model. No information was found in the literature describing fractions of fish mortality represented by predation. Nor was information found regarding the fate of such fish which die by causes other than predation (eg. whether they sink to the bottom and transport the mercury to sediments and benthos).

Finally, when dealing with mercury fluxes by entire populations of fish, it is important to account for the mercury which passes through the fish undigested, in addition to the mercury cleared from fish tissue. Fluxes related to this process are discussed in the following sections.

9.0 APPLICATION OF THE COMPLETE MODEL TO A GENERIC SHIELD LAKE

With the development of the thermodynamic and bioenergetics components of the model completed, the entire model was applied to three systems:

1- A generic oligotrophic/mesotrophic shield lake in Ontario

2- Eastern Basin of Clay Lake, Ontario

3- Lake St. Clair, Ontario/Michigan

In addition, mercury cycling in East Fork Poplar Creek, Tennessee, and a generic hydroelectric reservoir were considered although not modelled comprehensively. This section of the report discusses simulations involving the generic shield lake. Applications of the model to real systems (Clay Lake and Lake St. Clair) are discussed in Section 10.

Application of the entire model to a generic shield lake allowed the credibility of many of the rate constants assumed typical for oligotrophic to mesotrophic freshwaters to be tested, and in some cases bounded. Process rates considered plausible in the generic simulations were then examined further for real systems in Section 10.

9.1 Definition of Generic Shield Lake Conditions

A hypothetical "generic" lake was used to represent conditions considered typical of a small oligotrophic or mesotrophic lake in the Canadian shield in Ontario. Generic conditions were assumed due to the lack of a comprehensive dataset for a real shield lake, upon which the entire model could be calibrated. The basic characteristics of the lake are outlined in Table 9.1. The lake was assumed to have a 2 year hydraulic residence time, 1 km^2 area, 10 m mean depth, suspended solids concentration of 2 mg L^{-1} and TOC concentration of 2-3 mg L^{-1}. The lake was also assumed to be well mixed. Hg(II) and methylmercury concentrations in solution in inflows were 2.5 and 0.1 ug m^{-3} respectively. Particulate mercury concentrations in inflows were 0.15 ug g^{-1} and 0.0075 ug g^{-1} for Hg(II) and methylmercury respectively.

Rate constants for several simulated processes in the generic shield lake are presented in Table 9.2. Settling velocities were assumed to be in the range of 0.15 to 0.5 m day^{-1}, resuspension velocities were on the order of 10^{-5} m day^{-1}, and burial rates between 0.2 to 1.0 mm $year^{-1}$ (lower than might be expected in many other systems). Parameters related to fish biomass and bioenergetics have been previously developed in Section 8 and are outlined in Table 8.3. Aerobic conditions were assumed and the thermodynamic equilibria developed in Section 8 were used for these simulations.

Table 9.1
Selected Physical Inputs Used in Simulations
of a Generic Shield Lake

Characteristic	Value	Units
Hydraulic Residence Time	2.0	Years
Volumes		
- Air	$6 * 10^9$	m^3
- Water	$1 * 10^7$	m^3
- Sediment	30000	m^3
- Suspended Solids (2 mg/L)	13.3	m^3
- Water Column Plankton (2 ppmv)	20	m^3
- Benthos (200 Kg/ha)	20	m^3
- Prey Fish (1.5 ppmv)	15	m^3
- Predatory Fish (0.25 ppmv)	0.25	m^3
Areas:		
- Air/Water	$1 * 10^6$	m^2
- Water/Sediment	$1 * 10^6$	m^2
Solids Density	1.5	Kg/L
Sediment TOC	25.0	% dry
Water Column TOC	1.75	mg/L
Water Column Dissolved Humics	$1 * 10^{-5}$	Molar
Porewater Dissolved Humics	$5 * 10^{-5}$	Molar
Water Column pH	7.0	
Water Column Dissolved Oxygen	8.0	mg/L
Porewater Dissolved Oxygen (active layer near surface)	6.0	mg/L
Sediment Porosity (top,bottom)	0.95, 0.9	

Table 9.2
Selected Model Rate Constants for a Generic Shield Lake

Process	Variable Name	Rate			
		MeHg	Hg(II)	DiMeHg	Hg°
Volatilization (air side) (m day^{-1})	MTC_{air}	-	-	100	100
Volatilization (water side) (m day^{-1})	MTC_{wat}	-	-	0.5	0.5
Porewater/Water Column exchange (m day^{-1})	MTC_{o}	0.01	0.01	0.01	0.01
Rain Deposition Velocity (m day^{-1})	V_{rain}	0.002	0.002	-	-
Henry's Law Constant (dimensionless)	H	$1.9 * 10^{-5}$	$6.4\ 10^{-7}$	0.3	0.3
Dry Particle Settling in Air (m day^{-1})	V_{dry}	860	860	-	-
Suspended Solids Settling (m day^{-1})	V_{settle}	0.5	0.5	-	-
Resuspension Velocity (m day^{-1})	V_{resusp}	$9.5 * 10^{-6}$	$9.5 * 10^{-6}$	-	-
Burial Velocity for Sediments (m day^{-1})	V_{burial}	$2.0 * 10^{-6}$	$2.0 * 10^{-6}$	-	-

Table 9.2 (Continued)
Selected Model Rates for a Generic Shield Lake

Process	Variable Name	Rate			
		MeHg	Hg(II)	DiMeHg	Hg°
Transformations: (day^{-1})					
Water Column Reduction	K_{redwat}	-	$2.5 * 10^{-4}$	-	-
Methylation and Demethylation Related:					
- Carbon Degradation Rate in Water	r_{wat}	0.001	0.001	-	-
- Carbon Degradation Rate in Sediment	r_{sed}	0.0001	0.0001	-	-
- Methylation Rate for total Hg(II) dissolved in water*		-	0.0001		
- Methylation Rate for total Hg(II) dissolved in porewater**		-	0.0025	-	-
- Demethylation Rate for total MeHg dissolved in water***		0.002	-	-	-
- Demethylation Rate for total MeHg dissolved in porewater****		0.045	-	-	-

* - This rate is actually a combination of several variables and assumes the TOC in water is 2 mg/L, a bacterial yield of 0.014 ug MeHg per ug TOC, and an available fraction of Hg(II) dissolved in water for methylation of 0.0017

** - This rate is actually a combination of several variables and assumes a sediment TOC content of 25% dry wt, a bacterial yield of 0.0005 ug MeHg per ug TOC, and an available fraction of Hg(II) for methylation in porewater of 0.0007

*** - This rate is actually a combination of several variables and assumes TOC in water is 2 mg/L, a bacterial yield of 0.005 ug Hg° per ug TOC, and an available fraction of MeHg dissolved in water for demethylation of 0.0047

**** - This rate is actually a combination of several variables and assumes a sediment TOC content of 25% dry wt, a bacterial yield of 0.0001 ug Hg° per ug TOC, and an available fraction of Hg(II) for methylation in porewater of 0.0027

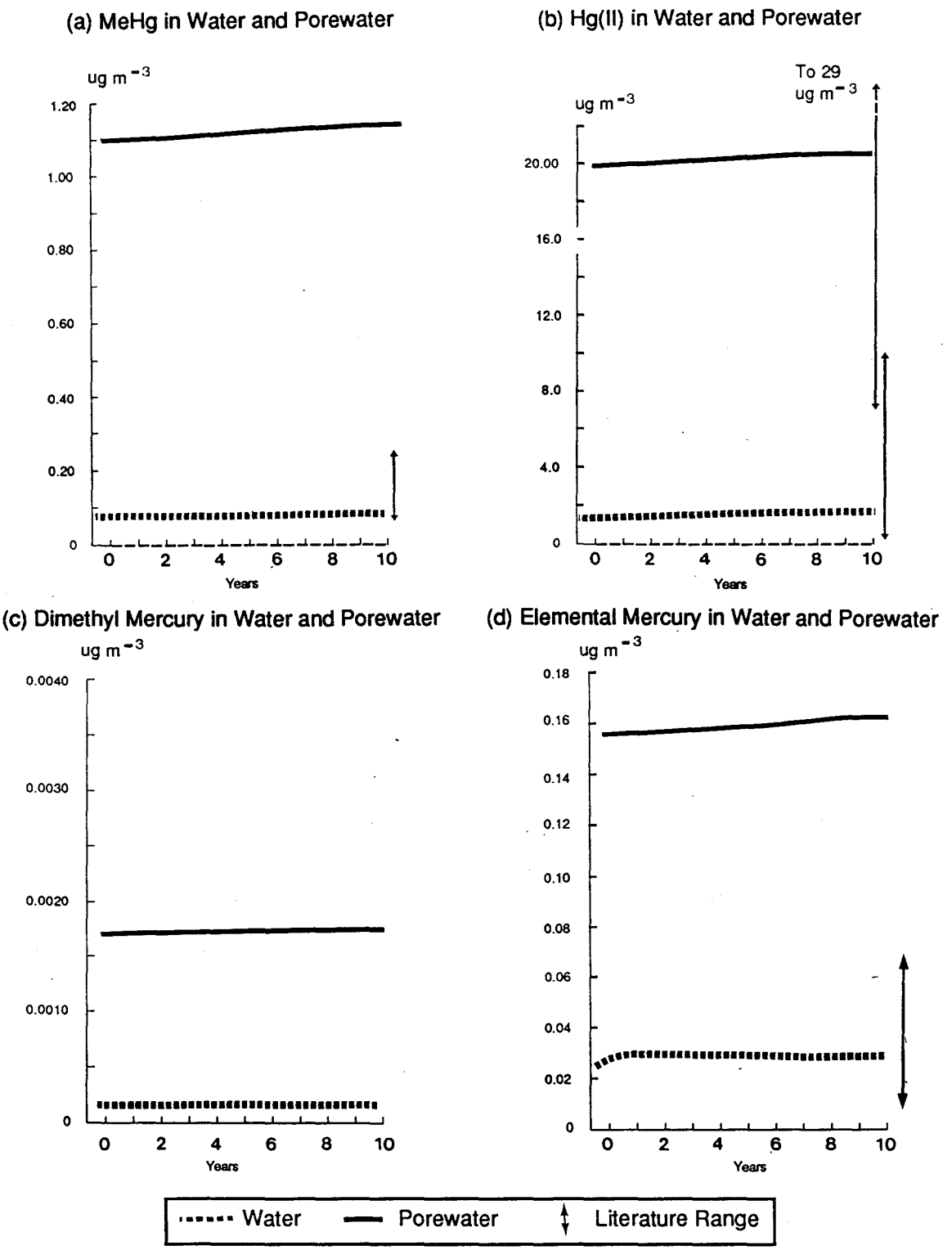
9.2 Simulation Results for the Generic Shield Lake

The model was run until essentially steady-state conditions developed. Figures 9.1 to 9.4 summarize the results of the simulation. There was a slight trend towards increasing Hg(II) and methylmercury in the system with time. The rates of increase were small (0.5% per year or less in either case), diminished as the simulation progressed, and do not affect the conclusions of the study. A longer simulation (30 years) was run using the same dataset, and resulted in stable conditions very nearly identical to those occuring after 10 years.

9.2.1 Mercury Concentrations in the Generic Shield Lake

Figure 9.1 shows mercury species in solution in surface water and porewater. Where possible, estimates of typical concentrations in unpolluted freshwaters are indicated in the Figure. Methylmercury concentrations in water (dissolved phase) ranged from 0.05 to 0.10 ug m^{-3}, and dissolved Hg(II) ranged from 1.3 to 1.6 ug m^{-3}. These values are within ranges of recently reported values for aerobic lakewaters (eg. 0.05 to 0.2 ug m^{-3} for methylmercury and 0.5 to 2.0 ug m^{-3} for Hg(II), see Section 4.2.4). Dimethyl mercury concentrations were virtually insignificant, since no significant production was included in the simulation. Elemental mercury concentrations in surface waters were in the range of 0.025 to 0.03 ug m^{-3}. Few measurements of elemental mercury in freshwaters have been made. Vandal et al. (in press) reported values in the range of 0.007 to 0.07 ug m^{-3} for remote waters in Wisconsin.

FIGURE 9.1
Simulated Mercury Concentrations in Solution in the Generic Shield Lake

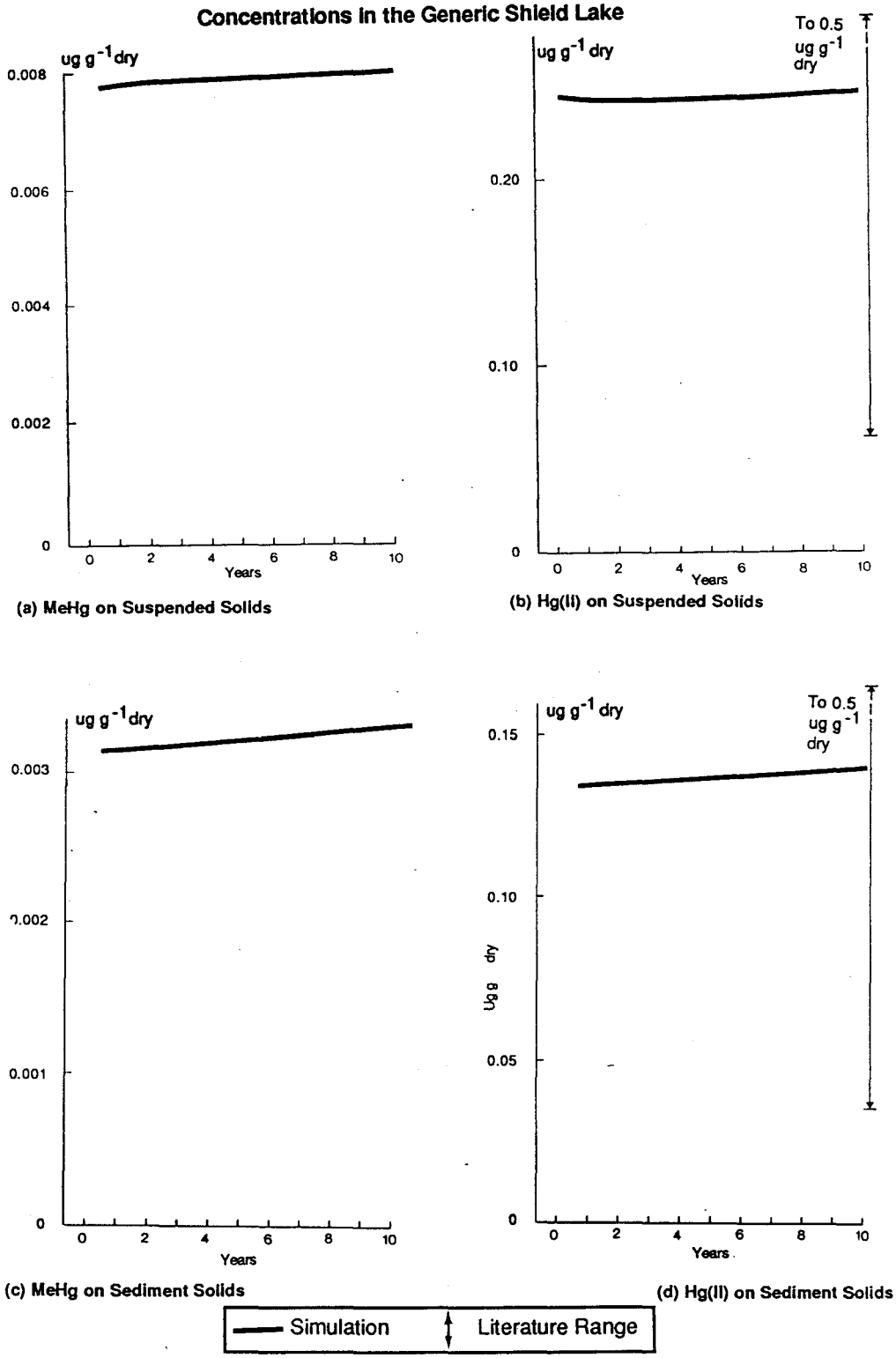


Limited field data were available to compare porewater Hg(II) predictions against. Simulated porewater Hg(II) concentration were in the vicinity of 20 ug m^{-3}, within the range of 7 to 29 ug m^{-3} total mercury reported by Andren and Babiarz (1990) in surficial porewaters from Little Rock Lake, Wisconsin. These results suggest a net diffusive flux of Hg(II) from porewater to overlying waters.

Figure 9.2 shows simulated particulate mercury concentrations in equilibrium with surface waters and porewater. Hg(II) on suspended solids was in the range of 0.20 to 0.25 ug g^{-1}, while on sediment solids the value was lower, approximately 0.15 ug g^{-1}. It is not clear from literature whether Hg(II) concentrations on suspended particulates in the water column are generally higher than on sediment solids. The simulated results also reflect an assumed lower Hg(II) partition constant for sediment solids than suspended solids. Lower partition constants in sediments may reflect particle interactions and different substrates for adsorption (eg. sediment solids may be lower in organic content). Simulated methylmercury in suspended solids ranged from 0.006 to 0.008 ug g^{-1}, while the concentration in sediment solids was lower, at 0.003 ug g^{-1}. Field data against which to compare these values are very limited for unpolluted systems. Bloom and Watras (1989a) reported particulate methylmercury concentrations in oxic surface waters of Little Rock Lake, Wisconsin, on the order of 0.01 ug g^{-1}.

At this point it is instructive to discuss the approach used in the model to partition mercury between fixed and exchangeable adsorption sites on particulates. One purpose of using fixed and exchangeable fractions of Hg(II) was to provide a framework to reconcile wide

FIGURE 9.2
Simulated Particulate Mercury Concentrations in the Generic Shield Lake



ranges of total mercury to methylmercury ratios for various systems. Although methylmercury may represent on the order of 5% of total mercury in typical aerobic freshwaters, Elwood et al. (1987) reported methylmercury and total mercury concentrations in water in the range of 0.5 and 3400 ug m^{-3} respectively, i.e. a ratio of less than 0.1%, in East Fork Poplar Creek, Tennessee. If methylation only involved dissolved Hg(II), irreversible partitioning of most Hg(II) onto solids could help explain low quantities of methylmercury relative to total mercury in some systems.

Simulations for the generic shield lake were initially structured to partition most particulate Hg(II) into the fixed component of particulates. Difficulties arose however in terms of obtaining plausible results. Since the model did not include any reactions which would transfer mercury between fixed and exchangeable particulate fractions, the concentrations of fixed Hg(II) in sediment solids always tended towards the fixed concentration on inflowing suspended solids. Other difficulties were encountered when most particulate mercury was assumed to be fixed. Most Hg(II) entering the lake via runoff or precipitation was assumed to be exchangeable. If most mercury in suspended solids was assumed to be fixed, it was difficult to remove exchangeable mercury via settling and outflows sufficiently that the lake would act as a significant sink for total mercury.

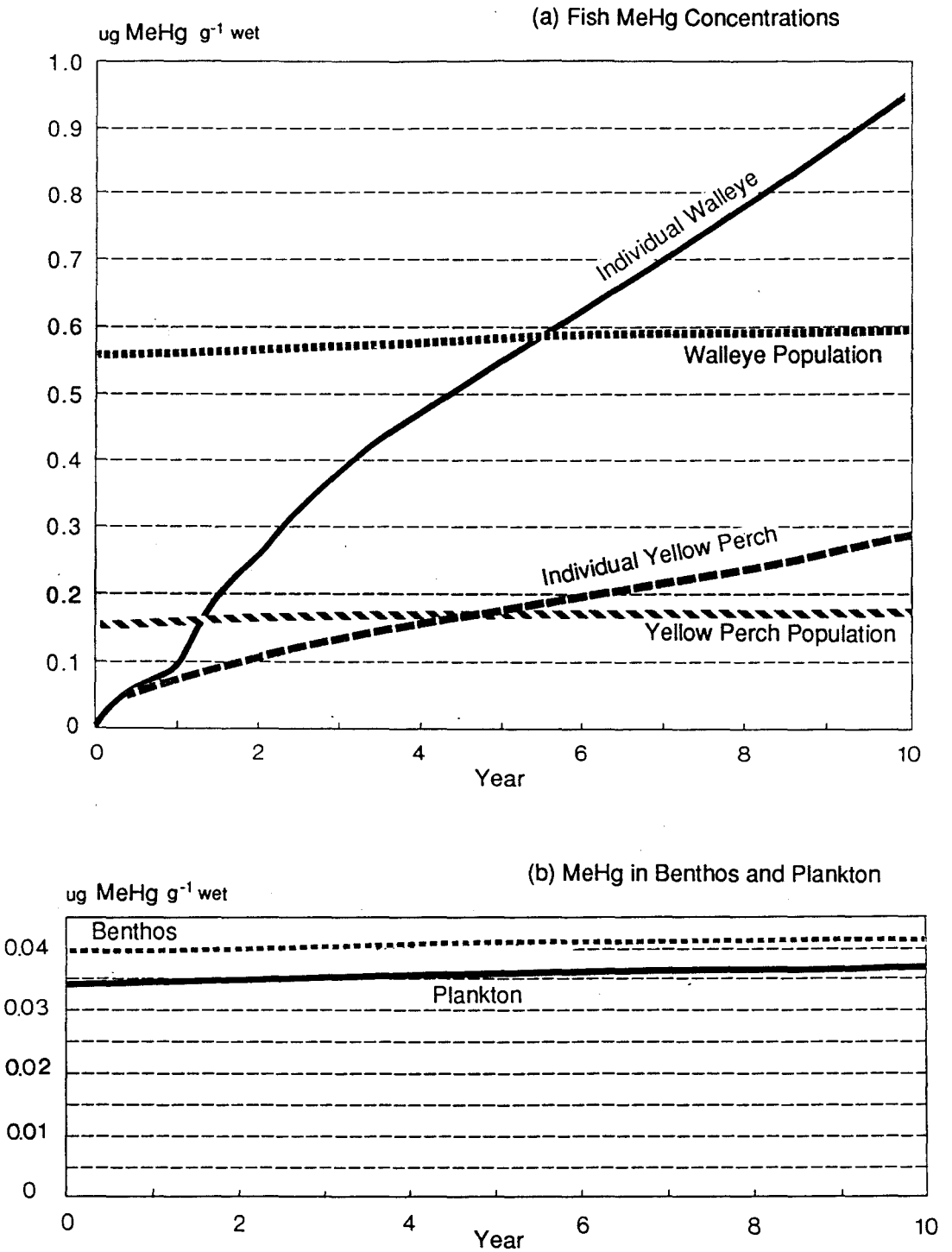
In lieu of the above difficulties, it was decided to use an alternate approach for this study where almost all Hg(II) on particulates (e.g. 99%) was exchangeable. To accommodate low ratios of methylmercury to total mercury in systems such as East Fork Poplar Creek, higher solids partition coefficients could be used to keep dissolved Hg(II) concentrations at

lower values. This would restrain methylation, which was assumed to utilize only dissolved Hg(II). There are shortcomings to this approach. One might overestimate quantities of exchangeable mercury on sediments which are resuspended to the water column, and predict unrealistic time periods for exchangeable Hg(II) to respond to system changes and reach a new steady-state. Further development of the fixed/exchangeable approach is recommended. Processes such as gradual fixation of mercury in sediments or perhaps by plankton in the water column (which subsequently die and become suspended particulate matter), or the gradual release of fixed mercury to the exchangeable pool should be considered in future versions of the model.

Figure 9.3 illustrates simulated methylmercury concentrations in biota for the generic shield lake. Methylmercury in plankton was in the range of 0.03 to 0.04 ug g^{-1} wet weight. Total mercury in plankton was in the range of 0.05 to 0.06 ug g^{-1} wet weight. These concentrations reflect assumed water/plankton partitioning rather than kinetic processes. Benthos methylmercury concentrations were in the range of 0.04 ug g^{-1} wet weight. Total mercury concentrations in benthos were approximately 0.07 ug g^{-1} wet weight. Wide ranges of plankton and benthos total mercury concentrations are reported in the literature (see Table 4.2). The simulated concentrations fall within reported ranges for unpolluted freshwaters.

Figure 9.3 also shows methylmercury concentrations in individual yellow perch and walleye hatched at the beginning of the generic simulation. Mean concentrations of methylmercury for fish populations are also shown in Figure 9.3. Simulated mercury concentrations increased during the lifetimes of walleye and yellow perch. Age 1+ yellow

FIGURE 9.3
Simulated Methylmercury Concentrations
in Biota in the Generic Shield Lake



perch methylmercury concentrations were in the range of 0.08 to 0.10 ug g^{-1}, increasing to about 0.17 ug g^{-1} by age 5 years. Simulated walleye concentrations were higher, and showed distinct jumps at ages 1 and 2 years, when changes in diet from benthos to yellow perch were simulated. A 1 kg walleye would be roughly 4 years old for this simulation, and the methylmercury concentration at this age was in the range of 0.45 to 0.50 ug g^{-1}. Wren et al. (in press) estimated a mean mercury concentration of 0.58 ug g^{-1} (range 0.09 to 3.24 ug g^{-1}) in standardized 41 cm walleye from a survey of 255 Ontario lakes. Older walleye (10-15 years old) in the simulation were predicted to exceed 1 ug g^{-1}. The mean population concentration of methylmercury simulated in yellow perch was in the range of 0.15 to 0.20 ug g^{-1}, reflecting a population distribution with most biomass in the 2-4 year old range. The mean methylmercury concentration for the walleye population was higher at 0.55 - 0.60 ug g^{-1}. This was due to higher concentrations in walleye than yellow perch at any given age, and a population distribution with most of the biomass occuring in slightly older fish (3-6 year olds, see Figure 8.14).

9.2.2 Mercury Fluxes in the Generic Shield Lake

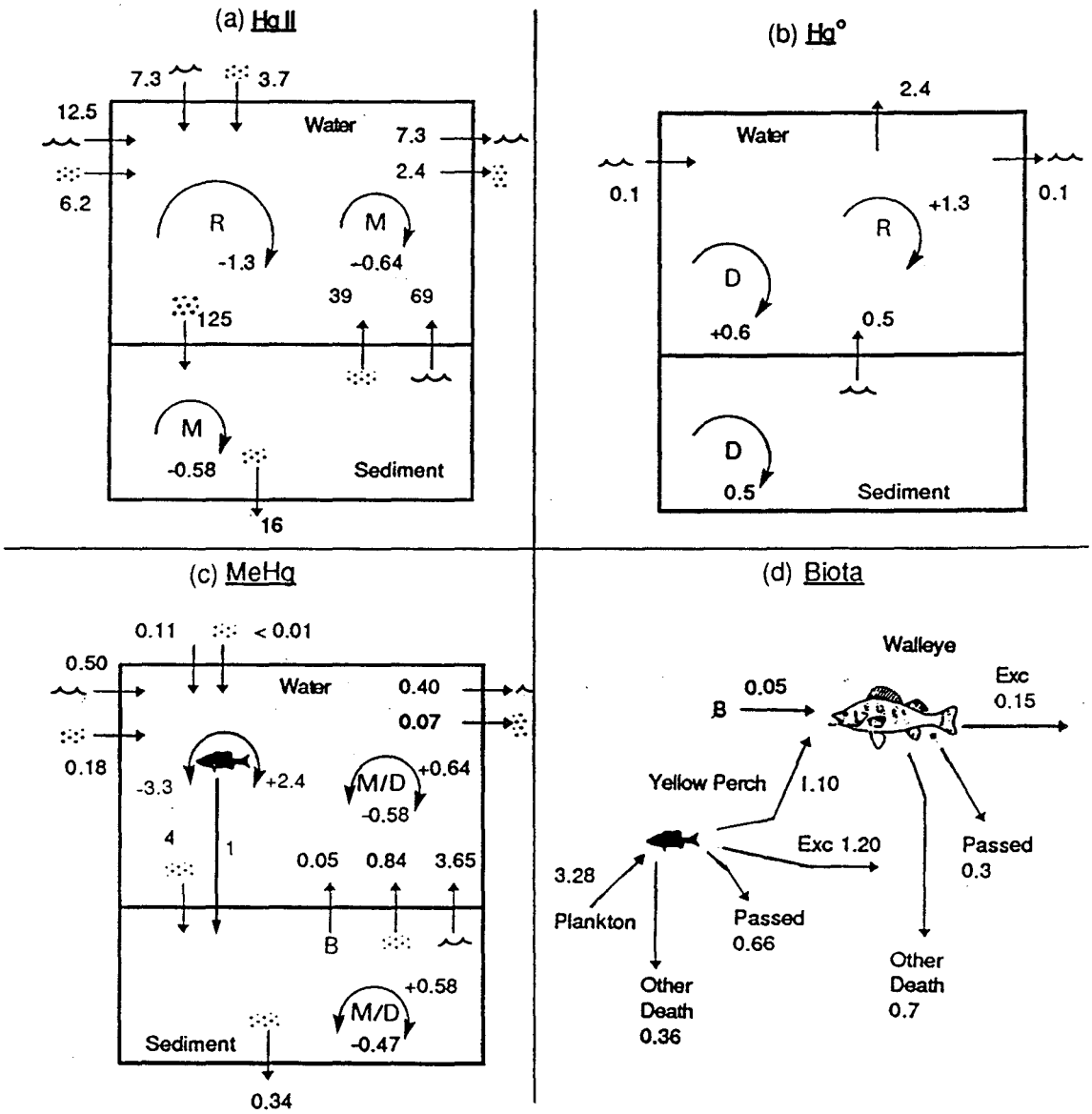
Figure 9.4 shows simulated mercury fluxes after 5 years had passed in the generic shield lake simulation. By this time in the simulation, stable trends were established.

Hg(II) Fluxes in the Generic Shield Lake

Figure 9.4 (a) shows simulated Hg(II) fluxes in water and sediments. The atmosphere deposited about 11 ug Hg(II) m^{-2} yr^{-1} on the lake, two thirds of which was in wet deposition. Runoff loaded 18-19 ug m^{-2} yr^{-1}. The simulated lake acted as a trap for Hg(II), with burial representing the largest sink, removing 16 ug m^{-2} yr^{-1}, or 55% of the total load. Although direct atmospheric and runoff loadings of Hg(II) were comparable for this scenario, system to system variability in residence time, humic matter in inflows, etc. will affect the relative importance of these two loading pathways. Either route has the potential to dominate in some situations.

The relative importance of various Hg(II) sinks could also change from system to system. In the generic lake simulations, internal mechanisms caused Hg(II) concentrations in surface waters to drop 40% from inflowing streams to lakewaters, i.e. from 2.5 to 1.5 ug m^{-3}. Such differences should be measurable in actual systems, but some attention to statistical design of monitoring efforts would be required. The largest single Hg(II) flux was settling of suspended solids. Once Hg(II) settled into the sediment compartment however, the net burial rate was a small flux relative to settling. Most mercury was redirected upwards back into the water column through resuspension and diffusion. Thus the net Hg(II) flux across the sediment/water interface was almost an order of magnitude lower than any of the unidirectional fluxes such as settling. Resuspension and diffusion rates are difficult to estimate and significant uncertainty is associated with these parameters.

FIGURE 9.4
Simulated Mercury Fluxes
for the Generic Shield Lake (ug Hg m^{-2} $year^{-1}$)



Methylation and reduction of Hg(II) were significant but relatively small fluxes in comparison to the physical transport processes (see Figure 9.4). Estimates of rates for these processes were based primarily on analyses of methylmercury and elemental mercury cycling and are discussed below.

Hg° Fluxes in the Generic Shield Lake

The dominant input processes for elemental mercury in the generic shield lake were reduction of Hg(II) and demethylation of methylmercury in sediments and the water column. The fluxes shown in Figure 9.4 (b) reflect the assumption that the air/water interface is a net source of mercury to the lake. Volatilization was the dominant sink for the system, and at steady-state would nearly equal loading of Hg°. This effectively constrained the sum of Hg(II) reduction and demethylation to 11 g yr^{-1} or less at steady state (see Figure 9.4 (a) for atmospheric loading of Hg(II)). Due to a lack of information regarding the relative magnitude of Hg(II) reduction and demethylation, the two processes were assumed comparable in magnitude. The resulting reduction rate was about 10% of Hg(II) per year in the water column. As discussed in Section 7.7.1, rates of Hg(II) reduction in unpolluted systems are not well quantified. Much higher Hg(II) reduction rates (eg. 10-60% per day) have been observed in some polluted systems (Turner et al., 1989). The potential exists for Hg(II) reduction to be more significant than simulated in this scenario. The high Hg° production rates described above for some polluted situations however would likely generate Hg° concentrations far above those assumed representative of unpolluted systems for this study.

Higher rates of demethylation than those used would also cause simulated elemental mercury concentrations to rise significantly. As simulated in this scenario, demethylation consumed methylmercury at a rate of about 3-5% of the total amount in sediments per year, and 50-75% per year in the water column. These estimates are speculative due to a lack of field data. Research regarding these rates would be very instructive.

Once demethylation rates were estimated in the water column and sediments, specific methylation rates could be estimated such that net methylation would occur. It should be noted that net bacterial production of methylmercury in the aquatic system is an assumption. It is hypothetically possible that bacteria could act as net demethylators.

Assuming the concentration of elemental mercury in freshwaters is typically in the range of 0.01 to 0.05 ug m^{-3} and piston velocities are in the range of 0.25 to 1.0 m day^{-1}, volatilization would represent the major removal mechanism for Hg°, assuming oxidation rates for elemental mercury are slow. Figure 9.4 (b) indicates that simulated volatilization of Hg° at the air/water interface was in the range of 2.0 to 2.5 ug m^{-2} $year^{-1}$ in the generic system. As stated above, this represented the dominant Hg° loss mechanism from the system. This flux was also significant in terms of total mercury cycling, representing about 20% of atmospheric deposition of total mercury. Considerable uncertainty is assigned to these estimates, since piston velocities are not well defined across the air/water interface and few observations of elemental mercury concentrations in surface waters or air/water flux measurements are available. An air/water piston velocity of 0.5 m day^{-1} and an air concentration of elemental mercury of 0.003 ug m^{-3} were assumed. Kim and Fitzgerald (1986) reported a piston velocity

of 5.1 m day^{-1} for tropical oceanic waters. This higher value may be due to increased wind mixing and circulation in oceanic waters relative to fresh waters, and does not necessarily preclude a lower value for small freshwater systems.

Abiotic Methylmercury Fluxes in the Generic Shield Lake

Figure 9.4 (c) shows methylmercury fluxes in the water column and sediments. Inflows from the watershed represented 0.7 ug m^{-2} $year^{-1}$, or 85% of total external loading of methylmercury to this system. Atmospheric deposition represented 0.1 ug m^{-2} $year^{-1}$ (15%). Burial represented about 0.3 to 0.4 ug m^{-2} $year^{-1}$, or about 40% of the external load to the lake. As noted for Hg(II) previously, significant variation is possible regarding methylmercury loading in runoff and via direct atmospheric deposition in different regions and circumstances. It was assumed that the inflowing water concentration of methylmercury was 0.1 ug m^{-3} while the methylmercury concentration in rain was 0.15 ug m^{-3}. Field measurements of methylmercury concentration in runoff are sparse. Lee and Iverfeldt (1990) reported methylmercury concentrations in streamwaters ranging from 0.01 to 0.64 ug m^{-3}, while values in lake waters ranged from 0.04 to 0.80 ug m^{-3}. Data are also lacking to indicate whether lakes are net sources or sinks for methylmercury.

In-Situ Methylation and Demethylation in the Generic Shield Lake

To examine the potential significance of in-situ methylation and demethylation, a simulation was carried out with no methylation or demethylation in the system. Under these circumstances, water methylmercury concentrations stabilized at approximately 0.06 ug m^{-3}. This is slightly less than the results obtained with active methylation in-situ (eg. 0.07 - 0.09 ug m^{-3}). In the simulation with no in-situ methylation, methylmercury concentrations in porewater and sediment solids were in the range of 0.9 ug m^{-3} and 0.003 ug g^{-1} respectively. These values do not seem unreasonably low. Based on this simulation, the watershed could be a significant source of methylmercury in some shield lakes. Field data documenting methylmercury loading and sinks in a shield lake would be very useful in combination with methylation/demethylation measurements. Such data could help resolve the significance of internal and external methylmercury loading sources.

It was somewhat arbitrarily decided to make in-situ net methylation significant but not dominant, equal to approximately 30% of external methylmercury loading. The majority of in-situ methylation was assumed to occur in sediments (50-75%) as opposed to the water column. These numbers are speculative. To prevent an unrealistic buildup of methylmercury in the generic system, the specific rates of methylation and demethylation used were about an order of magnitude lower than rates developed initially in Appendix D. Both processes were assumed significant, with methylation typically exceeding demethylation by 10% to 100%. An alternative method of simulating lower rates of net methylation would be to assume rapid bacterial cycling of methylmercury (high rates of production and degradation), but little net

production (demethylation nearly equalling methylation). As discussed previously however, high rates of demethylation could result in higher concentrations of elemental mercury. Pending improvements in analytical techniques to measure methylation and demethylation at natural rates will be very useful.

Methylmercury Cycling by Biota in the Generic Shield Lake

As shown in Figures 9.4 (c) and 9.4 (d), biota are estimated to play a significant role in methylmercury cycling. When fluxes for walleye, yellow perch, plankton and benthos are examined, internal cycling of methylmercury between the water column and biota is described by fluxes well in excess of external sources or sinks. For the conditions assumed in the simulation (total fish biomass density of 1.75 ppm), incorporation of methylmercury into yellow perch via consumption of plankton was one of the largest fluxes in the system. Once taken up by yellow perch, methylmercury was cycled by biota in the simulation as shown in Figure 9.4 (d). Some of the mercury consumed in plankton was not absorbed and passed unassimilated through the fish. Based on the assumed conditions, about 20 percent of the mercury in eaten plankton passed through the yellow perch population unassimilated. For yellow perch, losses from excretion represented another 40 percent of the total amount of methylmercury eaten. "Other mortality" represented another 10 percent and was assumed to represent a flux to sediments.

Roughly one-third of the methylmercury in consumed plankton was transferred up the food chain via consumption of yellow perch by walleye. This flux represented 95% of the

uptake of methylmercury by walleye. The remaining 5% was estimated to occur through consumption of benthos. Walleye cannibalism would redistribute methylmercury in the population but was ignored for the purposes of examining fluxes into and out of the population as a whole.

Although individual fish increase their mercury content throughout their lives, the population must establish a steady-state burden of mercury. Methylmercury losses from the fish pool via mortality must make up the difference between uptake and depuration. These losses include death by disease or old age, fishing and consumption by predators. If dead fish indeed sink to the bottom and decompose, settling biota could represent significant fluxes from water to sediments. In these simulations, the main loss of methylmercury from the walleye population was via mortality other than predation (approximately 65% of the methylmercury eaten by the walleye population). This flux was assumed to settle to the sediments. Methylmercury in settling fish represented about 1/4 of the methylmercury flux due to other settling suspended solids. Excretion eliminated only 15-20%% of the mercury eaten by walleye, while another 25% to 30% of this intake passed through the fish undigested. It was assumed that methylmercury passing through a fish unassimilated ultimately ended up in solution in the water column.

"Other mortality" was calculated on the basis of the difference between population productivity and losses from the population by being eaten by predators. Various checks were made in terms of the productivity and biomasses predictions for walleye and yellow perch. For the assumed conditions, productivity was 11.6 kg ha^{-1} yr^{-1} for walleye and 106 kg ha^{-1} yr^{-1}

for yellow perch. These fall within rather wide ranges of productivity noted in the literature. Wetzel (1983) suggested a productivity range of 10 to 200 kg ha^{-1} yr^{-1} for standing waters in temperate regions with one dominant species. Productivity to biomass ratios (a measure of the rate of turnover of the population) were also calculated. The predicted values of 0.45 and 0.7 yr^{-1} for walleye and yellow perch respectively fall with a range of estimates (0.18 to 5.5 yr^{-1}) discussed by Wetzel (1983) for freshwaters. No information could be found in the literature against which to compare estimates of the fraction of mortality represented by disease or old age, nor was any information found on the fate of fish dying by such causes. For this simulation, 80% of yellow perch mortality (on a mass basis) was represented by predation. Only 8% of the walleye mass lost via death was due to predation. These numbers are very preliminary estimates and further research in this area would be instructive.

Significant uncertainty is associated with these methylmercury fluxes, since such fluxes depend on fish species, growth rates, diets, sources of mortality, population distributions and biomass. The results should be viewed from the perspective that they indicate the potential for biota to represent significant methylmercury fluxes within aquatic systems, both in the water column and across the sediment/water interface. Further model refinements and data for calibration would be very useful.

9.2.3 Response Times in the Generic Shield Lake

In this study, response time is a measure of the time required to achieve a new steady-state if a system is perturbed, and can be expressed in terms of a half-life. Response time half

lives were determined on an instantaneous basis at any desired time in the simulations. The response time half-life was calculated on the basis of the time required for mercury sinks in a compartment to remove 50% of the mercury burden in that compartment.

Table 9.3 shows response times estimated for methylmercury and Hg(II) in various compartments in the generic shield lake. It is important to note that in the event of a variation from steady state conditions (eg. a sudden Hg(II) load to lake), the time observed for concentrations to drop 50% is not necessarily the same as the response time half-life in a given compartment. For example, the water column was predicted to respond relatively rapidly to changes in Hg(II) loading (eg. 1-2 months response time half-life). If, however, the loading change was a gradual change in load with time (eg. 50% drop every few years) rather than a step function, then the Hg(II) concentration in water would tend to mimick the longer term change in loading.

Table 9.3
Simulated Response Times for a Generic Shield Lake

Compartment	Response Time Half-Life
Methylmercury:	
- Water, Sus. Solids, and Plankton	50 days
- Sediment Solids and Benthos	1.5 years
- Yellow Perch Population	0.6 years
- Walleye Population	1.3 years
Hg(II):	
- Water, Sus. Sol. and Plankton	40 days
- Sediment Solids	3.0 years

Furthermore, feedback loops are possible between compartments, with mercury being cycled relatively rapidly between compartments, but not leaving the overall system. It was predicted for example that if Hg(II) loading to the generic shield lake was increased by an order of magnitude for five years and returned to normal loading by a step function, concentrations of Hg(II) dropped in the water column and sediments at a rate of about 50% each 15 years. This rate was far slower than response time kinetics might suggest in any given compartment, but reflected the response of the overall system.

The processes controlling recovery of the generic system in terms of total mercury were burial and outflow at the system boundaries. It is quite possible that Hg(II) reduction to Hg° or methylation could occur at faster rates, lowering the recovery time of the system considerably. Other systems may have greater burial rates or outflow rates as well, which would improve recovery times.

Simulated methylmercury dynamics in the generic shield lake also exhibited a trend towards internal response kinetics more rapid than the overall system response. For the above hypothetical scenario (5 year increased Hg(II) load), methylmercury concentrations responded quite slowly to increased in-situ methylation. The major restorative processes for methymercury were demethylation, burial and resuspension of sediment solids in combination with outflows. A noteworthy feature of the simulation was the tendency of methylmercury concentrations in water, sediments and biota to continue to increase for several years after the Hg(II) load was reduced. This occured since Hg(II) levels started to decline after 5 years, but remained above background levels and resulted in increased methylmercury loading for many

years. Decades were required for methylmercury concentrations to decline to background levels. These recovery rates would apply only to the scenario simulated. Increased demethylation, burial or outflows in other systems could improve system recovery times considerably. Demethylation rates are unknown in natural systems and could be considerably faster (eg. by an order of magnitude) than simulated for this scenario.

9.2.4 Mercury Distribution in the Generic Shield Lake

Table 9.4 shows the mass distribution of mercury in the generic system 5 years into the simulation. More than 90% of Hg(II) was estimated to be in sediments. This value varies with the depth of active sediment assumed (3 cm in this case). Methylmercury represented a small but significant fraction of total mercury in the system (3%), and was distributed primarily in sediments and biota. Sediments contained about 60% of methylmercury in the system while biota accounted for another 30%, and water 5%. The ratio of methylmercury in fish to water was approximately 4:1. It is important to remember that these estimates reflect assumed biota densities of 2 ppm each for benthos and plankton, 1.5 ppm for yellow perch and 0.25 ppm for walleye. Significant system to system variations will occur in lakes with varying degrees of productivity. Furthermore, the use of walleye and perch in this model is simply intended to provide examples of predatory and prey species. Obviously, many variations in terms of species composition and abundance will occur from system to system.

Table 9.4
Simulated Mercury Distribution in a Generic Shield Lake
(% in Each Compartment, by Mercury Form)

	MeHg	Hg(II)	Dimethyl	Elemental	Total
Air	0.01	0.08	<.01	3.0	3.1
Water	0.15	2.55	<.01	0.05	2.7
Sus. Sol.	0.03	0.85	N/A	N/A	0.88
Total Sediment	1.93	90.1	<.01	<.01	92.1
Plankton	0.12	0.07	N/A	N/A	0.2
Benthos	0.14	0.1	N/A	N/A	0.25
Yellow Perch	0.41	<.01	N/A	N/A	0.41
Walleye	0.25	<.01	N/A	N/A	0.25
TOTAL	3.0	93.7	<.01	3.1	100

10.0 Application of the Complete Model to Real Systems

Application of the entire model to a generic lake in Section 9 allowed the plausibility of several rate constants assumed "typical" for oligotrophic to mesotrophic freshwaters to be tested, and in some cases bounded. Based on the results of the generic shield lake simulation, the complete model was applied to two real systems:

1- Eastern Basin of Clay Lake, Ontario

2- Lake St. Clair, Ontario

The datasets for these two waterbodies are not adequate for model validation. The simulations in this section were additional calibrations which tested the plausibility of several rate constants developed in the generic shield lake simulation. These simulations also tested the ability of the model to reflect observed mercury trends in two aquatic systems and provide further insights regarding response times of aquatic systems.

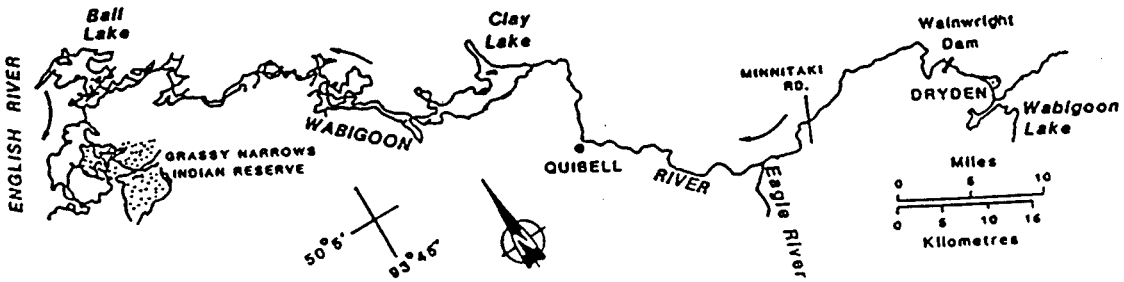
Section 11 will present an overall discussion of simulation results in the context of mercury cycling in natural lakes and industrially polluted systems. Mercury cycling in reservoirs and East Fork Poplar Creek, Tennessee (a mercury polluted system not simulated in this study), will also be discussed in Section 11, based on insights gained from simulations in this section.

10.1 Application of the Model to the Eastern Basin of Clay Lake, Ontario

Mercury pollution in the Wabigoon-English River system in Ontario is a well known and intensively studied situation (Parks et al. 1989, Schroeder et al. 1989, Parks and Hamilton 1987, Parks et al. 1986, Government of Canada/Government of Ontario, 1984). Particularly detailed studies were carried out in the 1979-1981 period as a result of a provincial/federal agreement established in 1978. Figure 10.1 shows the Wabigoon River between Dryden and Ball Lake. Elevated levels of mercury have been reported in this system in aquatic biota since 10 tonnes of inorganic mercury were loaded into the Wabigoon River at Dryden between 1962 and 1970 from a chloralkali plant (Parks et al., 1989). Mercury discharges from the plant were decreased by 99% in the early 1970's. Although declining concentrations in sportfish and crayfish have been observed in the system from values as high as 10-20 ug g^{-1} in the early 1970's (Government of Canada/Government of Ontario, 1984), mercury concentrations remain elevated relative to background values.

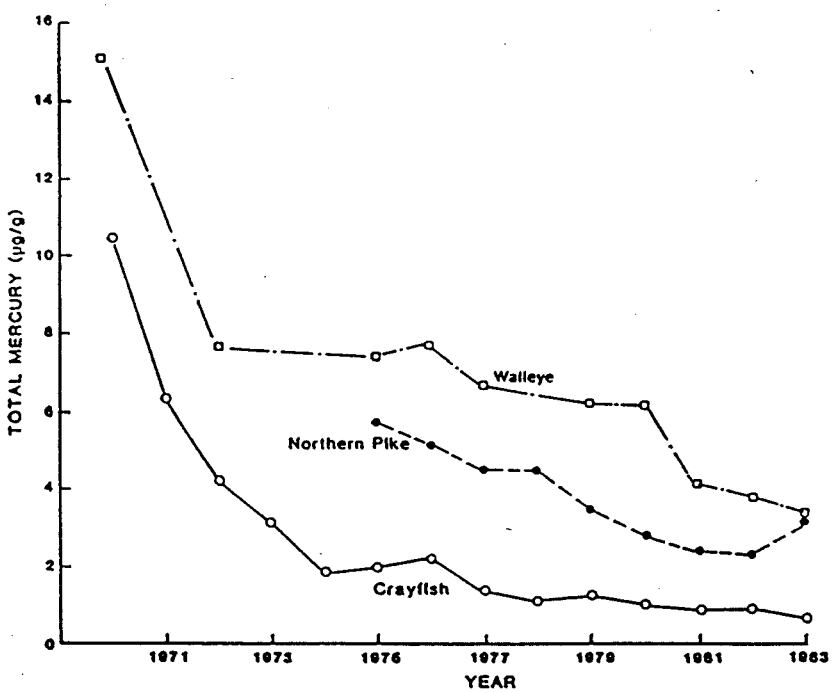
Based on average flows, Clay Lake is situated approximately 5 days time-of-travel downstream from Dryden (Parks et al., 1989). The lake has two main basins. Parks and Hamilton (1987) estimated that Clay Lake sediments contained 2000 kg of anthropogenic mercury as a result of upstream industries. The entire lake has a mean depth of 8 m and an average hydraulic residence time of 57 days. Based on data from Government of Canada/Government of Ontario (1984), an estimate was made for this study that the eastern, upstream basin had a volume of $6 * 10^7$ m^3, a mean depth of 4.5 m, and a mean hydraulic retention time of 14 days. The western basin stratifies but the eastern basin does not. Clay

FIGURE 10.1
Wabigoon River System from Dryden to Ball Lake



(Source: Parks, 1988)

FIGURE 10.2
Observed Total Mercury Concentrations in Biota in Clay Lake from 1971-83



(Source: Parks and Hamilton, 1987)

Lake is highly productive. The hypolimnion in the western basin experiences anaerobic conditions in late summer and winter (Government of Canada/Government of Ontario, 1984). Water quality in the Wabigoon River prior to 1983 was seriously degraded by effluents from the pulp and paper complex at Dryden. Primary and secondary treatment facilities were constructed in 1980 and 1983 respectively (Parks, 1989).

Concentrations of total mercury in Clay Lake sediments were approximately 20-50 times above background during the late 1970's and early 1980's (eg. 3 ug g^{-1}). Water concentrations of total mercury in the lake were on the order of 10-20 times background (eg. 15-25 ug m^{-3} unfiltered) and methylmercury concentrations were in the range of 1.3 ug m^{-3} (unfiltered), also 10-20 times background concentrations, during the same period. Mercury concentrations in sportfish have been monitored regularly in Clay Lake since 1970. Figure 10.2 illustrates decreasing mercury concentrations in Clay Lake in walleye, northern pike and crayfish for the period 1970-83.

Although analytical limitations during the 1970's and 1980's precluded accurate measurements of total and methylmercury in surface waters in unpolluted systems, the Wabigoon River system was probably sufficiently polluted to allow credible measurements. A simulation was therefore undertaken for the period 1979-88, using data from 1979-80 field studies as initial conditions. The simulation examined the ability of the model to predict partitioning and temporal trends for total and methylmercury in water, sediments and biota in the eastern basin of Clay Lake.

The eastern basin was selected rather than the entire lake, since this basin is well mixed year round and is more suited to a one-box representation of surface waters than the western, sometimes stratified, basin. Two way exchange of waters and movement of fish between the two basins is possible but not considered for the present simulation.

Inflowing waters to Clay lake averaged 26.5 ug m^{-3} of total mercury for the August 1978 to August 1980 period, while the east and west basins contained average total mercury concentrations of 23.5 and 16.5 ug m^{-3} respectively. (Parks and Hamilton, 1987). These values were based on unfiltered samples. A portion of the drop in total mercury between basins may have been due to higher suspended solids concentrations in the western basin. The trend towards a downstream decline in mercury concentrations was less apparent for methylmercury, with 1.4 ug m^{-3} in the inflow to Clay lake, 1.3 ug m^{-3} in the east basin and 1.2 ug m^{-3} in the west basin, for the same 2 year period (Parks et al., 1989). Further information regarding initial conditions and rate constants used in the simulation is provided in Table 10.1.

Since mercury concentrations in the Clay Lake system have declined with time, it was assumed that the mercury burden in upstream sections of the Wabigoon River between Dryden and Clay Lake also declined with time. Field data for mercury in sediments and crayfish in Clay Lake were used to estimate loading patterns. One simulation was run with Hg(II) and methylmercury loads decreasing by 50% each 5 years for the period 1979-88. A second simulation was performed for comparative purposes, holding loads constant.

Table 10.1
Selected Inputs for Clay Lake Simulation

Input Parameter	Value	Units
Hydraulic Residence Time	14	days
Surface Area	13.2	km^2
Estimated Mean Depth	4.5	m
Mean Suspended Solids Concentration:		
- Inflow to Eastern Basin	12	mg L^{-1}
- Eastern Basin	7.1	mg L^{-1}
Solids Density	2.5	kg L^{-1}
Initial Hg(II) Concentrations*:		
- Inflow (dissolved)	20	ug m^{-3}
- Inflow (particulate)	0.5	ug g^{-1}
- Eastern Basin (Dissolved)	12.5	ug m^{-3}
- Eastern Basin (Particulate)	1.5	ug g^{-1}
- Sediment Solids	3.0	ug g^{-1}
Initial Methylmercury Concentrations:		
- Inflow (dissolved)	1.25	ug m^{-3}
- Eastern Basin (dissolved)	1.25	ug m^{-3}
- Eastern Basin (particulate)	0.02	ug g^{-1}
- Sediment Solids	0.015	ug g^{-1}
Biomass:		
- Plankton (2 ppmv)	120	m^3
- Benthos (2 ppmv)	120	m^3
- Yellow Perch (1.5 ppmv)	90	m^3
- Walleye (0.25 ppmv)	15	m^3

* To estimate the distribution between particulate and dissolved Hg(II), concentrations of total mercury in the east and west basins of the lake were used in conjunction with suspended solids concentrations to develop two equations (one for each basin) with two unknowns (particulate and dissolved concentrations of total mercury). The result was an estimate of total mercury in water of 12.5 ug m^{-3} and a particulate concentration of 1.5 ug g^{-1} for 1979-80. The concentration of total mercury on inflowing suspended solids was estimated to be significantly less (0.5 ug g^{-1}) assuming 25% of annual loading of total mercury to Clay Lake was via particulate mercury (Government of Canada/Government of Ontario, 1984), and assuming an average inflowing suspended solids concentration 12 mg L^{-1} (Parks et. al 1986). The increase in total mercury concentration on particulates (per gram of solids) from the inflow to Clay Lake to the eastern basin of the lake could be explained through resuspension of highly polluted sediment solids.

Table 10.1 (Continued)
Selected Inputs for Clay Lake Simulation

Input Parameter	Value	Units
Rate Constants:		
- Water Column Reduction of Hg(II)	2.5E-4	day^{-1}
- Methylation and Demethylation Related:		
- Carbon Degradation in water	0.001	day^{-1}
- Carbon Degradation in sediments	0.0001	day^{-1}
- Methylation rate for total Hg(II) dissolved in water	0.0004	day^{-1}
- Methylation rate for total Hg(II) dissolved in porewater	0.003	day^{-1}
- Demethylation rate for total MeHg dissolved in water	0.003	day^{-1}
- Demethylation rate for total MeHg dissolved in porewater	0.018	day^{-1}
Porewater/Water Column Exchange	0.01	m day^{-1}
Suspended Solids Settling Velocity	0.5	m day^{-1}
Resuspension Velocity	1.65E-5	m day^{-1}
Burial Velocity	2.7	mm $year^{-1}$
Volatilization (air side)	100	m day^{-1}
Volatilization (water side)	0.5	m day^{-1}
Dry Particle Settling in Air	860	m day^{-1}

10.1.1 Mercury Concentrations Versus Time in the Eastern Basin of Clay Lake

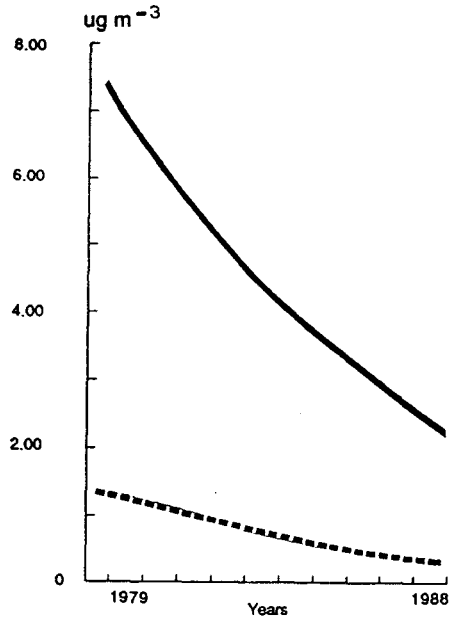
Mercury Versus Time in Abiotic Compartments

For the scenario with mercury loads in inflows decreasing with time, Figure 10.3 shows simulated methylmercury and Hg(II) concentrations in surface waters, porewater and sediment solids. Concentrations of Hg(II) and methylmercury in the water column and sediment solids in the eastern basin of the lake declined steadily at rate of about 50% each 5 to 6 years. The rate of decline of Hg(II) in sediment solids was in reasonable agreement with observed mercury profiles in sediment cores, also presented in Figure 10.3. Sediment cores from the eastern basin of Clay Lake showed decreasing total mercury concentrations in surficial sediments between 1971 and 1980. Near-surface concentrations of total mercury dropped from approximately 8 ug g^{-1} in 1971 to 3 ug g^{-1} in 1980 (50% drop in about 6 years). Long term temporal trends for methylmercury concentrations in water or sediments were not found in the literature.

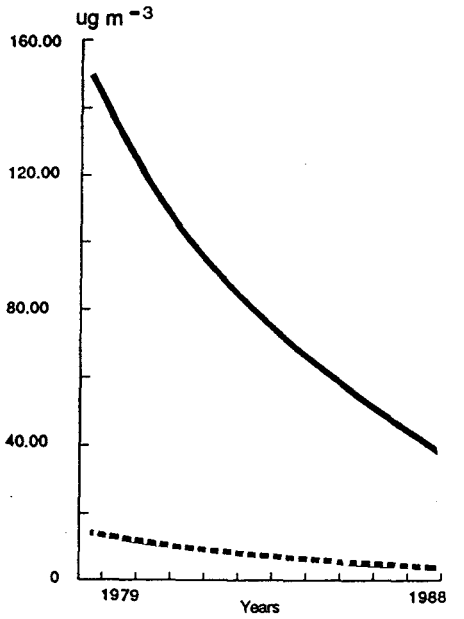
Based on the simulation, concentrations of Hg(II) and methylmercury in abiotic compartments in the eastern basin of Clay Lake would take decades, eg. 25-40 years, after remedial measures in the early 1970's to recover to background levels. This rate of recovery was similar to, and influenced by, the rate of decline of loading assumed for inflows. The simulation with constant inflow mercury loads indicated rates of recovery during the 10 year simulation period about twice as slow as the above simulation.

FIGURE 10.3
Simulated Methylmercury and Hg(II) Concentrations in the Eastern Basin of Clay Lake (1979-1988)

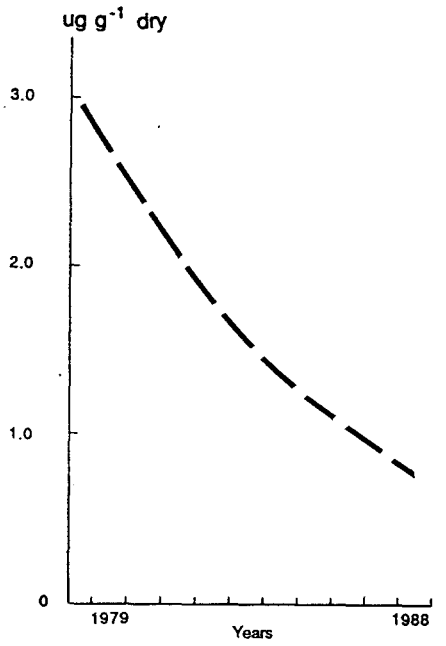
(a) Simulated MeHg in Water and Porewater



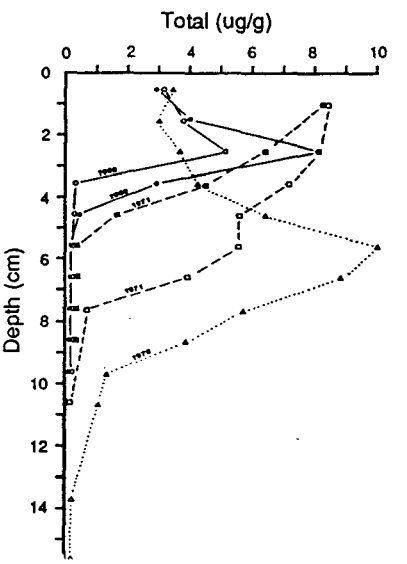
(b) Simulated HgII in Water and Porewater



(c) Simulated Hg(II) in Sediment Solids



(d) Observed Total Mercury in Sediments from the Eastern Basin of Clay Lake (1971-80) (Source: Government of Canada, Government of Ontario1984)



Mercury Concentrations Versus Time in Biota

Figure 10.4 illustrates simulated mean methylmercury concentrations for yellow perch and walleye populations. As was the case for abiotic compartments, these biota also showed steady declines in methylmercury concentrations with time, with concentrations declining by 50% over a period of 5-6 years. It is important to note that the observed concentration trends with time in fish do not necessarily reflect the ability of fish to establish new steady-state concentrations when conditions change. Yellow perch and walleye populations were estimated to have response time half-lives of 0.6 and 1.3 years respectively (i.e. the time required to reach 50% of the new steady-state concentration). Declining mercury concentrations in the fish pools reflected both the ability of the pools to respond and temporal decreases in uptake from food.

Figure 10.5 shows simulated total mercury and methylmercury concentrations in plankton and benthos. Observed crayfish concentrations of total mercury in Clay Lake are also presented in the figure, and agree reasonably with the simulated benthos concentrations.

FIGURE 10.4
Simulated Methylmercury Concentrations in Walleye and Yellow Perch Populations in the Eastern Basin of Clay Lake (1979-1988)

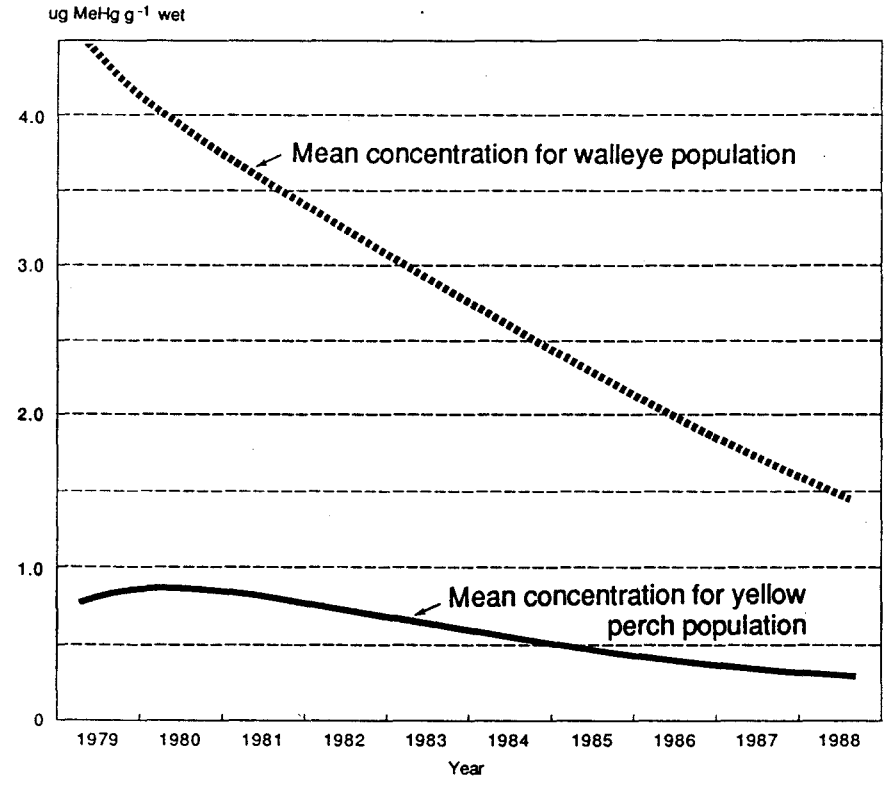
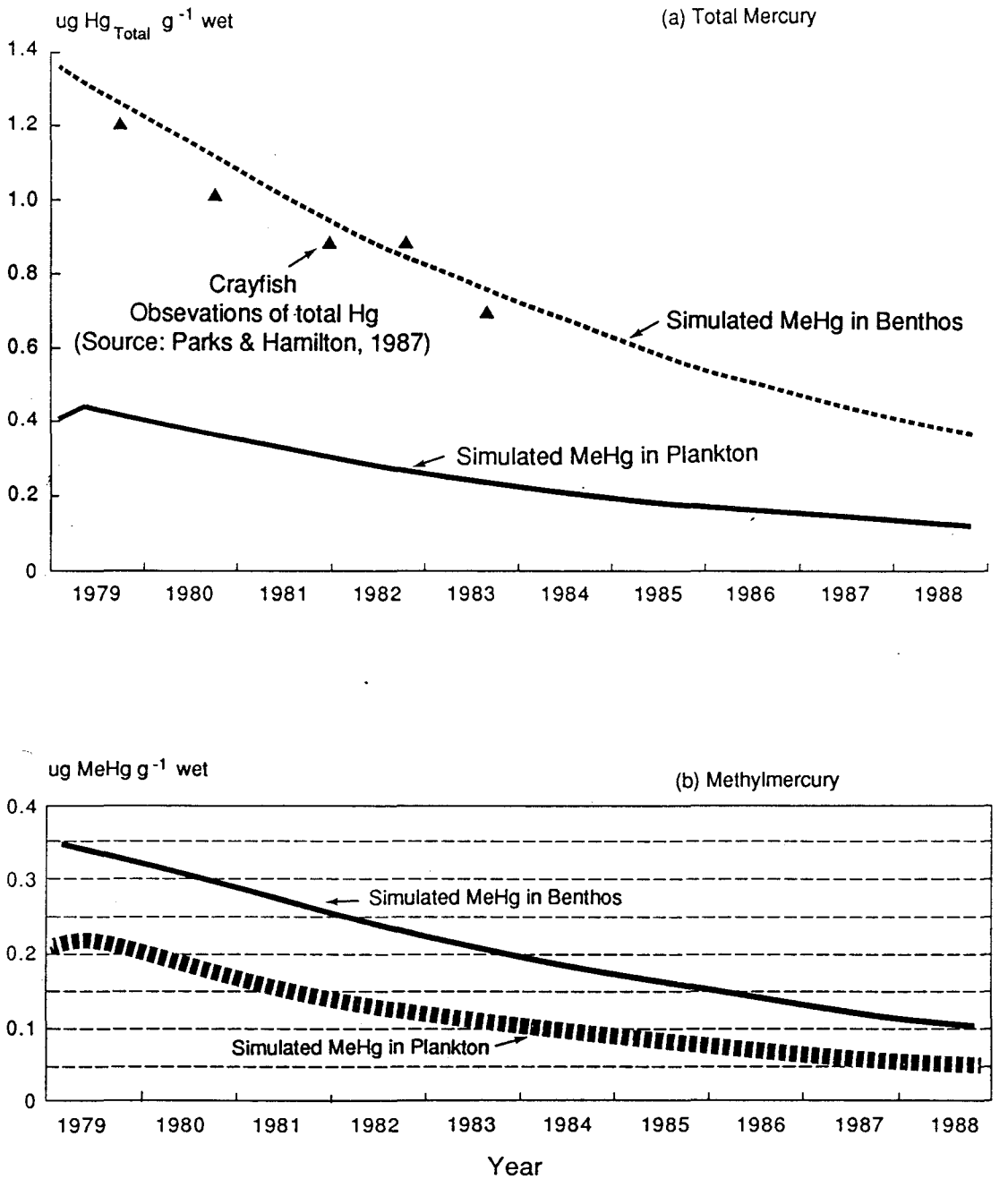


FIGURE 10.5
Simulated Total Mercury and Methylmercury in Plankton and Benthos (1979-1988) in the Eastern Basin of Clay Lake

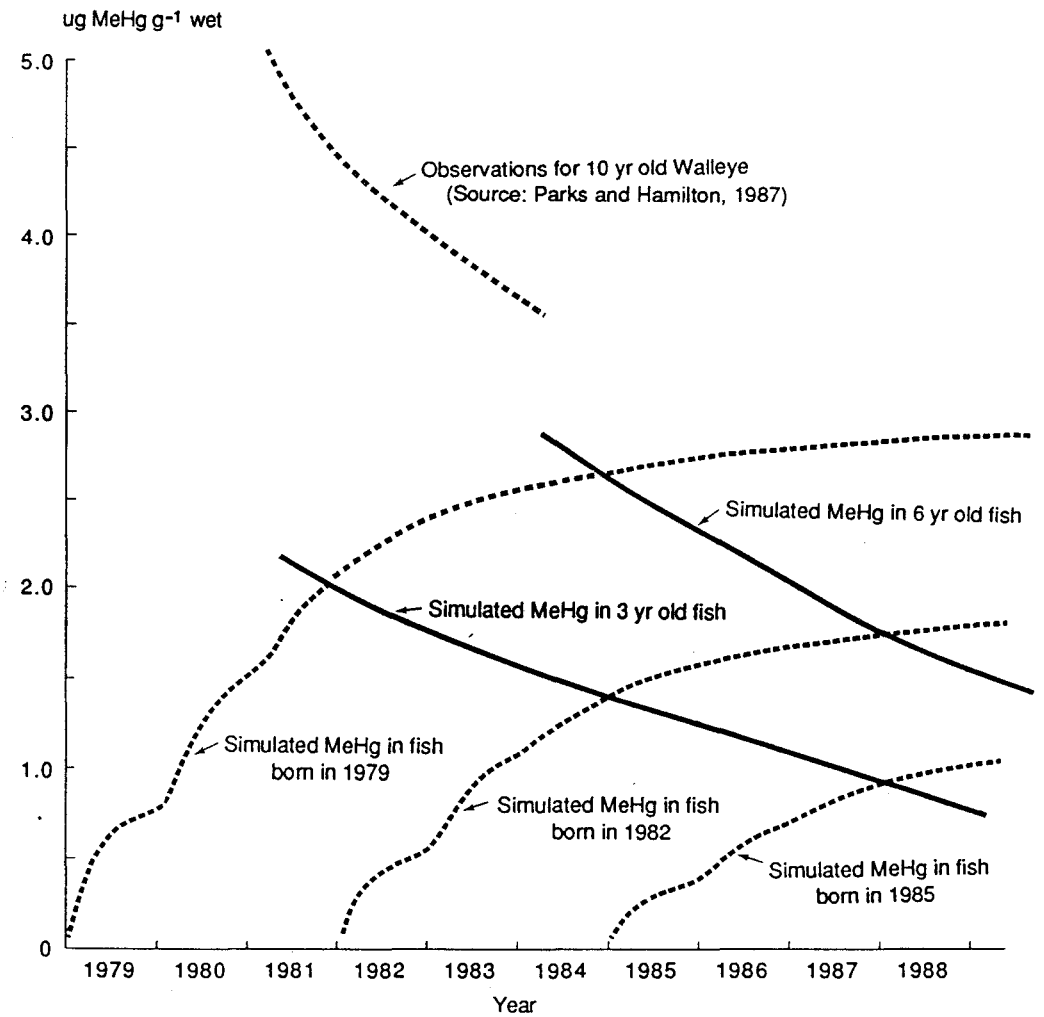


Observed crayfish mercury concentrations for the entire period from 1970 to 1983 did not follow a simple exponential decay with time. There was a trend towards a rapid initial decrease in mercury concentrations during the first few years, followed by a slower second phase of recovery. This trend was also observed for walleye in Clay Lake. Further discussion of possible causes of this trend in Clay Lake and Lake St. Clair are presented in Section 11. This simulation started in 1979, and was thus compared to observations during the slower recovery phase.

Data regarding plankton concentrations of total and methylmercury were lacking. To estimate initial methylmercury concentrations in plankton, simulations of yellow perch mercury accumulation were used. The methylmercury concentration in the perch diet (plankton) was varied to generate mercury concentrations in age 1+ yellow perch similar to values reported between 1979 and 1981. For this period, observed concentrations in age 1+ yellow perch ranged from 0.12 to 0.66 ug Hg g^{-1} wet weight at the inflow and outflow to Clay Lake. No data were found for age 1+ yellow perch within the lake. A mean value for age 1+ yellow perch of 0.4 ug Hg g^{-1} was estimated. The diet (plankton) concentration which generated this concentration using the bioenergetics equations was approximately 0.2 ug Hg g^{-1} wet weight. It was then assumed that methylmercury represented 50% of total mercury in plankton, such that the total mercury concentration in plankton was initially set at 0.4 ug Hg g^{-1}.

Although results have been discussed for fish in terms of mean mercury concentrations for entire populations, observations of fish mercury levels are usually referenced to a fish of standard length, weight or age. Figure 10.6 shows simulated methylmercury concentrations for

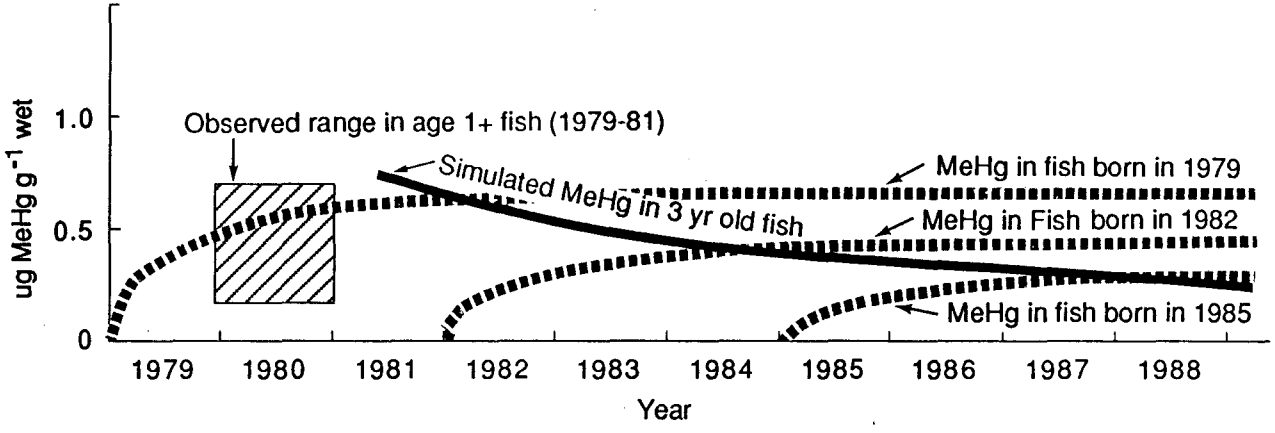
FIGURE 10.6
Simulated MeHg Concentrations for Individual Walleye in the Eastern Basin of Clay Lake (1979-1988)



individual fish hatched in various years. From these estimates, curves were constructed to represent concentrations in walleye which were 3 or 6 years old at any selected time during the simulation. The figure shows that as time progressed, mercury concentrations for 3 and 6 year old fish declined. Also shown in the figure are observations of mercury concentrations in 10 year old walleye. The simulated 3 and 6 year old fish were lower in mercury content than the observed 10 year olds, as would be expected, and the rates of decline agree reasonably between simulated and observed specimens. The simulations resulted in mercury levels decreasing at a rate of about 50% each 4.5 to 5.5 years in 3 to 6 year old walleye.

A similar exercise was conducted for individual yellow perch. Results are shown in Figure 10.7. The mercury content of simulated yellow perch which were 3 years old at any given time decreased as the simulation progressed. Simulated methylmercury concentrations were 0.41 to 0.52 ug g^{-1} for an age 1+ fish hatched in 1979. This range compared reasonably to estimates for methylmercury in age 1+ yellow perch based on field data (range 0.12 to 0.66 ug g^{-1} during 1979-81). The reader is reminded that the agreement between observed and simulated concentrations is more a case of calibration than prediction.

FIGURE 10.7
Simulated MeHg Concentrations for Yellow Perch in the Eastern Basin of Clay Lake (1979-1988)



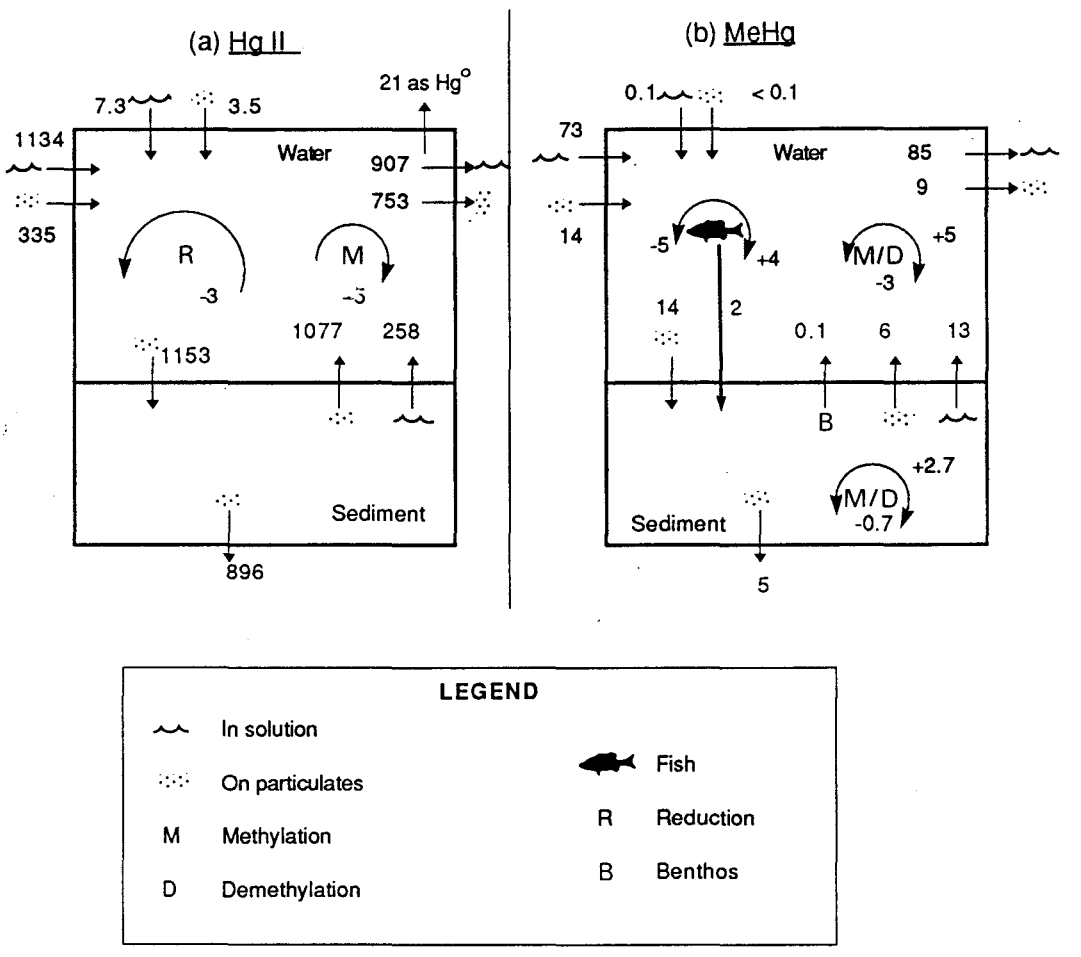
10.1.2 Mercury Fluxes in the Eastern Basin of Clay Lake

Hg(II) Fluxes in the Eastern Basin of Clay Lake

Figure 10.8 (a) shows simulated Hg(II) fluxes in water and sediments, for a date 5 years into the simulation (during 1984). Reduction and methylation of Hg(II) in the water column were estimated to be relatively minor in comparison to Hg(II) exchange with sediments or inputs from upstream. This was due to the short retention time of 14 days in the eastern basin, and significant settling and resuspension rates for solids. The net flux of Hg(II) across the sediment water interface was calculated to be out of the sediments due to highly polluted sediments. Sediment Hg(II) concentrations decreased due to resuspension, diffusion to the water column, and burial. Outflows had Hg(II) concentrations about 10-15% higher than inflows, 5 years into the simulation. If upstream loading of Hg(II) were sharply reduced, sediments would likely become a more significant source of Hg(II) to outflowing waters.

Sediment burial was also found to be a significant mechanism for recovery, with burial representing 60% of the Hg(II) load in the inflow. Atmospheric loading and volatilization of Hg(II) was negligible, although it was interesting that volatilization (21 ug m^{-2} $year^{-1}$) was predicted to exceed deposition (11 ug m^{-2} $year^{-1}$) on the date selected for analysis (5 years into the simulation) in these polluted waters. This trend is opposite to that estimated for unpolluted systems in Section 9.

FIGURE 10.8
Simulated Mercury Fluxes in the Eastern Basin of Clay Lake, 5 Years into Simulation
(ug Hg m^{-2} $year^{-1}$)



Methylmercury Fluxes in the Eastern Basin of Clay Lake

Figure 10.8 (b) shows simulated fluxes for methylmercury in the water column, sediments and biota. Inflows represent the major methylmercury load to the eastern basin of the lake for the simulated scenario. The net methylmercury flux across the sediment/water interface was into the water column. Outflows contained 5-10% more methylmercury than inflows, suggesting the basin was a net source of methylmercury. Burial of methylmercury was a less effective removal mechanism than for Hg(II), representing only 5% of the methylmercury load in the inflowing waters. Atmospheric deposition of methylmercury was negligible, and fluxes related to biota were less significant in this simulation than for a generic shield lake. The same biomass densities were used as in the generic lake, in lieu of field data to the contrary.

Due to the short hydraulic residence time (14 days) in the eastern basin of Clay Lake, inflows and outflows were the primary methylmercury source and sink respectively. Methylation and demethylation in the water column and sediments were not overly significant, based on the rates from Table 10.1. The development of these rates is discussed in Appendix D. There is a large degree of uncertainty associated with the assumed methylation and demethylation rates. It is not possible to say with confidence that these processes are of minor consequence in-situ.

An implication of the methylation rates used in the simulation was that methylmercury concentration trends were not controlled by in-situ Hg(II) levels. Rates of recovery for methylmercury and Hg(II) were similar because loadings for both these species in inflows were assumed to decline at similar rates.

10.1.3 Response Times in the Eastern Basin of Clay Lake

Since methylmercury and Hg(II) in abiotic compartments exhibited similar rates of recovery, relatively constant concentration ratios were calculated between these compartments (ie. apparently stable partitioning in this waterbody). Insights regarding this trend can be gained by looking at predicted response times for various compartments. Table 10.2 shows response times (in terms of half-lives to respond to system perturbations) and the times required in this simulation for concentrations to drop 50% for several compartments. These two indicators do not necessarily have the same value. For example, although the water column was estimated to respond quickly (eg. 6-10 day half-life response times) to changes in Hg(II) and methylmercury loads, the actual concentrations were simulated to decrease at a much slower rate. A 50% drop in Hg(II) or methylmercury concentration took 5-6 years, mimicking changes in loading with time. Sediments were slower to respond, with response time half-lives of 1.25 and 2.5 years for methylmercury and Hg(II) respectively.

Table 10.2
Response Times for Clay Lake Simulation

Compartment	Time for $C/C_o = 0.5$	Response Time Half-Life
Methylmercury:		
- Water, Sus. Solids, and Plankton	4.5-5.0 years	10 days
- Sediment Solids and Benthos	5.0-6.0 years	1.25 years
- Yellow Perch Population	4.5-5.0 years	0.65 years
- Walleye Population	5.0-6.0 years	1.25 years
- Individual Yellow Perch (age 3)	4.5-5.0 years	varies with age
- Individual Walleye (age 3-6)	4.5-5.5 years	varies with age
Hg(II):		
- Water, Sus. Sol. and Plankton	5.0-6.0 years	6-10 days
- Sediment Solids	5.0-6.0 years	2.5 years
Inflowing Hg(II) and Methylmercury	4.6 years	N/A

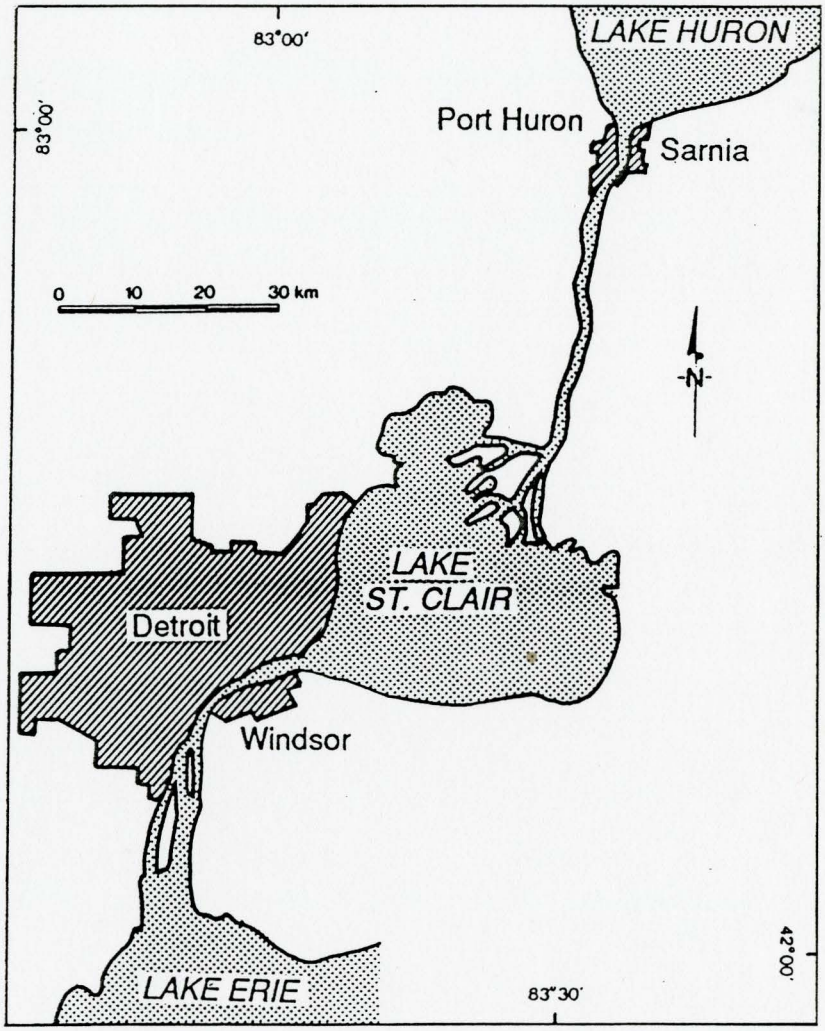
It is not necessarily true that concentration ratios between water and sediments would be constant in the long term (years) in all circumstances, even though rapid stabilization could occur in the short term. Consider, for example, a scenario whereby upstream inputs of Hg(II) are sustained at constant levels indefinitely and water column Hg(II) loading is dominated by inflows. Under such conditions, water column Hg(II) levels could remain relatively stable with time while polluted sediments might gradually head towards a steady-state condition with overlying waters. Thus the ratio of Hg(II) in the water column to Hg(II) in sediments could vary with time.

Several studies of the Wabigoon River system have suggested rapid development within hours to days of a "pseudo-equilibrium" between methylmercury and Hg(II) in sediments and the water column (Parks et al., 1986; Parks et al., 1989; Parks, 1989). Such rates are somewhat faster than, but not necessarily inconsistent with, the response times presented in Table 10.2. Factors which could lead to more rapid response kinetics in the river upstream of Clay Lake include higher suspended solids concentrations in the river (greater rate of removal by settling), higher rates of microbial activity (eg. BOD_5 values of 21-28 mg L^{-1} upstream at Wainwright Dam versus 2.1 mg L^{-1} at the inflow to Clay Lake (Parks et al., 1986), microbial adaptation in more highly contaminated river sections, and increased diffusion and/or resuspension rates as a result of more mixing in a riverine environment. These same factors could also lead to faster response kinetics in the productive eastern basin of Clay Lake relative to oligotrophic shield lakes with longer hydraulic retention times on the order of years.

10.2 Application of the Complete Model to Lake St. Clair

Lake St. Clair, in conjunction with the St. Clair River and Detroit River, forms the connecting waterway between Lake Huron and Lake Erie (see Figure 10.9). It has a maximum depth of 6.5 m, a mean depth of 3.4 m, surface area of 1115 km^2 and a mean hydraulic retention time of about 9 days (Environment Canada/USEPA, 1988; Edwards et al., 1989; Halfon et al., 1990). The lake is fed primarily by the St. Clair River, which has a mean hydraulic retention time of approximately 21 hrs (Edwards et al., 1989). Tributary flows are typically less than 5% of the St. Clair River flowrate (Halfon et al., 1990). Lake St. Clair is highly productive, with extensive wetlands and a delta area at the mouth of the St. Clair River. The lake is well buffered, and does not stratify (Environment Canada/USEPA, 1988). Despite the productivity of the overlying waters, the sediments are low in organic content. Lang and Fontaine (1990) cited an estimate for sediment composition of 50% sand and gravel, 33% silt and 17% clay. The mean organic content in the upper 2 cm of sediments was estimated to be 1.3%. Suspended solids concentrations were estimated to be 7.7 mg L^{-1} in the inflow and lake waters, based on data from Environment Canada/USEPA (1988). Sediment accumulation rates are low, since at most 30 cm of sediments have accumulated in post glacial times (Lang and Fontaine, 1990). Particulate settling and resuspension appear to be active, important processes in the lake. Mudroch and Hill (1989) considered the lake non-depositional for fine grained recent sediments, with such material being transported on a transitional basis from the St. Clair River through Lake St. Clair and eventually to Lake Erie. Sediment samples from the western basin of Lake Erie showed mercury concentrations as high as 3 ug g^{-1} in 1970 (Mudroch and Hill, 1989).

FIGURE 10.9
Lake St. Clair and Surrounding Area



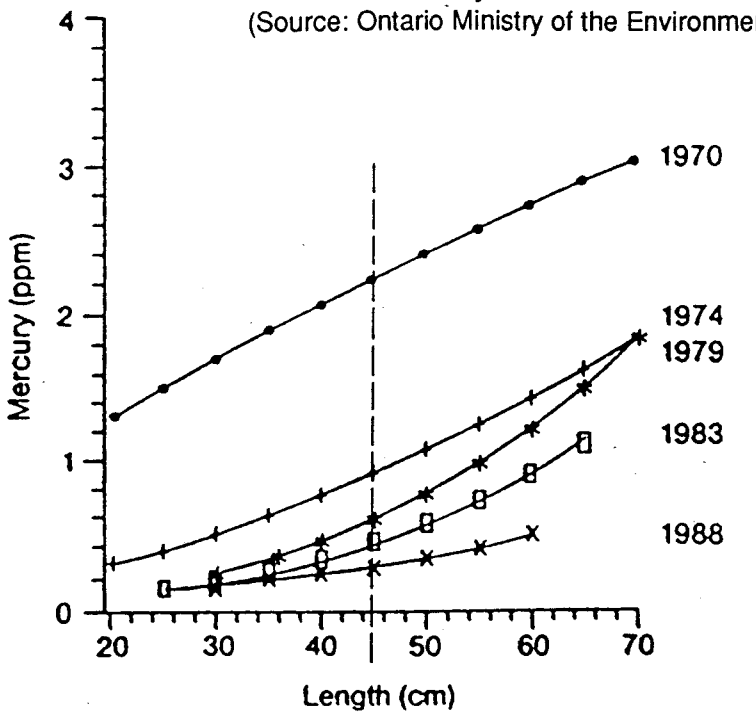
Source: Mudroch and Hill (1989)

Measurements have been made of total mercury concentrations in sediments and fish in the lake since the 1970's. Until the early 1970's, Dow Chemical Limited operated a mercury cell chloralkali facility upstream of the lake on the St. Clair River. Sediments in the St. Clair river show a history of mercury pollution, with samples taken in 1986 by Mudroch and Hill (1989) showing values as high as 43 ug Hg g^{-1}. Maximum concentrations tended to be several centimeters below the surface, suggesting a decrease in mercury loadings in recent years. Estimates of mean mercury concentrations in surficial sediments in Lake St. Clair from 1970 and 1974 also provide evidence of reduced mercury loadings in recent years, showing a 63% drop from 1.55 ug Hg g^{-1} in 1970 to 0.57 ug Hg g^{-1} in 1974 (Mudroch and Hill, 1989). Based on data from Environment Canada/USEPA (1988), concentrations in lake sediments in 1983 were on the order of 0.1 to 0.5 ug Hg g^{-1}, being higher in deeper regions of the lake. Using these data, the 1983 mean concentration of total mercury for all sediments was estimated in the range of 0.25 to 0.3 ug Hg g^{-1}, suggesting a continued decrease in mean lake sediment mercury concentration with time after 1974.

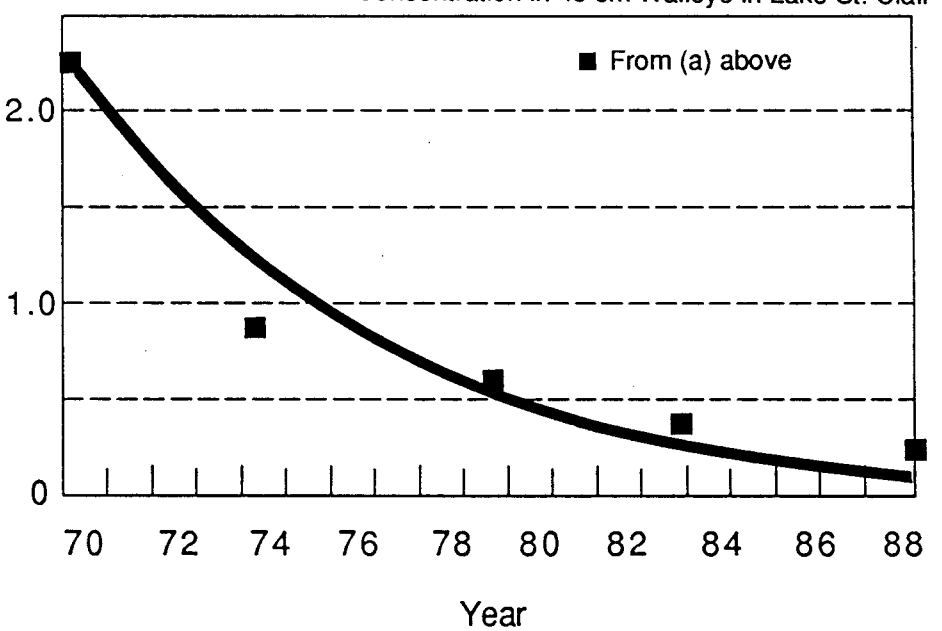
Concentrations of mercury in walleye in Lake St. Clair have also been decreasing since the early 1970's. Based on Figure 10.10, the mercury concentration in a standardized 45 cm walleye would have dropped 60% from 2.25 ug Hg g^{-1} in 1970 to 0.91 ug Hg g^{-1} in 1974. This was virtually the same rate of decline as observed for total mercury in sediments.

FIGURE 10.10
Observed Mercury Concentrations in 45 cm Lake St. Clair Walleye (1970-88)

(a) Lake St. Clair Walleye 1970-88
Declines in Mercury for 5 Selected Years
(Source: Ontario Ministry of the Environment, 1989)



(b) Estimated Rate of Decline of Mercury Concentration in 45 cm Walleye in Lake St. Clair



It was assumed that mercury loadings from the St. Clair River were cut off completely as of 1970. It is acknowledged that residual emissions from industry may continue to occur, and the mercury polluted St. Clair River sediments may have been acting as a source to the overlying river waters since the industrial loads were restricted. The Lake St. Clair simulation was undertaken to examine the ability of the model to simulate restorative processes, particularly fluxes across the sediment/water interface, in a system with heavily polluted sediments. A significant difference between this simulation and the Clay Lake scenario was the lack of upstream mercury inputs assumed for Lake St. Clair. Restorative processes were simulated in abiotic and biotic compartments and compared to observations of mercury concentrations versus time in biota. The simulation also allowed a test of the credibility of applying several rate constants and partition coefficients used in the simulation of a generic shield lake to this scenario.

No reliable measurements of mercury concentrations in water in the lake or its inflow were found in the literature. Hg(II) concentrations in the water column and sediments were initially (for 1970) set to 10 times the values used in the generic shield lake simulation. This was based on a 10:1 ratio between total mercury concentrations in sediments in Lake St. Clair in 1970 and sediment concentrations assumed in the generic shield lake (1.5 ug Hg g^{-1} and 0.15 ug Hg g^{-1} respectively). A similar approach was used for methylmercury in the water column, using a factor of 4.5 to represent the increase in methylmercury concentrations in abiotic and biotic compartments in the water column between Lake St. Clair in 1970 and the generic shield lake. This ratio was based on walleye concentrations of 2.25 ug Hg g^{-1} for a 45 cm fish in 1970 in Lake St. Clair, and a mercury concentration of 0.55 ug Hg g^{-1} for the mean

walleye population in the generic shield lake.

Due to the rapid cycling of suspended matter between the water column and sediments, it was found that mercury concentrations (methyl and Hg(II)) on suspended solids were usually 80-90% of the concentrations in the polluted sediments, even though inflow suspended matter was assumed to be relatively unpolluted in terms of mercury. Once the methylmercury concentration in suspended matter in the water column was estimated, initial methylmercury concentrations in sediment solids, porewater and benthos could also be projected using the partition coefficients from the generic shield lake simulation. The result of this approach was an estimate that initial methylmercury concentrations in sediments and benthos were about 10 times the concentrations used in the generic shield lake simulation.

Values of selected inputs used in this simulation are listed in Table 10.3. Two recent modelling efforts provided valuable guidance regarding model inputs for the Lake St. Clair simulations. Lang and Fontaine (1990) applied TOXIWASP, a USEPA contaminant mass balance model to Lake St. Clair for chloride, cesium 137, octachlorostyrene and PCB's. Halfon et al. (1990) applied TOXFATE, also a contaminant mass balance model, to study the fate of seven volatile hydrocarbons in the lake.

Table 10.3
Selected Inputs for Lake St. Clair Simulation

Input Parameter	Value	Units
Hydraulic Residence Time	9	days
Surface Area	1115	km^2
Estimated Mean Depth	3.4	m
Mean Suspended Solids Concentration:		
- Inflow	7.7	mg L^{-1}
- Lake	7.7	mg L^{-1}
Solids Density	2.5	kg L^{-1}
Initial Hg(II) Concentrations:		
- Inflow (dissolved)	1.5	ug m^{-3}
- Inflow (particulate)	0.17	ug g^{-1}
- Lake (dissolved)	15	ug m^{-3}
- Lake (particulate)	1.1	ug g^{-1}
- Sediment Solids	1.55	ug g^{-1}
Initial Methylmercury Concentrations:		
- Inflow (dissolved)	0.1	ug m^{-3}
- Lake (dissolved)	0.32	ug m^{-3}
- Lake (particulate)	0.03	ug g^{-1}
- Sediment Solids	0.033	ug g^{-1}
Biomass:		
- Plankton (2 ppmv)	9440	m^3
- Benthos (2 ppmv)	9440	m^3
- Yellow Perch (1.5 ppmv)	7080	m^3
- Walleye (0.25 ppmv)	1180	m^3

Table 10.3 (Continued)
Selected Inputs for Lake St. Clair Simulation

Input Parameter	Value	Units
Rate Constants:		
- Water Column Reduction of Hg(II)	0.00025	day^{-1}
- Methylation and Demethylation Related:		
- Carbon Degradation in water	0.001	day^{-1}
- Carbon Degradation in sediments	0.0001	day^{-1}
- Methylation rate for total Hg(II) dissolved in water	0.0003	day^{-1}
- Methylation rate for total Hg(II) dissolved in porewater	0.035	day^{-1}
- Demethylation rate for total MeHg dissolved in water	0.0015	day^{-1}
- Demethylation rate for total MeHg dissolved in porewater	0.20	day^{-1}
Porewater/Water Column Exchange	0.01	m day^{-1}
Suspended Solids Settling Velocity	3.0	m day^{-1}
Resuspension Velocity	$2.3 * 10^{-5}$	m day^{-1}
Burial Velocity	1.0	mm $year^{-1}$
Volatilization (air side)	100	m day^{-1}
Volatilization (water side)	0.5	m day^{-1}
Dry Particle Settling in Air	860	m day^{-1}

10.2.1 Mercury Concentrations Versus Time in Lake St. Clair

Figures 10.11 and 10.12 show simulated mercury species in solution and on particulates in surface waters and sediments. Hg(II) concentrations declined steadily in sediment solids and suspended solids, at similar rates of approximately 50% each 6 to 6.5 years. The simulated rate of decline of Hg(II) concentration in sediments from 1970-74 was slower than the observed rates of (see Figure 10.12 (d)). Reasons for this will be discussed later in this section. Based on the assumed partitioning, initial concentrations of Hg(II) in surface waters would have been the range of 15 to 20 ug m^{-3} in 1970, dropping to 2-3 ug m^{-3} by 1988. Methylmercury in surface waters was simulated to drop from about 0.3-0.4 ug m^{-3} in 1970 to 0.1 to 0.2 ug Hg g^{-1} by 1988. The 1988 predictions for methylmercury would still be elevated above expected background concentrations, but only slightly.

Field data for the 1970-88 period revealed a tendency for rapid initial decrease in mercury concentrations in sediments and fish during the first few years, followed by a slower second phase of recovery. A similar trend was observed in the walleye data for Clay Lake. A discussion of these recovery patterns is presented in Section 11.

FIGURE 10.11
Simulated Methylmercury and Hg(II)
Concentrations in Solution in Lake St. Clair (1970-88)

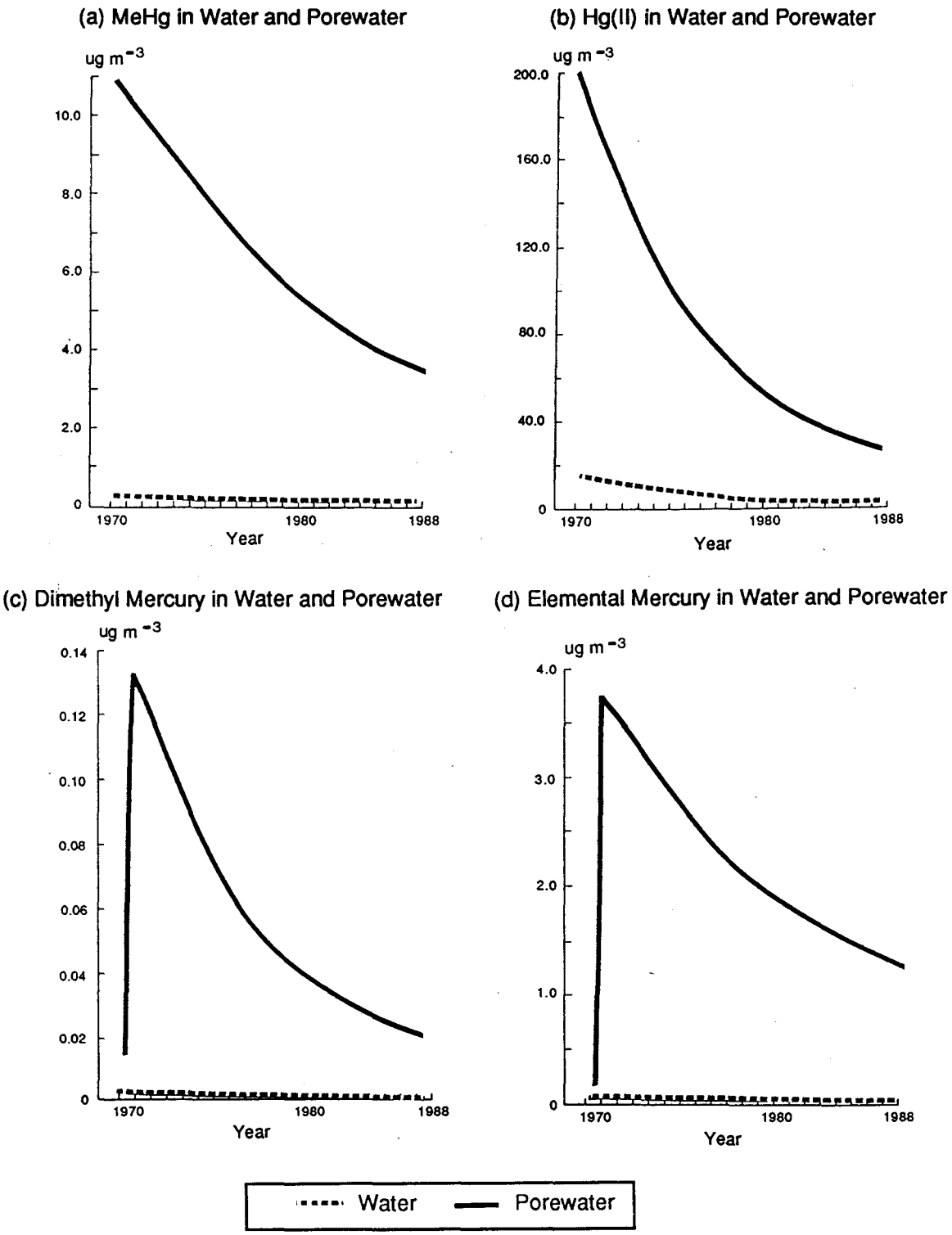
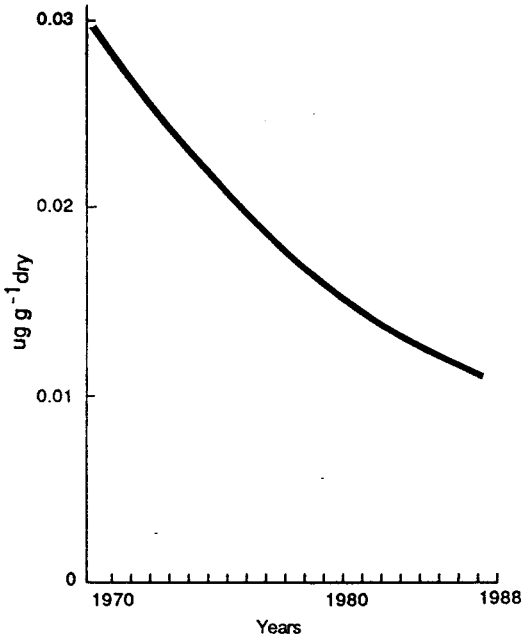
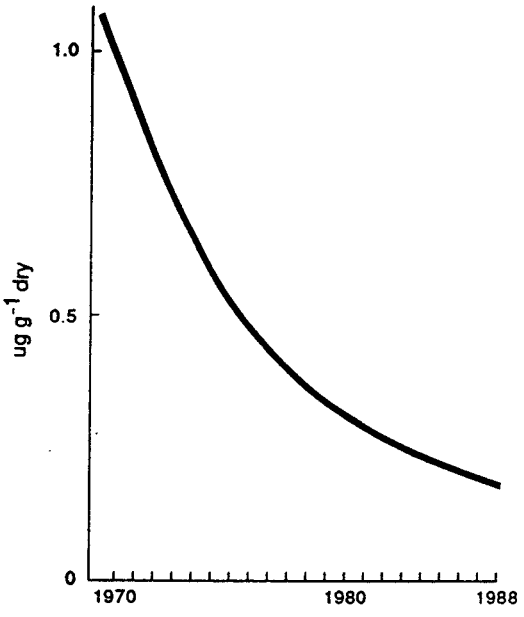


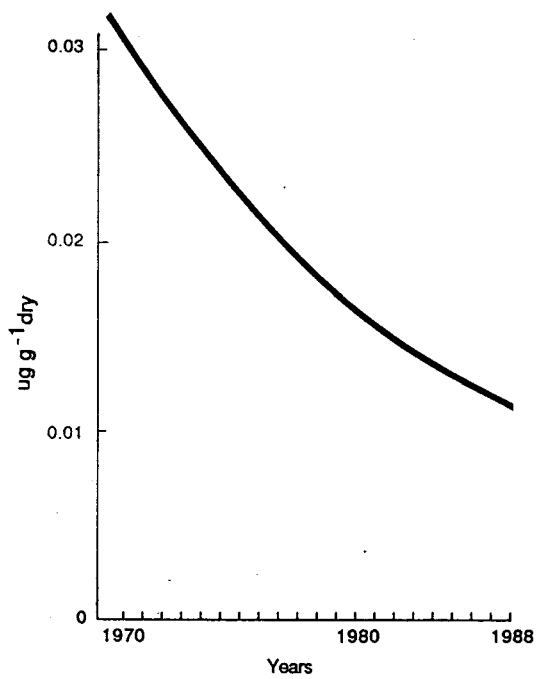
FIGURE 10.12
Simulated Particulate Hg(II) and Methylmercury Concentrations In Lake St. Clair Water Column and Sediments (1970-1988)



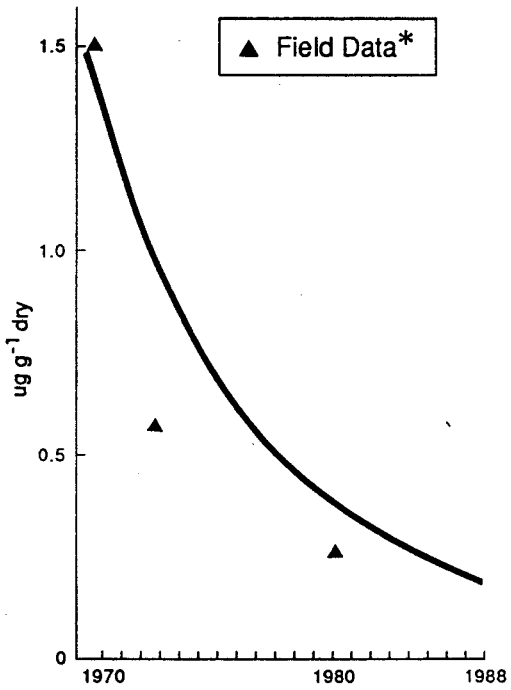
(a) MeHg on Suspended Solids



(b) Hg(II) on Suspended Solids



(c) MeHg on Sediment Solids



(d) Hg(II) on Sediment Solids

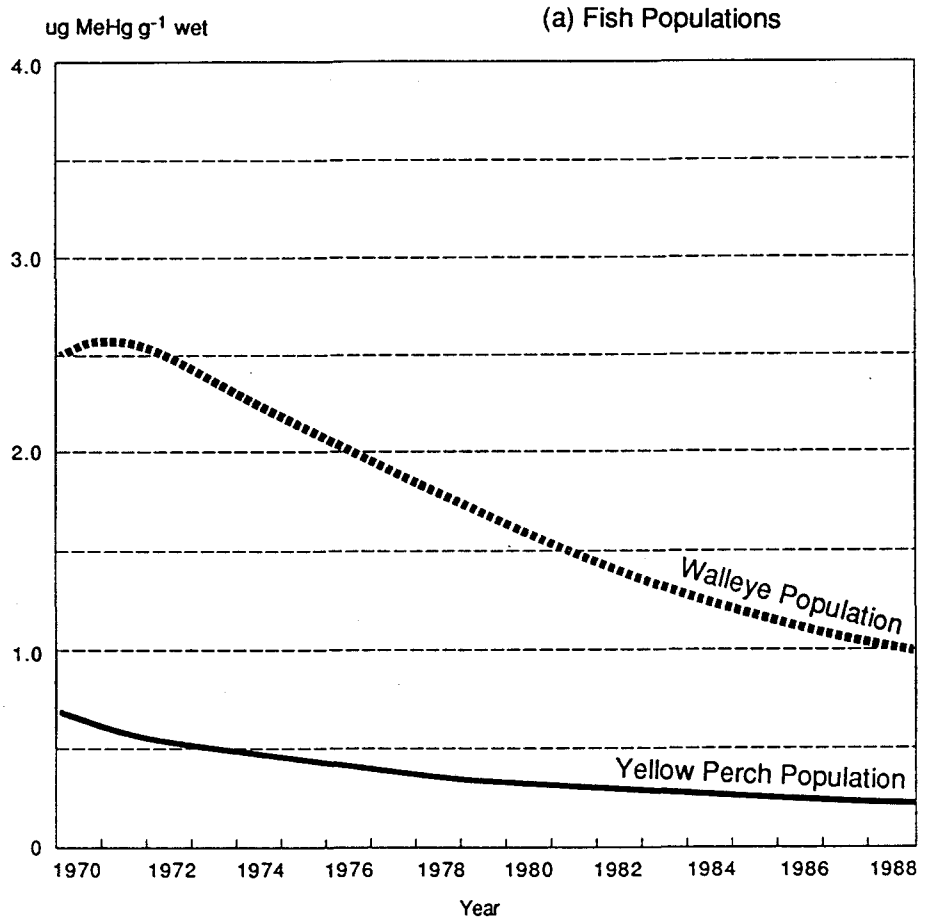
* Source: Mudroch & Hill,1989;
Environment Canada/USEPA (1988)

Figure 10.13 illustrates modelled methylmercury concentrations in plankton, benthos and mean population mercury concentrations for yellow perch and walleye. As was the case for abiotic compartments, these compartments showed steady declines in methylmercury concentrations with time. Methylmercury concentrations declined by 50% over a period of 11 to 12 years. Rates of mercury decline in simulated 3 and 6 year old walleye (see Figure 10.14) are also in the range of 50% over an 11-12 year period. Figure 10.14 also shows estimated mercury concentrations for 45 cm walleye in Lake St. Clair from 1970 to 1988 (Ontario Ministry of the Environment, 1989). It is apparent that simulated rates of decline of walleye mercury content are considerably slower than field data suggest. This discrepancy will be discussed below.

10.2.2 Mercury Fluxes in Lake St. Clair

Figure 10.15 shows selected mercury fluxes 5 years into the simulation (during 1975). Figure 10.15 (a) shows Hg(II) fluxes in water and sediments, and suggests in-situ processes (reduction and methylation) in the water column were relatively small in comparison to Hg(II) loading in inflows or exchange with sediments. This was due to the short retention time of 9 days. The net flux of Hg(II) across the sediment water interface was out of the sediments due to highly polluted sediments. Sediment concentrations decreased due to resuspension, diffusion and burial.

FIGURE 10.13
Simulated Methylmercury Concentrations in Biota in Lake St. Clair (1979-1988)



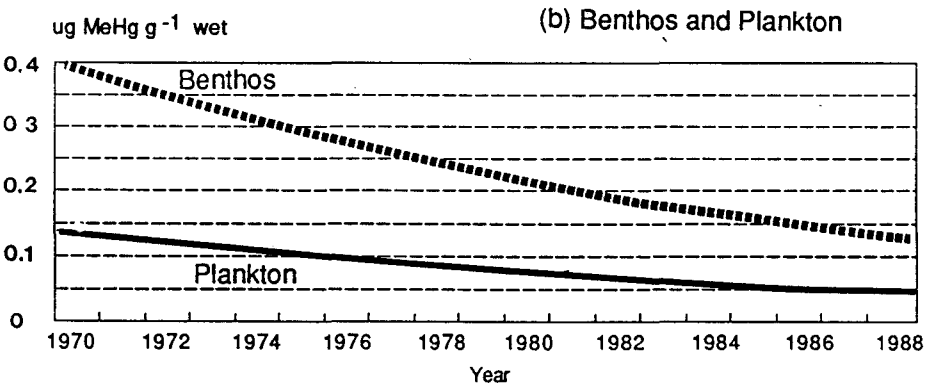


FIGURE 10.14
Simulated Methylmercury Concentrations in 3 and 6 Year Old Walleye in Lake St. Clair (1970-1988)

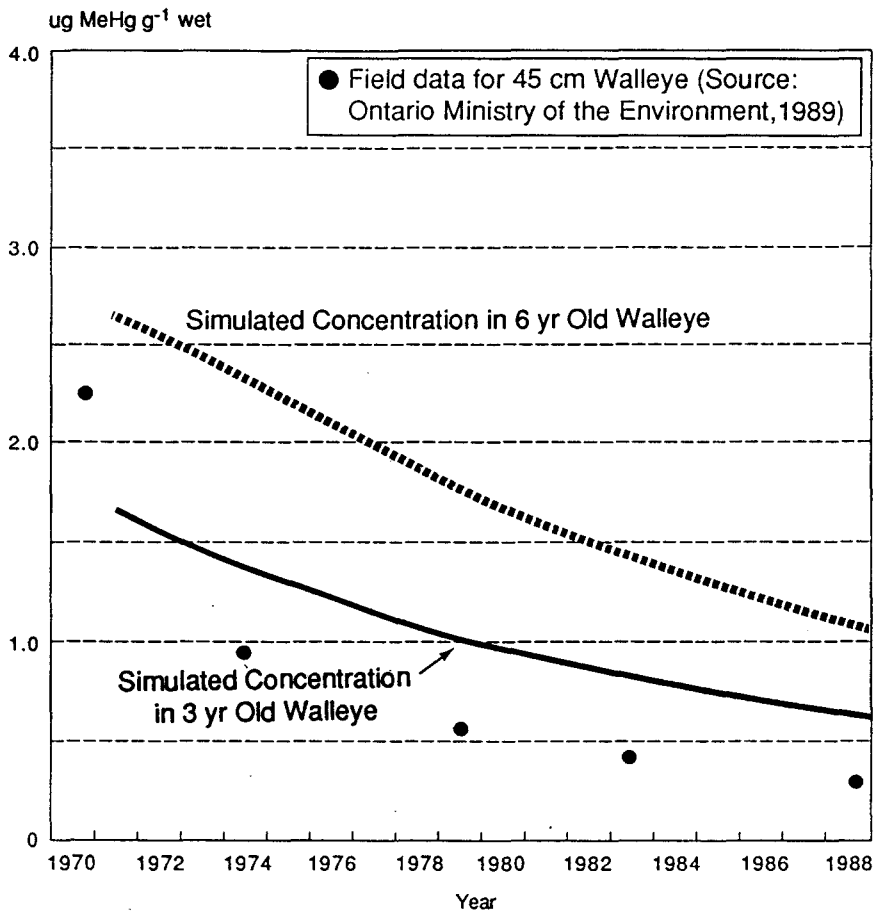
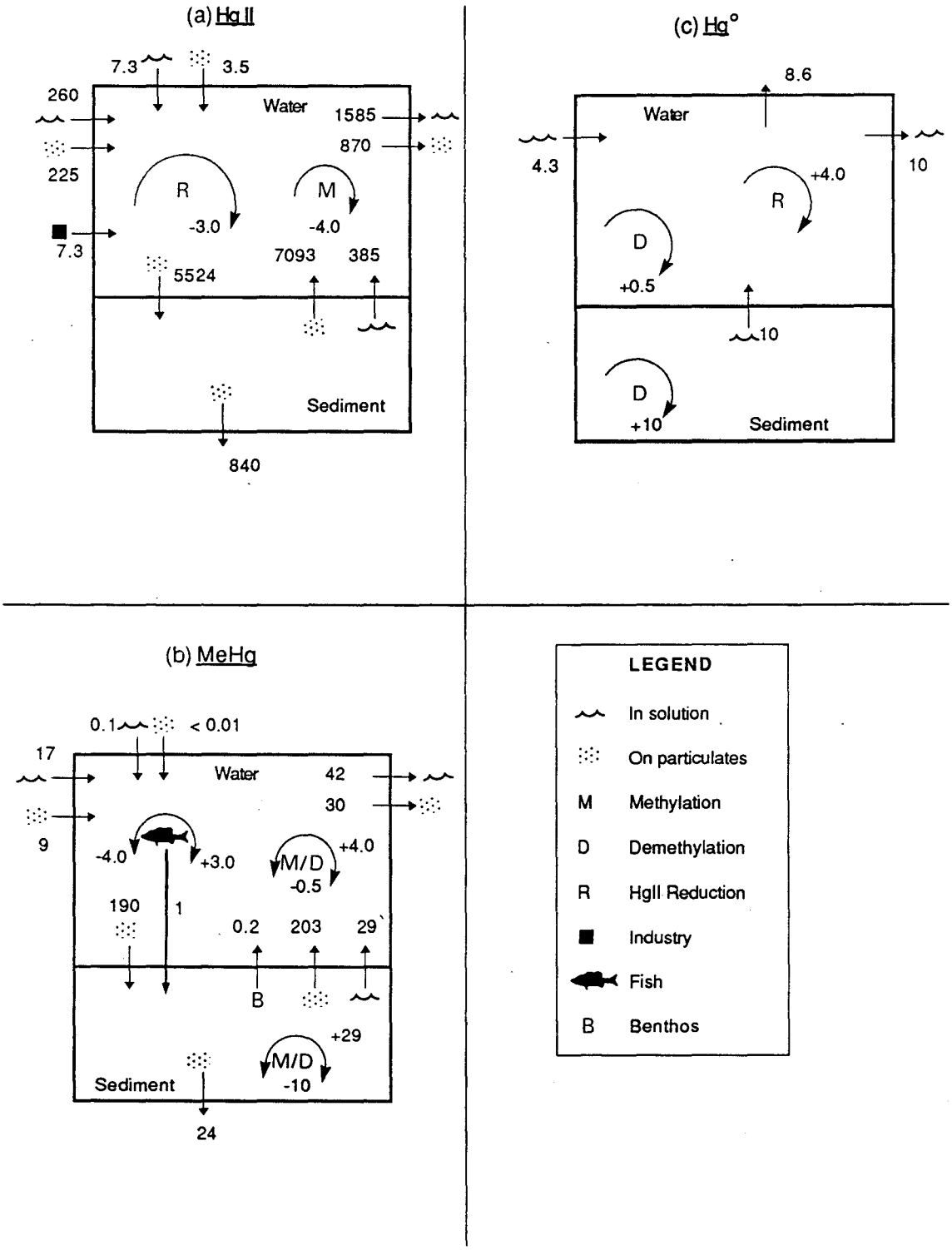


FIGURE 10.15
Simulated Mercury Fluxes (ug/m^2 /yr) in Lake St. Clair, 5 Years Into Simulation



Since the inflow to the lake was assumed to contain background mercury concentrations, the return of sediment Hg(II) to the water column resulted in outflows contained 500% more Hg(II) than inflows, 5 years into the simulation, suggesting the lake was a net source of mercury under the assumed conditions.

Burial was also a significant Hg(II) removal mechanism, but less so than outflows, with a burial rate of 840 ug m^{-2} $year^{-1}$. Roughly twice as much mercury tended to leave polluted sediments via return to the water column (net flux) as opposed to burial.

Hg(II) partitioning between the water column and sediments can be interpreted from the simulation to be driven by fluxes of particulate matter. Rapid rates of settling of suspended solids and resuspension tended to direct particulate mercury concentrations in sediments and the water column towards the same value, although dilution by hydraulic throughput in the water column resulted in lower particulate concentrations in the water column. Consequently, mercury resuspension exceeded settling and the net flux was out of the sediments.

Figure 10.15 (b) shows fluxes for methylmercury in the water column, sediments and biota. As was the case for Hg(II), the net methylmercury flux across the sediment/water interface was into the water column. Outflows contained 275% more methylmercury than inflows (5 years into the simulation), suggesting the basin was a net source of methylmercury. Atmospheric deposition of methylmercury was negligible and fluxes related to biota were less significant in this simulation than for a generic shield lake. The same biomass densities were

used as in the generic shield lake. Biota fluxes of methylmercury may therefore have been underestimated, since Lake St. Clair is highly productive. Methylation and demethylation in the water column and sediments were not overly significant, based on the use of rate constants developed in Appendix D. There is a large degree of uncertainty associated with the methylation and demethylation rates assumed however, and it is not possible to say these processes are definitely of minor consequence.

10.2.3 Response Times in Lake St. Clair

Methylmercury and Hg(II) in abiotic compartments did not exhibit similar rates of recovery. Hg(II) recovered roughly twice as fast as methylmercury. The simulated rates of decline of methylmercury and Hg(II) concentrations in this scenario were controlled by the ability to load the water column with methylmercury and Hg(II) from sediments and remove mercury through outflows, and by burial.

The rate of removal of Hg(II) and methylmercury via the water column was sensitive to the solids/water partition coefficients assumed. If a high partition coefficient was used, removal was less effective. Under such conditions, much of the mercury in the water column was on particulates and simply resettled back into the sediments. If, however, the partition coefficient was lowered, significant quantities of mercury were exported in outflows in the dissolved phase, while settling returned less water column mercury to the sediments. The partition coefficients used in the simulation were nearly identical to those used in the generic shield lake simulation (intentionally) to examine the effect of using such coefficients in

different systems. Lowering partitioning constants for methylmercury and Hg(II) in the water column would have improved the fit between observed and simulated rates of recovery.

Table 10.4 shows response times (in terms of half-lives to respond) and the times required for concentrations to drop 50% for several compartments for the Lake St. Clair simulation. As was the case for the Clay Lake simulation, concentrations did not drop as quickly as the response times might lead one to assume at first. This was primary due to recycling of mercury between compartments without actually leaving the overall system.

Table 10.4
Response Times for Lake St. Clair Simulation

Compartment	Time for $C/C_o = 0.5$	Response Time Half-Life
Methylmercury:		
- Water, Sus. Solids, and Plankton	10-12 years	2-3 days
- Sediment Solids and Benthos	10-11 years	2 years
- Yellow Perch Population	10-12 years	0.6-0.7 years
- Walleye Population	10-12 years	1.3 years
- Individual Walleye (age 3-6)	10-12 years	varies with age
Hg(II):		
- Water, Sus. Sol. and Plankton	6-7 years	2-3 days
- Sediment Solids	6-7 years	2.0-2.5 years

11.0 GENERAL DISCUSSION

This section of the report presents an overall discussion of mercury cycling in aquatic systems, taking into consideration the simulations presented earlier. As will be discussed below, it seems likely that the relative importance of various sources and sinks for total mercury, methylmercury and Hg° depends on circumstances specific to the type of system being studied, e.g. seepage lakes versus runoff dominated lakes, productive versus unproductive lakes, lakes with short versus long retention times, polluted versus unpolluted systems, reservoirs etc. For this reason, a traditional sensitivity analysis was not carried out, since a process might be very significant in one system and negligible in another. The discussions address the potential significance of processes, and whether they should be kept in future versions of the model or warrant research.

11.1 Cycling and Distribution of Total Mercury in Aquatic Systems

11.1.1 Total Mercury Loading

Most of the total mercury load to an unpolluted shield lake is Hg(II) of external origin, i.e. atmospheric loading and runoff. Significant sources of in-situ Hg(II) generation (e.g. oxidation of elemental mercury) have not been identified in unpolluted lakes, however Rasmussen et al. (in press) are currently investigating mercury loading to lakes via geologic

faults in the Muskoka region of Ontario.

For the generic shield lake simulated in this study, atmospheric and terrestrial mercury sources were comparable in magnitude. Atmospheric sources represented about 11 ug Hg m^{-2} $year^{-1}$ and runoff represented about 18 ug m^{-2} $year^{-1}$. Wet deposition was approximately 7.5 ug Hg(II) m^{-2} $year^{-1}$ while dry deposition was about half this amount (3.5 ug m^{-2} $year^{-1}$). These numbers suggest that dry deposition is significant but smaller than wet deposition in remote areas. Dry deposition may be more significant in urban areas with higher concentrations of atmospheric particulates. A simplified mercury cycle for the atmosphere was included in the model (see Figure 7.2) but not tested in this study. Instead, steady-state concentrations of various mercury species were assumed in the atmosphere.

Several factors affect atmospheric deposition of mercury. Mean annual precipitation rates, for example, can vary by about a factor of two in Ontario, from 0.5 to 1.1 m yr^{-1} (Government of Ontario, 1984). Anthropogenic factors affecting atmospheric mercury deposition include atmospheric pH, soot content, ozone, and direct mercury emissions. Brosset (1987) noted the potential for ozone to react with water to produce H_2O_2, which in turn could oxidize elemental mercury to Hg(II) in the presence of hydrogen ions. Thus the potential exists for acidic atmospheric conditions to lead to increased deposition of Hg(II) on the water surface and in the watershed. Based on the variability in precipitation rates and concentrations of total mercury in precipitation, it seems reasonable to assume atmospheric deposition rates of total mercury may vary by a factor of 5 to 10 times in Ontario, e.g. from 5 to 30 ug m^{-2} $year^{-1}$.

Terrestrial loading of total mercury to a lake can also be influenced by several factors, including the lake hydraulic retention time, humic content in runoff waters, concentration of suspended solids in runoff and possibly soil pH. Thermodynamic calculations in this study suggest that humic and fulvic acids dominate Hg(II) complexation in aerated surface waters. This supports positive correlations reported by several authors between humic content in runoff and Hg(II) loading to waterbodies (Borg and Johansson 1989, Meili 1988b). Particulate matter was simulated to carry a significant, but not dominant, fraction of the total mercury in runoff. In the generic shield lake scenario, suspended solids in runoff was relatively low (1.5-2.0 mg L^{-1}) and carried about one third of the runoff mercury load. Suspended solids in inflows in the Lake St. Clair simulation were assumed to be 7.7 mg L^{-1} and carried almost half the runoff mercury load. These results also suggest that suspended solids could dominate runoff loading of total mercury during the spring freshet.

Soil pH may also affect Hg(II) loading in runoff. The net influence of soil pH on runoff loading of total mercury is unclear, since several competing factors are involved. Lodenius and Autio (1989) found less total mercury in leachate from peat at reduced pH (3.6 to 5.4) than from distilled water. Similarly, Hakanson (1974) observed less added mercury in solution in a sediment sample at pH 5 than pH 9. A possible explanation could involve aggregation and settling of DOC at low pH. This trend would result in less mercury in solution in runoff at low pH. On the other hand, this effect would be offset somewhat if mercury precipitated with carbon were resuspended and transported as particulate mercury. Furthermore, until the pH is lowered sufficiently to aggregate and settle out humic acids, the process of H^{+} competition with Hg^{++} for complexation sites may be of significance.

Depending on the relative influence of H^+ on the complexation capability of organics in solution and adsorption capability of solids, pH may influence the distribution between mercury in solution and on particulates. Additional research regarding the effects of pH on runoff loading of mercury would be useful.

It is likely then that considerable variation is possible in both atmospheric and terrestrial loading of total mercury. Wet deposition, dry deposition, dissolved mercury in runoff, and particulate mercury in runoff are all potentially significant sources of total mercury in lakes, depending on specific circumstances. These processes should be kept in future versions of the model. The relative magnitudes of these loads are likely case specific for shield lakes, influenced for example by the ratio of lake area to drainage basin area. It is important to note that atmospheric and terrestrial loading of total mercury are not independent processes. Increased atmospheric deposition of mercury will also load more mercury to the watershed, some fraction of which ends up in runoff. Anthropogenic impacts on atmospheric deposition may therefore affect terrestrial loading of mercury as well.

In reservoirs, the tendency of soil inundation to load Hg(II) to the system is unclear. Increased methylmercury content in fish in reservoirs has been attributed by many authors primarily to increased bacterial methylation activity, rather than a greater supply of Hg(II). Bodaly et. al (1987) examined this issue for the Churchill River diversion in Manitoba through a study of mercury concentrations in unflooded soils, flooded soils 5 years after flooding, and sediments in established lakes (see Section 4.2.1). The overall mean depletion of total mercury in paired samples (flooded versus unflooded) was only 6.7%, and a wide range

of variability was associated with the data. A plausible scenario upon flooding is that Hg(II) could be leached from soils, then effectively bound to suspended organic particles which settle, generating relatively high mercury concentrations in newly forming sediments. This process could be followed finally by a gradual return to Hg(II) concentrations typical of natural lakes, equal or lower than the original soil mercury content, when the trophic surge ends. Field studies to test such hypotheses would be very useful. Verta et al. (1986b) reported newly formed sediments in 6 Finnish reservoirs contained significantly more mercury than underlying older sediments or the soils before flooding, except for the new Kalajarvi reservoir for which no new organic sediments were found. Field experiments to monitor Hg(II) in soils before and after flooding, and in the water column, would be very useful. Leaching of Hg(II) from flooded soils would be a simple addition to the model.

The Potential for Mercury Loads two Induce Two Phase Recovery Trends

In the mercury polluted systems simulated (Lake St. Clair and Clay Lake), similar mercury trends were observed in the field. Mercury concentrations in walleye tended to decrease in a two-phase manner. Rates of recovery in the early years following remedial actions were more rapid than later rates of recovery. In both systems, measures were taken to reduce mercury inputs originating upstream from the lakes. It is possible that the two-phase recovery is indicative of one or more of the following:

1- Sediment return of mercury from polluted sediments *upstream* of the lakes. This would result in residual loading of mercury to the lakes and could partially explain the slower second phase of recovery; and/or

2- Sediment return of mercury from polluted sediments *in* the lakes. This would result in residual loading of mercury to the lakes and could partially explain the slower second phase of recovery; and/or

3- Gradual reductions of industrial mercury inputs in a series of steps, rather than a single step.

The two phase recovery trends observed in walleye in Clay Lake and Lake St. Clair reflect methylmercury levels. It is possible that the second slower phase of recovery could be related to direct inputs of methylmercury inputs from upstream sources or lake sediments. It is also possible that residual Hg(II) inputs from upstream sources or Hg(II) return from sediments could induce a two-phase methylmercury recovery in the system. For this to occur, in-situ methylation would have to be a significant source of methylmercury relative to external inputs.

Two-phase recoveries could occur in other systems as well. For example, if watershed loading of mercury was elevated by anthropogenic activities and then curtailed, a two-phase recovery might be observed. Examples of such activities might be increased atmospheric emissions of mercury or anthropogenic influences on atmospheric or terrestrial pH levels. A gradual decline of mercury levels in the terrestrial system might occur which could

cause sustained inputs of mercury via runoff.

11.1.2 Total Mercury Sinks

The simulations suggested that unpolluted lakes are sinks for total mercury. Sediments in mercury polluted systems may be net sources of total mercury however. The Clay Lake and Lake St. Clair simulations suggest that this may be particularly relevant when external (e.g. upstream) loads of mercury are curtailed and polluted sediments change from being recipients of mercury to become an important source of mercury to the water column, via resuspension or diffusion.

In the generic shield lake, burial and outflows both represented significant removal mechanisms for total mercury from the overall water column/sediment system, together representing 85% of all sinks. The remaining 15% of losses were accounted for by volatilization of elemental mercury to the atmosphere. The relative importance of burial and outflows as removal mechanisms will depend on system characteristics. Burial would be expected to increase in significance in lakes with longer hydraulic retention times (lower volumetric outflow removal of mercury), lakes with high sediment accumulation rates, or lakes with shallow mean depths (greater surface area to volume ratio for settling). Short retention times, low sedimentation rates, and greater mean depth (less volumetric rate of removal of mercury via settling) would all contribute to a lake being a less efficient trap for total mercury via burial.

The lesser significance of volatilization of Hg° as a total mercury sink needs to be qualified with some uncertainty. It was assumed that mercury exchange across the air/water interface results in a net load to the lake in unpolluted systems. This implies that volatilization is less than atmospheric deposition of mercury. Assuming steady-state concentrations for elemental mercury in the water column, production of elemental mercury via Hg(II) reduction and demethylation would be constrained to rates less than atmospheric deposition of total mercury. In the generic shield lake, the volatilization rate was approximately 2.0 - 2.5 ug m^{-2} $year^{-1}$. This represented about 20% of atmospheric deposition. Volatization was based on the use of 0.5 m day^{-1} as a piston velocity for Hg° across the air/water interface, an Hg(II) reduction rate of 10% per year in the water column, and demethylation rates of 3-5% per year of all methymercury in sediments and 50-75% per year of methylmercury in the water column.

The above inferences about Hg(II) reduction and demethylation rates are preliminary, having been based on the simulated cycle of elemental mercury. Although Hg(II) reduction was not a major sink for total mercury in unpolluted systems in the simulations, it would be premature to discard this process from the model as unimportant. Field studies should be undertaken to investigate these processes. Both may be influenced significantly by conditions within the waterbody. It is possible for example that in mercury polluted systems with Hg(II) concentrations orders of magnitude above background, the significance of volatilization could increase as a system sink. The Clay Lake simulation indicated the potential for the overall air/water mercury flux to be into the atmosphere in polluted systems. Field information is required to calibrate these components of the model.

11.1.3 Response Times for Total Mercury in Aquatic Systems

The time required for various compartments and the entire system to reach a new steady-state has been examined using the model. Response times for total mercury in individual compartment vary considerably. The response time half-life for total mercury, essentially Hg(II), was on the order of 1-2 months in the water column in the generic shield lake and 2.5 to 3 years in sediments (3 cm thickness). The processes which controlled the response times in individual compartments tended to be those which moved mercury from one compartment to another within the system. In particular, settling, resuspension and diffusion, which transferred Hg(II) between the water column and sediments, were important. These fluxes tended to be about an order of magnitude greater than fluxes removing mercury from the system altogether. The response time of the combined water column/sediment system was therefore considerably slower. In the generic shield lake, total mercury concentrations would move towards a new steady-state with a half life in the range of 10-20 years. Considerable variability in the overall system response time is expected for different scenarios. The Clay Lake simulations for instance, responded with sufficient speed to reflect mercury loads which decreased at a rate of about 50% each 6 years. Burial, volatilization, and outflow rates were all higher in this system relative to the generic shield lake.

For the lake scenarios simulated in this study, the sediments and water column would tend to reach a steady-state for total mercury after a time period on the scale of weeks to months. Essentially the water column would adapt to conditions in sediments rather than the reverse. Faster establishment of a steady-state is quite plausible in other systems. For

example, rivers or very shallow lakes may experience higher suspended solids concentrations and a greater rate of mercury removal by settling. Increased diffusion and/or resuspension rates as a result of more mixing are also possible in rivers or shallow lakes. The mass transfer coefficient used in this study for porewater/water exchange was 0.01 m day^{-1}. Higher values are plausible (e.g. 0.1 m day^{-1}) and would result in more rapid attainment of steady-state conditions between the water column and sediments.

An important consideration in terms of Hg(II) response time is the exchangeable and fixed fraction of mercury on solids. As discussed previously, the simulations were run assuming virtually all the Hg(II) on solids was exchangeable. It is quite possible however that a significant or even dominant portion of sediment solids may not be readily exchangeable. If this were the case, then porewater and compartments in equilibrium with porewater (benthos and exchangeable solids) might respond at different rates than assumed in these simulations. It is also worth noting that if most sediment solids mercury were not exchangeable, resuspension would load particulate mercury to the water column, but much of this mercury might remain on solids rather than become available to influence surface water concentrations. Future modifications to the model will better handle the question of fixed and exchangeable fractions.

The distribution of a significant fraction of sediment Hg(II) into a relatively fixed compartment could prevent methylation and help reconcile some of the variability between systems for the ratio of methylmercury to total mercury in solution. For example, New Hope Pond in East Fork Poplar Creek, Tennessee, is a system highly polluted with inorganic

mercury. Water concentrations of total mercury are in the ug L^{-1} range. Methylmercury concentrations in water are also elevated, but not to the same extent as Hg(II). In this system methylmercury represents less than 0.05% of total mercury in water. This is about two orders of magnitude lower than the percentage one might expect for an aerobic unpolluted system (e.g. 5%).

11.2 Cycling and Distribution of Methylmercury in Aquatic Systems

As is the case for Hg(II), the steady-state concentration of methylmercury in a lake is a function of the balance between loads and sinks in the system. It is not clear from limited field data or the simulations in this study whether lakes generally act as traps or sources of methylmercury. There are presently insufficient field data to establish trends in this regard. Plausible rate constants could be used in simulations to lead in either direction.

11.2.1 Methylmercury Loading

The Relative Importance of External and Internal Sources of Methylmercury

There is presently insufficient information available to accurately simulate in-situ production of methylmercury and make comparisons with external loads. A simulation of the generic system with no in-situ methylation whatsoever still generated plausible concentrations in abiotic and biotic compartments (e.g. 0.06 ug m^{-3} in surface waters). This suggests that for some shield lakes, external methylmercury inputs may be important.

Alternatively, it is possible that in-situ methylation and removal via burial were both underestimated in the simulations. Field data are required to identify whether unpolluted shield lakes are net sinks or sources of methylmercury (i.e. methylmercury in outflows exceeds inflows), and to assess the significance of in-situ production of methylmercury. Since little, if any, additional methylmercury formation was required to generate plausible results in the generic shield lake simulation, net methylation (sediments and water column combined) was intentionally constrained to a rate of production equal to about 30% of external loading. The steady-state concentration of methylmercury in the water column then increased from 0.06 to about 0.08 ug m^{-3} due to in-situ methylation.

The Relative Importance of Terrestrial and Atmospheric Inputs of Methylmercury

The simulations suggest that for many shield lakes, terrestrial based methylmercury inputs may exceed atmospheric deposition. For the generic shield lake hypothesized in this study, with a 2 year hydraulic retention time, only 15% of external methylmercury loading was via direct atmospheric deposition. Another 65% of external methylmercury inputs was dissolved in the inflow and about 20% was carried on inflowing particulates. Dry deposition was negligible, but this reflected an assumption rather than having any basis in field data.

The relative importance of atmospheric and terrestrial loads of methylmercury depends on many factors, including the lake hydraulic retention time, ratio of lake surface area to drainage area, and concentration of suspended solids in runoff. The simulations suggested that particulate methylmercury in runoff is significant, but usually smaller than the dissolved

component (e.g. 25% of total runoff methylmercury in the generic shield lake when the suspended solids concentration was 2 mg L^{-1}). The results also suggest that increased suspended solids concentrations could significantly increase methylmercury loading via runoff, particularly during the spring freshet.

pH also has the potential to be implicated in rates of both atmospheric and terrestrial loading of methylmercury. Wood (1989) noted Swedish studies which indicated acidification may liberate cobalt in soils. This could in turn elevate rates of methylcobalmin mediated methylation in soils or runoff waters. As with Hg(II), low pH could result in precipitation of DOC and associated methylmercury in runoff. Thermodynamic calculations used in the model suggest DOC is the dominant complexing agent for methylmercury as well as Hg(II) in aerated waters. The affinity for methylmercury and carbon would also suggest positive correlations between humic matter and methylmercury concentrations in runoff, as have been established for Hg(II).

It was beyond the scope of the model at present to simulate variations in external methylmercury loading as a function of environmental conditions. Methylmercury loads from the atmosphere and land were specified as inputs. Development of models to assess methylmercury loading to lakes via the atmosphere and land are important steps required to develop a full understanding of methylmercury cycling in lakes. Abiotic methylation of mercury by humic substances, particularly fulvic acids has been identified in the literature (Weber et al., 1985; Nagase et al., 1982; Lee et al., 1985) and should be considered as a possible methylating mechanism in terrestrial systems.

Factors Affecting Methylmercury Production

Internal formation of methylmercury in lakes and reservoirs is a subject of considerable uncertainty, as discussed previously. Bacterial methylation is likely the major in-situ source of methylmercury. Direct leaching of methymercury from flooded soils and abiotic methylation are other potential sources. Factors affecting in-situ methylation, demethylation and net methylation have been discussed in Section 5 and are summarized in Tables 5.1 and 5.2.

The model is sufficiently mechanistic to allow an examination of possible trends regarding effects of DOC, pH, and temperature on mercury bioavailability, bacterial activity, methylation and demethylation rates in lakes and reservoirs. However, given the present lack of an ability to measure in-situ methylation and demethylation rates at natural levels, the above concepts were often treated qualitatively rather quantitatively in this study.

Methylation and demethylation rates are influenced by the total amount of Hg(II) or methylmercury in solution and the available fraction of this total which is utilized by bacteria. Thermodynamic calculations used in simulations in this study to represent well oxygenated waters suggest that only a small fraction of Hg(II) or methylmercury is available for methylation or demethylation in the water column or sediments. Table 8.1 suggests a range of 0.05 to 0.2 % of Hg(II) in solution being available for methylation. Table 8.2 suggests 0.25 to 0.5% of methylmercury in solution is available for demethylation. These estimates are very preliminary and assume mercury complexes with organics are unavailable to bacteria. The

estimates also assume free sulphide levels in aerobic waters are negligible. Based on thermodynamic estimates discussed in Section 8, even traces of sulphide in aerobic waters could play a role in mercury bioavailability.

The approach used in the model for partitioning suggests that if the mass of suspended solids or plankton were to increase in the water column, more methylmercury would partition into these compartments and reduce concentrations in solution.

Although anaerobic systems were not simulated using the overall model, thermodynamic calculations were carried out to study mercury speciation in anaerobic conditions. The model framework considered competition for Hg^{++} ions by dissolved compounds, solid substrates, plankton (in the water column only) and benthos (in sediments only). Most Hg(II) and methylmercury was predicted to be bound to sulphide complexes in anaerobic conditions. The total amount of mercury in solution could increase significantly if sulphides successfully compete with solid substrates for mercuric ions (see Figures 8.2 and 8.4). If sulphide complexes with Hg(II) are not methylated, then the total mercury concentration in solution could increase with greater sulphide concentrations, while the concentration of bioavailable species such as $HgCl_2$ could decrease, since most of the mercury is bound to sulphides. Since methylation of sulphide complexes has been reported, although at very low rates, it is not clear whether movement of Hg(II) into sulphide complexes would result in greater or lower rates of methylation. It is plausible that a shift of Hg(II) away from organics into a sulphide pool which can be methylated, albeit at a slower rate, could ultimately result in greater production of methylmercury. This could help reconcile increased

concentrations of methylmercury observed in anoxic hypolimnia in Little Rock Lake (Bloom and Watras, 1989a) and the western basin of Clay Lake (Furitani and Rudd, 1980). Alternatively, the affinity between sulphide and mercury could result in diffusion of methylmercury from sediments into overlying anoxic waters containing sulphide during summer stratification. Increased diffusion into anoxic hypolimnia of Hg(II) bound to sulphides could also help explain higher Hg(II) concentrations observed in Little Rock Lake under such conditions (Bloom and Watras, 1989a).

The thermodynamic approach used in the model also allowed inferences regarding possible effects of DOC levels on mercury availability for methylation and demethylation. Although high humic concentrations in runoff may be associated with Hg(II) loading to a shield lake, elevated DOC levels *within* the waterbody would thermodynamically be expected to remove mercury from the pools available for methylation or demethylation, assuming DOC/Hg complexes are not available to bacteria. This would offset to an unknown extent the effect on methylation of Hg(II) loaded from the watershed. Furthermore, stimulation of microbial activity by allochthonous carbon may be low in some runoff dominated lakes if this DOC has been degraded prior to reaching the watershed.

Acidity levels may also play a role in the influence of DOC on bioavailability of Hg(II) and methylmercury for net in-situ methylmercury production. As discussed previously, low pH could aggregate and settle out DOC. This would lead to lower concentrations of dissolved Hg(II) in solution, although the fraction of Hg(II) in solution available for methylation would thermodynamically be expected to increase.

Methylmercury loading in Reservoirs

In reservoirs, loading of methylmercury via leaching from flooded soils and via in-situ methylation are both possibilities. Increased DOC levels in new reservoirs would be expected to stimulate bacterial activity since a significant carbon fraction would be easily degradable, and Hg(II) levels may (or may not) increase due to leaching from soils. These factors would tend to increase methylation rates in-reservoirs. Opposing this trend would be the lower fraction of mercury in solution which is methylated, since higher DOC levels would be expected to complex Hg(II), leaving less to be methylated. Increased levels of methylmercury found in fish in new reservoirs suggest increased in-situ production of methylmercury, although other causes are possible, including leaching of methylmercury from flooded soils and changes in fish growth rates, behaviour and diet.

Estimates of Methylmercury Production

Estimates of methylation rates developed in Appendix D were initially applied to the generic shield lake simulation. However, these rates resulted in very high concentrations of elemental mercury in the water column, due to demethylation. Methylation and demethylation rates were therefore reduced by about an order of magnitude for the generic shield lake to remedy this problem. Minor relative adjustments to rates of specific methylation and demethylation were also required to maintain a desired level of net methylation.

Simulated rates of methylation in sediments ranged from about 0.05% to 1.0% per year of the total Hg(II) burden in sediments. Rates of methylation of Hg(II) in surface waters in the simulations were in the range of 5-15% of Hg(II) per year in solution in surface waters. Demethylation rate constants were more rapid than methylation rate constants in the water column and sediments, by about an order of magnitude. Sediment demethylation consumed methylmercury at a rate in the range of 1-10% of total sediment methylmercury per year. Water column rates were higher, in the range of 50-200% of methylmercury in solution in surface waters per year.

Simulated net production of methylmercury in the generic shield lake was about 0.05 to 0.10 ug MeHg m^{-2} $year^{-1}$ in the water column and 0.10 to 0.15 ug MeHg m^{-2} $year^{-1}$ in sediments in the generic system. Approximately one third of net methylmercury production in-situ was therefore in the water column. Rates of net methylation in polluted sytems were higher, up to 10-20 ug MeHg m^{-2} $year^{-1}$ in sediments and 2-4 ug m^{-2} $year^{-1}$ in the water column. In the simulations, net production of methylmercury in the water column varied from 15% to 40% of the combined total for sediments and the water column, indicating both sites are potentially significant. It would be inappropriate to draw conclusions based on the simulations regarding the relative magnitude of water column and sediment methylation.

All of the methylation and demethylation rates discussed above are preliminary. These processes may be very important however in terms of methylmercury cycling. Further research in this area is essential to understand methylmercury cycling in lakes and reservoirs.

11.2.2 Methylmercury Sinks

Demethylation, burial and outflows all represented significant removal mechanisms in the generic shield lake simulation for methylmercury (see Figure 9.4). The relative importance of these loss terms depends on individual system characteristics. For the simulations in this study, sediment demethylation consumed methylmercury at rates in the range of 1-10% of total sediment methylmercury per year, while water column rates were higher, in the range of 50-200% of methylmercury in surface waters per year. In the generic shield lake system, demethylation in sediments and the water column were comparable in absolute magnitude, and combined to remove methylmercury at a rate of about 1 ug MeHg m^{-2} $year^{-1}$. Rates of demethylation were chosen partly on the basis of producing plausible concentrations of elemental mercury in sediments and the water column.

11.2.3 The Importance of Biota to Methylmercury Cycling

The simulations suggested that if biomass densities are in the range of 1-5 ppm (plankton, benthos and fish combined), these biota are a significant repository for methylmercury in terms of the entire aquatic system. Plankton, benthos, and fish may all contain quantities of methylmercury comparable or greater to that present in water, depending on the biomass densities in each case. Table 9.4, for example, shows that for the simulation of a generic shield lake, plankton and benthos contained roughly equal masses of methylmercury as surface waters, and fish contained about 4 times the quantity in the water column. These results reflect estimated biota densities of 2 ppm each for benthos and plankton, 1.5 ppm for

yellow perch and 0.25 ppm for walleye. In productive systems such as Lake St. Clair, biota may be even more significant repositories of methylmercury. Biota were second only to sediments in terms of methylmercury distribution in the generic system (about 60% in sediments, 30% in biota). Placing a significant fraction of the methylmercury in compartments which do not leave the system rapidly would tend to slow down the potential of the overall system to respond and establish a new methylmercury steady-state.

The simulations also suggested that biota were responsible for large methylmercury fluxes in the water column, in excess of external loads in the generic lake (see Figure 9.4). Biota may also contribute significantly to fluxes across the water/sediment interface.

Based on the bioenergetics approach used in the model, the food pathway would represent more than 95% of methylmercury uptake by fish in aerobic waters. This prediction applied to walleye and yellow perch. Methylmercury uptake across the gills has the potential to be somewhat more significant if water methylmercury concentrations increased about 1-2 orders of magnitude into the range of 1-5 ng L^{-1} (e.g. anoxic hypolimnia), *without* a corresponding increase in the methylmercury concentrations in food. This is unlikely however, and fish may not wish to pursue a meal in such a harsh environment in any case.

Fish populations achieved a steady-state where intake of methylmercury was offset by excretion and loss of biomass from the fish pool via death. In the case of yellow perch in the generic shield lake simulation, about 1/5 of the methylmercury in eaten plankton passed through the fish unassimilated. Another 1/3 of the methylmercury in eaten plankton moved up

through the food chain when yellow perch were eaten by walleye. In terms of clearing mercury from tissue in yellow perch population, the primary removal mechanisms were excretion (about 45%) and consumption by predators (about 40%).

The main loss of methylmercury from the walleye population was via mortality other than predation (approximately 65% of the methylmercury eaten by walleye). This flux was assumed to settle to the sediments. If dead fish indeed sink to the bottom and decompose, and if a significant fraction of predatory fish die by means other than predation, fish could be significant in terms of water/sediment fluxes.

There is significant uncertainty associated with these methylmercury fluxes, since they depend on fish species, growth rates, diets, sources of mortality, population distributions and biomass. The results should be viewed from the perspective that they indicate the potential for biota to represent significant methylmercury fluxes within aquatic systems, both in the water column and across the sediment/water interface. Further model refinements and data for calibration would be very useful.

11.2.4 Response Times for Methylmercury in Aquatic Systems

When conditions in a system are not at steady-state, it is the first (or higher) order methylmercury sinks which control the ability of various compartments and the entire system to respond and establish new steady-state methylmercury concentrations. The response time half-life for methylmercury was on the order of 1-2 months in the water column and 1.5 years

in sediments in the generic shield lake simulations. As was the case for Hg(II), the processes which tended to control the response times for individual compartments were those which moved methylmercury from one compartment to another within the system. In particular, settling, resuspension and diffusion, which moved methylmercury between the water column and sediments were important. These fluxes tended to be about an order of magnitude greater than fluxes removing methylmercury from the system altogether. The response time of the combined water column/sediment system was therefore slower. In the case of the generic system simulated in this study, the methylmercury burden in the overall system would move towards a new steady-state with a half-life on the order 10 years.

For the generic shield lake scenario simulated in this study, the sediments and water column would tend to reach a methylmercury steady-state after a time period on the scale of months, with the water column moving more rapidly to achieve steady-state than sediments. It is quite plausible that steady-state conditions between the water column and sediments could occur more quickly in other situations, for example rivers, shallow lakes or mercury polluted systems. Factors promoting a more rapid attainment of steady-state conditions include higher rates of microbial activity or microbial adaptation in contaminated environments (faster rate of demethylation), increased diffusion, and/or increased resuspension rates as a result of more mixing. The Lake St. Clair scenario involved a productive shallow waterbody with a retention time of 9 days. A methylmercury steady-state between the water column and sediments in this system would likely happen more quickly than for the generic shield lake scenario, perhaps in a matter of days to weeks, rather than months.

Since methylmercury and Hg(II) were predicted to have similar response times in the generic shield lake, one would expect an apparent steady-state relationship to develop between methymercury and Hg(II) within a period of months as well. Changes in Hg(II) steady-state conditions would not necessarily be paralleled by comparable changes in methylmercury concentrations however. For example, if Hg(II) levels doubled in a system, methylmercury concentrations would reach a new steady-state, but might not double unless in-situ methylation was the dominant methylmercury load in the system. Ratios of methylmercury to Hg(II) concentrations may therefore vary in a given system from one steady-state scenario to another.

Although plankton and benthos were assumed to be in instantaneous equilibrium with the water and porewater phases respectively, fish populations responded more slowly to system changes. The methylmercury content in the yellow perch population in all simulations was predicted to respond to changes with a half life in the range of 0.6 to 0.7 years, while the corresponding value for the walleye population was in the range of 1.3 years. Processes dominating these responses in yellow perch were primarily (i) consumption by predators and (ii) excretion. In the walleye population, response time was affected the most by "other undefined death" (old age, disease, etc.). Estimates of sustainable rates of fishing as a possible mercury removal mechanism should be carried out. These results are subject to assumptions regarding productivity rates and behaviour patterns and causes of death, factors for which considerable variability is possible.

12.0 SUMMARY

A mechanistic model has been developed to study mercury cycling in freshwater systems. The model was used in a diagnostic manner rather than predictively. It would be premature to attempt accurate predictive applications until more field data are obtained and a more quantitative perspective is gained regarding processes important in the mercury cycle. Such information is now beginning to emerge.

A model based only on total mercury would not be sufficiently flexible to address methylmercury cycling. At least two mercury forms, methylmercury and Hg(II), should be included in a mechanistic model for aquatic systems. Consideration of elemental mercury improves the ability to simulate losses from the system through volatilization. From the perspective of a diagnostic model which includes mercury in fish, it was necessary to include 5 mercury forms: methylmercury, Hg(II), elemental mercury, dimethylmercury and solid HgS.

In the aerobic systems simulated in this study, Hg(II), methylmercury and elemental mercury were found to play significant roles in the mercury cycle. Volatile dimethylmercury and unreactive solid HgS were not important in these aerated systems, but it is quite plausible that they assume a greater significance in anaerobic environments as mechanisms to remove mercury from biologically active pools in surface waters and sediments.

Several abiotic and biotic compartments need to be included in a mechanistic model for lakes and reservoirs. Air, water, sediments, suspended solids, and 4 biotic compartments were included. To address the issue of biomagnification and the effect of diet on mercury levels in fish, it was necessary to consider water column plankton, benthos, prey fish species and predatory fish. As discussed below, biota likely represent important repositories and fluxes for methylmercury. A model framework was therefore developed which adapted bioenergetics equations for individual fish to treat mercury burdens and fluxes for fish year classes and entire fish populations.

Mercury Distribution

Hg(II) was the dominant mercury form in all systems studied. In freshwater aquatic systems, most Hg(II) is in sediments. Elemental mercury was simulated to represent the dominant mercury form in air but represented only a small fraction of mercury in the water column and sediments (e.g. 0.1 percent). Biota do not appear to be overly significant regarding Hg(II) distribution, but are important regarding methylmercury distribution. Depending on the biomass densities assumed, plankton, benthos and the water column may all contain comparable quantities of methylmercury, while fish may be the largest methylmercury repository in the water column. The simulation of a generic Ontario shield lake in this study resulted in fish containing about 4 times as much methylmercury as water, assuming a fish "density" of 1.75 ppm.

The Hg(II) Cycle

In the simulations, Hg(II) loading from the atmosphere and runoff were both important. For shield lakes in Ontario with significant runoff, the relative magnitude of these two loads will depend on specific environmental factors. Either source is capable of dominating Hg(II) loading to a lake.

Based on the simulations, shield lakes with significant runoff were net sinks for total mercury in unpolluted systems. In mercury contaminated environments, such as Clay Lake and Lake St. Clair, sediment return of Hg(II) via resuspension and/or diffusion caused the lake to be a net source of mercury to downstream areas, particularly if mercury inputs from upstream were curtailed. Return of mercury from polluted sediments in a lake or upstream could partially explain observed two-phase recoveries of methylmercury in some polluted systems. Observed mercury concentrations in walleye in Lake St. Clair and Clay Lake, Ontario both showed an initial rapid rate of recovery following remedial actions, followed by a slower second phase.

The primary sinks for the generic shield lake simulations were Hg(II) burial and outflows, representing about 85% of total mercury losses from the overall aquatic system. Volatilization of Hg° to the atmosphere represented the remaining 15%. Considerable system to system variability is probable for sources and sinks of total mercury in shield lakes. Methylation and reduction of Hg(II) were not calculated to be major Hg(II) sinks, but considerable uncertainty is associated with rates for these processes. In the generic shield lake

simulation, Hg(II) was reduced to elemental mercury at a rate of 10% per year in the water column. Simulated demethylation rates were 3-5% per year of total methymercury in sediments and 50-75% per year of methylmercury in the water column.

The time required for Hg(II) concentrations in various compartments to respond to changes in loads was simulated. In this study, response time was a measure of the time required to achieve a new steady-state if a system was perturbed. The response time half-life was the time required for mercury sinks in a compartment to remove 50% of the mercury burden in the compartment. Overall system response time half-lives were also calculated, based on the ability of the overall system sinks (outflows, burial and internal decay) to bring the system to a new steady-state.

Water column Hg(II) in the generic shield lake simulations had a response time half-life in the range of 1-2 months. The corresponding value for sediments was longer, on the order of 2-3 years. These times tended to be controlled by fluxes to other internal compartments, rather than by fluxes out of the overall system. There was therefore a tendency towards relatively rapid internal cycling of Hg(II), but slower overall system response times. The generic shield lake was estimated to recover from elevated Hg(II) levels at a rate in the range of 50% each 10-20 years. This rate applied to all compartments in the lake, since internal cycling was relatively rapid. Rates of recovery in other systems could vary considerably, depending on burial rates, resuspension, outflows and internal degradation of Hg(II) through reduction and perhaps methylation. The Clay Lake simulation, for example, suggested declines in overall mercury burdens in the system (and in

individual compartments) at a rate of about 50% each 5-6 years.

The Elemental Mercury Cycle

Based on an evaluation of measurements of elemental mercury concentrations in surface waters and an air/water piston velocity, Hg° volatilization was estimated to be in the range of 2.0-2.5 ug m^{-2} $year^{-1}$ in the generic shield lake. The air/water interface was accordingly a net source of mercury to the lake for unpolluted systems, since atmospheric deposition of total mercury was in the range of 11 ug m^{-2} $year^{-1}$. Mercury polluted systems may volatilize more mercury than they receive via atmospheric deposition. Volatilization was simulated to be the main Hg° sink for the water column in the generic shield lake. At steady-state this loss is approximately balanced by internal Hg° formation via Hg(II) reduction and demethylation. This steady-state relationship was used to help bound plausible rates of Hg(II) reduction and demethylation.

The Methylmercury Cycle

It is not possible based on existing field studies or the simulations carried out in this study to determine whether remote shield lakes act as net downstream sources or sinks of methylmercury. Further measurements are required of methylmercury concentrations in runoff, precipitation and in the waterbody, and of in-situ methylation rates, to assess this issue. Based on simulations for a generic shield lake in Ontario, the watershed has the potential to be an important source of methylmercury in some shield lakes. It would be inappropriate to draw

conclusions based on the simulations in this study regarding the relative magnitude of water column and sediment methylation. The simulations did indicate however that water column and sediment production of methylmercury have the potential to be comparable in magnitude.

Thermodynamic calculations used in this study to represent well oxygenated waters suggest that only a small fraction (eg. less than 1%) of Hg(II) is available for methylation in the water column or sediments. Similarly, less than 1% of methylmercury was thermodynamically expected to be available for demethylation in the water column or sediments. Most Hg(II) and methylmercury in oxygenated waters was calculated to be complexed by DOC (e.g. 99%) and assumed unavailable for utilization by bacteria. The strong affinity between Hg(II) and sulphide suggests thermodynamically that even trace quantities of sulphide in aerobic waters could play a previously unforeseen, substantial role in mercury bioavailability. Anaerobic conditions were thermodynamically predicted to cause most Hg(II) and methylmercury to be bound to soluble sulphide complexes, even in the presence of DOC. Thermodynamic calculations also suggested that the total amount of mercury in solution, particularly porewater, could increase significantly if sulphides successfully compete with solid substrates for mercuric ions. Sulphide complexes with Hg(II) were considered unavailable for methylation, although low rates of methylation of solid phase HgS have been reported in the literature. The ability of sulphide/Hg(II) complexes to be methylated could be an important factor influencing methylation in anoxic conditions.

The influence of DOC upon mercury levels in fish has been closely examined in the literature. Oligotrophic lakes and dystrophic with significant runoff often show positive correlations between DOC and fish mercury content. Eutrophic waterbodies however, may tend towards lower mercury levels in fish. The model framework was used qualitatively to help reconcile the existence of both positive and negative correlations between DOC levels and fish mercury levels in differing environments. The thermodynamically predicted affinity between mercury and carbon suggests that lakes receiving a large fraction of their DOC from the watershed are also receiving increased watershed inputs of Hg(II) and possibly methylmercury. However, watershed based DOC may tend to keep dissolved mercury in a biochemical pool which is mainly unavailable for methylation or demethylation. This could at least partially offset the positive effect on methylation of increased Hg(II) loading from the watershed. Furthermore, watershed DOC may be relatively degraded prior to reaching the lake, and may not stimulate methylation as much as labile carbon would. Elevated fish mercury concentrations in some high colour, low productivity lakes with significant runoff may therefore reflect higher external loading of methylmercury rather than in-situ production.

Increased DOC in eutrophic waters with low terrestrial inputs would be internally generated and would not reflect an increase in Hg(II) or methylmercury loading from the watershed. Although the DOC may reflect increased bacterial activity in such waters, in-situ methylation might be low due to DOC complexation of Hg(II). These conditions could lead to negative correlations between DOC and fish mercury content in some systems, such as productive seepage lakes.

The potential for methylmercury formation in reservoirs was considered. A new reservoir may induce a pulse of Hg(II) and/or methylmercury from flooded soils, and provide a plentiful supply of degradable carbon. The labile carbon might stimulate bacterial activity to a greater relative extent than DOC complexation removes Hg(II) from the bioavailable pool. These conditions could lead to higher fish mercury concentrations in reservoirs. Other factors could also be implicated in elevated mercury levels in fish in reservoirs, including changes in fish growth rates, behaviour and diet.

The model suggests pH could be implicated in relationships between DOC and fish mercury levels. Low pH conditions could induce DOC aggregation and settling, causing lower concentrations of dissolved Hg(II). This process would also be expected on a thermodynamic basis to *increase* the fraction of Hg(II) in solution assumed available for methylation (represented by Hg^{++} and other inorganic Hg(II) complexes). It is unclear whether the absolute concentration of Hg(II) available for methylation would increase or decrease due to DOC aggregation and settling.

Simulations suggested that biota were responsible for large methylmercury fluxes in the water column in unpolluted lakes. These biotic fluxes may be comparable to abiotic fluxes across the sediment/water interface and are likely in excess of external rates of methylmercury inputs (see Figure 9.4). Based on the bioenergetics approach used in the model, uptake of mercury via the food pathway would represent 95-99% of methylmercury to fish in aerobic waters. This prediction applied to walleye and yellow perch. Fish populations achieved a steady-state where intake of methylmercury was offset by excretion and loss of

methylmercury containing biomass via death. If dead fish sink to the bottom and decompose, this process may be significant in terms of water column/sediment methylmercury fluxes. There is a wide range of uncertainty associated with methylmercury fluxes involving fish populations. Estimates of such fluxes depend on fish species, growth rates, diets, sources of mortality, population distributions and biomass. The results should be viewed from the perspective that they indicate the potential for biota to represent significant methylmercury fluxes within aquatic systems, both in the water column and across the sediment/water interface.

The time required for methylmercury concentrations in various compartments to respond to changes in loads was examined. Water column methylmercury concentrations had response time half-lives in the generic shield lake simulations in the range of 1-2 months, while the corresponding value for sediments was longer, on the order of 1.5 years. These response times tended to be controlled by fluxes to other compartments in the system, rather than by fluxes out of the system. The result was a tendency for relatively rapid internal cycling of methylmercury, but slower overall system methylmercury response times (e.g. decades). Recovery rates for methylmercury likely vary considerably from system to system, depending on rates of burial, resuspension, outflow and demethylation.

Response times for fish populations were estimated to be on the scale of 6-8 months for prey species and roughly twice as long for predatory species. The longer response times for the predatory fish population were caused by lower rates of depuration at higher mean weights, and slower population turnover times for predators. It is concluded that the use of

bioenergetics to simulate mercury uptake by individual fish and populations is a very useful mechanistic approach to define response times.

For the generic shield lake simulated in this study, the sediments and water column would tend to reach a methylmercury steady-state after a time period on the scale of months, with the water column moving more rapidly to achieve steady-state than sediments. Attainment of a steady-state between the water column and sediments could occur more rapidly in situations involving higher rates of microbial activity, microbial adaptation in contaminated environments (faster rate of demethylation), increased diffusion, and/or increased resuspension rates as a result of more mixing (e.g. in a river or shallow lake). Steady-state ratios of methylmercury to Hg(II) concentrations may vary in a given system from one steady-state scenario to another.

Finally, the model provided a sound basis for diagnostic comparisons of processes involved in mercury cycling in aquatic systems. Total mercury and methylmercury cycling are affected by a wide range of physical, chemical and biological processes which defy simple treatment of the issue. Many influences on mercury cycling exist and are included in the model, but need to be better quantified (eg. effects of DOC, pH, productivity). The simulations undertaken in the study were reasonably able to reflect observed trends. However, this agreement resulted partly from case by case adjustments of rate constants and lake specific characteristics (eg. mercury inputs), and partition coefficients, and is not a statement of a robust predictive strength. This case by case process constitutes part of the long-term work needed to define magnitudes of model coefficients. Such assessments will help the evolution

of an understanding of the important processes in mercury dynamics in aquatic systems. Much of the work needed to quantify these parameters is ongoing and the ability to model mercury should improve dramatically in the next few years. Recommendation for future research and model development are given in the next section.

13.0 RECOMMENDATIONS

Recommendations are grouped into 2 categories: those relating to information needs (field and laboratory studies), and those related directly to future model development. Within each category, recommendation are listed in order of priority.

Recommendations to Address Information Needs:

1- Improved methods for measuring methylation and demethylation rates at natural levels in aquatic systems are needed. Methods should be developed for sediments and the water column.

2- A mass balance measurement program for Hg(II), methylmercury and elemental mercury should be carried out for a typical shield lake, and for a reservoir situation, providing both pre and post impoundment conditions in the case of the reservoir. Physical, chemical and biological processes should also be monitored in these systems to allow calibration of the model. Multi-year studies would provide data to assess year to year variability.

3- Improved methods to assess bioavailable fractions of Hg(II) and methylmercury for methylation and demethylation respectively would be useful. Operational techniques should be considered which allow predictions of bioavailability for a variety of conditions, and compared to thermodynamic techniques presented in this study. The roles of sulphides and organics on bioavailability should be stressed.

4- Adsorption/desorption kinetics for methylmercury and Hg(II), and partitioning into kinetically fast and slow fractions should be investigated. A methodology to estimate partition coefficients for a variety of environmental conditions should be developed.

5- Food chain dynamics of mercury cycling need to be investigated more thoroughly, including studies to assess the prey/predator cycling of mercury. Data are lacking regarding methylmercury and Hg(II) speciation and concentrations in plankton and benthos as a function of different environmental conditions. Methods should be developed to assess the fate of mercury in fish which die by causes other than direct predation, since these fluxes may be significant.

6- Investigations of cycling of elemental mercury are needed, including rates of reduction of Hg(II) in the water column and sediments, rates of demethylation, air/water volatilization and oxidation of Hg°.

Recommendations Regarding Model Development:

7- If terrestrial loads of methylmercury are found to be significant relative to in-situ production (this study suggests this is quite possible given the presently available data), a model which assesses terrestrial loading of methylmercury would be very useful. The model should also consider terrestrial loading of Hg(II). Consideration should be given to the potential for environmental factors such as humic matter in runoff and pH to influence terrestrial Hg(II) and methylmercury loading to aquatic systems.

8- Follow parallel studies in atmospheric modelling. Consider using a simplified atmospheric cycle in this model once mercury cycling in the atmosphere is adequately quantified.

9- Improve the bioenergetics calibrations used for mercury dynamics for individual fish.

10- Improve the treatment of fish populations in the present model. Treat each year class as a compartment.

11- Focus the scope of the model from a diagnostic perspective which considers a wide range of likely and unlikely processes, to a smaller set of processes likely to be significant. Consider a two-phase approach, involving steady-state assessments and unsteady-state assessments for particular situations (e.g. reservoirs).

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APPENDICES

APPENDIX A

Hg(II) SPECIATION IN SURFACE WATERS

The following complexes are assumed present in fresh waters, in addition to the free Hg^{++} ion:

COMPLEX — COMPLEXATION EQUATION

Soluble Hg(II) complexes:

1) $HgCl_2$

$$\frac{[HgCl_2]}{[Hg^{++}][Cl^-]^2} = 10^{13.97}$$

Reference:

- Smith and Martell (1976c): 13.22 @ 25 C, 0.5 M ionic strength
  13.23 @ 25 C, 1.0 M ionic strength

- Dyrssen and Wedborg (1980): $B[Cl]^2 = 10^{6.6}$ @ $[Cl^-] = 10^{-3.7}$

  gives $B = 10^{13.97}$
  where $B = [ML_n]/[M][L]^n$
  (as above)

2) $HgCl^+$

$$\frac{[HgCl^+]}{[Hg^{++}][Cl^-]} = 10^{7.3}$$

Reference:

- Smith and Martell (1976c): 6.74 @ 25 C, 0.5 M ionic strength
  6.72 @ 25 C, 1.0 M ionic strength

- Dyrssen and Wedborg (1980): $B[Cl] = 10^{3.6}$ @ $[Cl^-] = 10^{-3.7}$

  gives $B = 10^{7.3}$
  where $B = [ML]/[M][L]$
  (as above)

3) $HgOHCl$ $\quad \frac{[HgOHCl]}{[Hg^{++}][OH^-][Cl^-]} = 10^{18.07}$

Reference:

- Dyrssen and Wedborg (1980): $B[OH-][Cl-] = 10^{8.9}$

@ $[Cl^-] = 10^{-3.7}$
and pOH=5.5
gives $B = 10^{18.1}$
where $B = [MOHL]/[M][OH^-][L]$
(as above)

and $B[OH-][Cl-] = 10^{7.7}$

@ $[Cl-] = 10^{-3.7}$
and pOH= 6.67
gives $B = 10^{18.07}$
where $B = [MOHL]/[M][OH^-][L]$
(as above)

4) $Hg(OH)_2$ $\quad \frac{[Hg(OH)_2]}{[Hg++][OH-]^2} = 10^{21.84}$

Reference:

- Smith and Martell (1976c): 21.8 @ 25 C, 0.0 M ionic strength
- Smith and Martell (1976b): 21.0 @ 25 C, 0.5 M ionic strength
- Smith and Martell (1976b): 21.1 @ 25 C, 1.0 M ionic strength

- Dyrssen and Wedborg (1980): $B[OH-]^2 = 10^{8.0}$

@ $[Cl^-] = 10^{-3.7}$
and pOH=5.5
gives $B = 10^{21.8}$
where $B = [M(OH^-)^2]/[M][OH^-]^2$
(as above)

and $B[OH^-]^2 = 10^{8.5}$

@ $[Cl^-] = 10^{-3.7}$
and pOH=6.67
gives $B = 10^{21.84}$
where $B = [M(OH^-)^2]/[M][OH^-]^2$
(as above)

5) $HgHS_2^-$ $\quad \dfrac{[HgHS_2^-]}{[Hg^{++}][HS^-][S^{2-}]} = 10^{45.5}$

Reference: Dyrssen and Wedborg (1980)

6) $Hg(HS)_2$ $\quad \dfrac{[Hg(HS)_2]}{[Hg^{++}][HS^-]^2} = 10^{37.7}$

Reference: Dyrssen and Wedborg (1980)

7) HgS_2^{-} $\quad \dfrac{[HgS_2^-][H+]^2}{[Hg^{++}][HS^-]^2} = 10^{23.3}$

This complexation constant was developed using the following constants from Smith and Martell (1976b):

$\dfrac{[HgHS_2^-]}{[HgS_2^-][H^+]} = 10^{8.30}$ (20 C, ionic strength 1.0)

$\dfrac{[Hg(HS)_2]}{[HgHS_2^-][H^+]} = 10^{6.19}$ (20 C, ionic strength 1.0)

$\dfrac{[Hg(HS)_2]}{[Hg^{++}][HS^-]^2} = 10^{37.7}$ (20 C, ionic strength 1.0)

8) HgS (soluble) $\quad \dfrac{[HgS]_{soluble}[H^+]}{[Hg^{++}][HS^-]} = 10^{28.5}$

Reference: Dyrssen (1989)

9) Hg/Humic complexes in solution $\frac{[HgRS^+]}{[Hg^{++}][RS^-]} = 10^{22.1}$

Reference: Dyrssen and Wedborg (in press)

Sample organic complexes from Smith and Martell (1976a):

Ligand	Complexation:	Temp	Ionic Strength
- Acetic acid:			
	$[ML]/[M][L] = 10^{5.89}$	25 C	0.1
	$[ML_2]/[M][L]^2 = 10^{9.30}$	30 C	1.0
	$[ML_3]/[M][L]^3 = 10^{13.28}$	30 C	1.0
	$[ML_4]/[M][L]^4 = 10^{17.06}$	30 C	1.0
- Oxalic Acid:			
	$[ML]/[M][L] = 10^{9.66}$	25 C	0.1
- D-Tartaric Acid:			
	$[ML]/[M][L] = 10^{7.0}$	25 C	0.1
- Formic acid:			
	$[ML]/[M][L] = 10^{5.43}$	25 C	0.1
- Citric Acid:	$[ML]/[M][L] = 10^{10.9}$	25 C	0.1
- (Alkyldiylidenetetrathio)tetraacetic acid ($C_mH_nO_8S_4$):			
	$[ML]/[M][L] = 10^{16.6}$	25 C	0.1
- 1,2-Phthalylidenetetrathiotetracetic acid:			
	$[MH_2L]/[M][H_2L] = 10^{18.8}$	25 C	0.1
	$[M(OH)_2L]/[M][OH]^2[L] = 10^{45}$	25 C	0.1
- Tiron ($C_6H_6O_8S_2$):			
	$[ML]/[M][L] = 10^{19.86}$	25 C	0.1

Bjornberg et al. (1988) reviewed literature and estimated values of humic/mercury complexation constants ranging from 10^{10} to 10^{20}.

Zepp et al. (1974) indicated that the phenolic component of humics were relatively unimportant when compared to the thiol component in terms of complexing methylmercury.

In this study, thiol groups are also assumed to be important Hg(II) sites in soluble humics. Protonation of thiols has been estimated as follows (Zepp et al. 1974):

$$[HRS]/[H^+][RS^-] = 10^{9.52}$$

Zepp et al. also assumed a fraction (0.0001) of the dissolved organic matter to be thiol groups. Using a value of 10^{15} as a representative complexation constant for a typical humic mixture and the above estimates regarding thiol fractions in humics and protonation, a complexation constant for Hg(II) in terms of the RS^- component of dissolved humic matter is $10^{21.5}$. Dyrssen and Wedborg (in press) reported a value of $10^{22.1}$ which was adopted for this study.

Solid Phase Mercuric Sulphide:	Solubility Product
10) HgS_{solid}	$[Hg^{++}][S^{--}] = 10^{-52}$

Reference:

- Smith and Martell (1976b): -52.7 @ 25 C, 0.0 M ionic strength
  -51.0 @ 20 C, 1.0 M ionic strength
- Hem(1970) -52.37 @ 25 C, standard conditions

APPENDIX B

Hg(II) and Methylmercury Equilibrium Partitioning

(I) Partitioning in Surface Waters

The approach used to determine the equilibrium Hg(II) distribution among competing soluble complexes and solid phase adsorption sites is as follows:

1) Each timestep, determine the mass (M):

$$M = a + b + c + d$$

where:

(a) soluble Hg(II) in surface waters;
(b) Hg(II) bound to exchangeable suspended solids;
(c) Hg(II) in plankton;
(d) solid phase HgS in the water column;

It is assumed that Hg°, methylmercury complexes and dimethyl Hg forms are not in equilibrium with other mercury forms in the water column, and thus do not enter into the following calculations.

Masses are calculated by adding together the previous timestep's values of (a), (b), (c) and (d) with fluxes for each heading occuring during the present timestep, to establish today's value for M.

2) The new value of M is then used to establish individual activities of Hg(II) species for the present timestep. It is assumed temporarily that no solid HgS will occur when M is distributed amongst Hg(II) forms in surface water, exchangeable suspended solids, and plankton for the present timestep's calculations. All of the terms (a) through (c) can be expressed in terms of constants and the activity of the Hg^{++} ion:

(a) - 9 soluble Hg(II) complexes and free Hg++ ion in the water column,

$$= V_{water} * ([HgCl_2] + [HgCl^{+}] + ... [HgRS^{+}] + [Hg^{++}])$$
$$= V_{water} * ([Hg^{++}] * fac1 + [Hg^{++}] * fac2 + ... [Hg^{++}] * fac9 + [Hg^{++}] * fac10)$$
$$= V_{water} * ([Hg^{++}] * (fac1 + fac2 + ... fac10))$$

where, according to complexation constants:

V_{water}= water volume
fac1 = $[Cl^-]^2 * 10^{13.97}$
fac2 = $[Cl^-] * 10^{6.74}$
.
.
fac9 = $[RS^-] * 10^{22.1}$
fac10 = 1

(b) - Hg(II) complexes in exchangeable suspended solids,

$=V_{ss}*K_{ss}*[Hg^{++}]$

where:

V_{ss}= volume of exchangeable suspended solids
K_{ss}= dimensionless partition coefficient:$[Hg(II)]_{ss}/[Hg^{++}]_{water}$ between exchangeable suspended solids and water.

(c) - Hg(II) complexes in water column plankton,

$= V_{pl}*K_{pl}*[Hg^{++}]$

where:

V_{pl}= volume of water column plankton
K_{pl}= dimensionless partition coefficient: $[Hg(II)]_{ss}/[Hg^{++}]_{water}$ between water column plankton and water.

The new value of M can now be related to a series of constants and one variable, the activity of Hg^{++}.

$$M = V_{water} * ([Hg^{++}] * (fac1 + fac2 + ... fac10)) + V_{ss}*K_{ss}*[Hg^{++}] + V_{pl}*K_{pl}*[Hg^{++}]$$

Letting sumfac= (fac1 + fac2 + ...fac10), and rearranging gives:

$$[Hg^{++}] = M * \{(sumfac * V_{water}) + (V_{ss}*K_{ss}) + (V_{pl}*K_{pl})\}^{-1}$$

From this value of $[Hg^{++}]$, other species activities (molar) are then determined using the appropriate factors.

3) Finally, in anaerobic condtions only, where sulphide levels are significant, it is necessary to check if the solubility product criterion $[Hg^{++}][S^{-}]=10^{-52}$ has been violated, based on the assigned value of $[S^{-}]$ for the system and the value of $[Hg^{++}]$ calculated above. If so, the activity of Hg^{++} is reduced to satisfy the criterion, and the number of moles of Hg^{++} precipitated are used to determine the mass of solid HgS. The new value of $[Hg^{++}]$ is then used to recalculate the other mercury complexes involved.

The approach to calculating the equilibrium distribution of methylmercury in surface waters, suspended solids and plankton is analagous to the approach for Hg(II), except that no solid phase precipitate is involved.

(II) Partitioning in Porewater

As is the case for surface waters, porewater Hg(II) is assumed to be dominated by nine soluble complexes and may be influenced by HgS in anaerobic conditions. The sediment solids are assumed to be in equilibrium with Hg^{++} in porewater. Benthos are assumed to be in equilibrium with Hg^{++} in porewater and exchangeable solids.

The approach used to determine the equilibrium distribution among competing complexing/bonding agents is as follows in the model:

1) Each timestep, determine the mass (M) :

$$M= a + b + c + d$$

where:

(a) water soluble Hg(II) in porewater;
(b) Hg(II) bound to exchangeable sediment solids;
(c) Hg(II) in benthos;
(d) solid phase HgS in sediments

These masses are calculated by adding together the previous timestep's values of (a), (b), (c) and (d) with fluxes for each occuring during the present timestep, to establish the present timestep's value for M.

2) The new value of M is then used to establish individual activitys of Hg(II) species for the present timestep. It is assumed temporarily that no solid HgS will occur when M is distributed amongst Hg(II) forms in porewater, sediment solids, and macroinvertebrates for the present timestep's calculations. All of the terms (a) through (c) can be expressed in terms of constants and $[Hg^{++}]$:

(a) - 9 soluble Hg(II) complexes and free Hg++ ion in porewater,

The approach to estimating term (a) is identical to the above approach used for surface waters:

$$(a) = V_{porewater} * ([Hg^{++}]_{pw} * (fac1 + fac2 + ... fac10))$$
$$= V_{sed} * Porsed * ([Hg^{++}]_{pw} * (fac1 + fac2 + ... fac10))$$

where, according to complexation constants:

$V_{porewater}$	= porewater volume
V_{sed}	= total sediment volume
Porsed	= sediment porosity
fac1	= $[Cl^-]^2 * 10^{13.97}$
fac2	= $[Cl^-] * 10^{6.74}$
.	
.	
fac9	= $[RS^-] * 10^{22.1}$
fac10	= 1

(b) - Hg(II) complexes in the exchangeable sediment mass:

$$= V_{exch\ solids} * K_{exch\ solids} * [Hg^{++}]_{pw}$$
$$= V_{exch\ solids} * K_{exch\ solids} * [Hg^{++}]_{pw}$$
$$= (V_{sed} * (1\text{-Porsed}) * exfrac) * K_{exch\ solids} * [Hg^{++}]_{pw}$$

where:

V_{sed}	=	total sediment volume
exfrac	=	exchangeable fraction of sediment mass
$K_{exch\ solids}$	=	dimensionless partition coefficient: $[Hg(II)]_{exch\ solids}/[Hg^{++}]_{pw}$

(c) - Hg(II) complexes in benthos

$= V_{mac} * K_{mac} * [Hg^{++}]_{avail\ sed}$

where:

V_{mac}= volume of macroinvertebrates
K_{mac}= dimensionless partition coefficient: $[Hg(II)_{mac}]/[Hg^{++}]_{avail\ sed}$

where:

$[Hg^{++}]_{avail\ sed}$	=	{Mass of Hg^{++} in porewater + Mass of Hg^{++} in sed solids} * V_{sed}^{-1}
Porewater Hg^{++} mass	=	V_{sed}*Porsed * $[Hg^{++}]_{pw}$
Sediment solids Hg^{++} mass	=	V_{sed} * (1-Porsed) * exfrac * $K_{exch\ solids}$ * $[Hg^{++}]_{pw}$ (assumes most sediment solids Hg(II) is Hg^{++})

simplifying gives:

$[Hg^{++}]_{avail\ sed}$	=	$[Hg^{++}]_{pw}$ * {(V_{sed}*Porsed) + (V_{sed}*(1-Porsed)*exfrac*$K_{exch\ solids}$)} * {V_{sed}*Porsed) + (V_{sed}*(1-Porsed)*exfrac)}$^{-1}$

The new value of M can now be related to a series of constants and one variable, the porewater activity of Hg^{++}.

Rearranging gives:

$[Hg^{++}]_{pw} = M/\{(sumfac*(i)) + (ii) + (iii)\}$

where (i) $= V_{sed}$ * Porsed
(ii) $= V_{sed}$ * (1-Porsed) * exfrac * $K_{exch\ solids}$
(iii) $= V_{mac}$ * K_{mac} * {(V_{sed}*Porsed) + (V_{sed}*(1-Porsed)*exfrac*$K_{exch\ solids}$)} * * {(V_{sed}*Porsed) + (V_{sed}*(1-Porsed)*exfrac)}$^{-1}$

From this value of $[Hg^{++}]$, other species activities (molar) are then determined using the appropriate factors.

3) Finally, the influence of solid phase HgS is investigated as described above for surface waters.

The approach to calculating the equilibrium distribution of methylmercury in porewater, benthos and sediment solids is analagous to the approach for Hg(II), except that no solid phase precipitate is involved.

APPENDIX C

METHYLMERCURY SPECIATION IN WATER

The following complexes are assumed present in fresh waters, in addition to the free CH_3Hg+ ion:

Soluble Hg(II) complexes:

1) CH_3HgCl Methylmercuric Chloride

$$\frac{[CH_3HgCl]}{[CH_3Hg+][Cl-]} = 10^{5.18}$$

Reference:
- Smith and Martell (1976b): 5.18 @ 25 C, 0.1 M ionic strength
  5.32 @ 25 C, 1.0 M ionic strength

2) CH_3HgOH Methylmercuric Hydroxide

$$\frac{[CH_3HgOH]}{[CH_3Hg+][OH-]} = 10^{9.17}$$

Reference:
- Zepp et al. (1974): 9.37 @ 0.1 M ionic strength

- Dyrssen and Wedborg (1980): $K_1[CH_3Hg+]= 2.5$ @ pOH= 6.67, 0.001 M ionic strength gives $K_1= 9.17$

3) CH_3HgS^- Methylmercuric sulphide

$$\frac{[CH_3HgS-]}{[CH_3Hg+][S--]} = 10^{21.2}$$

Reference:

- Smith and Martell (1976b): 21.0 @ 20 C, 0.1 M ionic strength

- Zepp et al. (1974): 21.2 @ 20 C, 0.1 M ionic strength

4) $(CH_3Hg)_2S$ Dimethylmercuric sulphide

$$\frac{[(CH_3Hg)_2S]}{[CH_3HgS^-]^2[S^{--}]} = 10^{37.5}$$

Reference:

- Zepp et al. (1974):

$$\frac{[(CH_3Hg)_2S][S^{--}]}{[CH_3HgS^-]^2} = 10^{-4.9}$$

Combining this equation with $\frac{[CH_3HgS^-]}{[CH_3Hg^+][S^{--}]} = 10^{21.2}$

gives the constant: $10^{37.5}$

5) CH_3HgRS Methylmercury/humic complexes where RS- is the thiol complexing component of the humic substance

$$\frac{[CH_3HgRS]}{[CH_3Hg^+][RS^-]} = 10^{16.12}$$

Reference:

- Dyrssen and Wedborg (in press)

- Zepp et al. (1974):

Cysteine: $\frac{[CH_3HgRS]}{[CH_3Hg^+][RS^-]} = 10^{15.7}$

@ 25 C, 0.5 ionic strength

- Carty and Malone (1979):

Glutathione: $\frac{[CH_3HgRS]}{[CH_3Hg^+][RS^-]} = 10^{15.9}$

Other complexing sulphur containing groups @ 25 C:

for

SC_2H_4OH , $\log k_1 = 16.1$
CH_3S- , $\log k_1 = 16.2$
C_6H_5S- , $\log k_1 = 15.1$
$C_6H_5CH_2S-$, $\log k_1 = 16.3$

Since the above complexing constants apply to specific sulphur compounds rather than total humic substances, it is necessary to estimate the fraction of humic substances which is made of sulphur complexing groups. Zepp et al. (1974) assumed a total dissolved organic concentration of 10^{-5} and a thiol organic concentration of 10^{-9}. Thus a fraction of 0.0001 thiols was used for this study. It was also necessary to estimate the fraction of the thiol groups which would be protanated (HRS). Only RS- ions were assumed to be available for bonding with positively charged methylmercury ions. The following complexation constant for hydrogen ions and CH_3Hg+ was used:

Reference: Zepp et al. (1974)

$$\frac{[HRS]}{[H+][RS-]} = 10^{9.52}$$

Rabenstein (1977) also presented the following protonation constants:

Glutathione: $10^{8.93}$
Cysteine : $10^{8.53}$
2- Mercaptoethanol: $10^{9.52}$

Solid Phase Methylmercury complexes:

Smith and Martell (1976) Volume 5: 1st Supplement contains the following solubility product:

$$[CH_3Hg+][OH-] = 10^{-13.66}$$

@ 25 C, 1.0 ionic strength

thus for a pH range 5 to 9, the following CH_3Hg+ concentrations could not be exceeded:

- pH 5: pOH=9 , $[CH_3Hg+] = 10^{-4.66}$ M (maximum)
- pH 9: pOH=5 , $[CH_3Hg+] = 10^{-8.66}$ M (maximum)

Speciation calculations indicated that in fresh waters the CH_3Hg+ activity would be well below the above levels, and solid phase CH_3HgOH precipitation would not be expected to be important.

APPENDIX D
INITIAL ESTIMATES OF COEFFICIENTS FOR METHYLATION AND DEMETHYLATION EQUATIONS

The model uses the following equations to simulate bacterial methylation and demethylation. These processes are represented in the water column and sediments.

In water:

$$M = r * [TOC] * Const_m * \{[Hg(II)]_{av} * (Monod_m + [Hg(II)]_{av})^{-1}\}$$

$$D = r * [TOC] * Const_d * \{[CH_3HgX]_{av} * (Monod_d + [CH_3HgX]_{av})^{-1}\}$$

In sediments:

$$M = r * [TOC] * porsed^{-1} * Const_m * \{[Hg(II)]_{av} * (Monod_m + [Hg(II)]_{av})^{-1}\}$$

$$D = r * [TOC] * porsed^{-1} * Const_d * \{[CH_3HgX]_{av} * (Monod_d + [CH_3HgX]_{av})^{-1}\}$$

where:

M	= ug MeHg produced * day^{-1} * m^{-3} (m^3 surface water or porewater)
D	= ug Hg(II) produced * day^{-1} * m^{-3} (m^3 surface water or porewater)
r	= TOC consumption rate (day^{-1})
[TOC]	= TOC concentration (ug TOC m^{-3}) (m^3 surface water or total sediment)
Const	= Constant (ug Hg * ug TOC^{-1})
Porsed	= Sediment Porosity (fraction)
$Hg(II)_{av}$	= bioavailable fraction of Hg(II) (ug Hg * m^{-3}) (m^3 surface water or porewater)
CH_3HgX_{av}	= bioavailable fraction of MeHg (ug Hg * m^{-3}) (m^3 surface water or porewater)
Monod	= half saturation constant (ug Hg * m^{-3}) (m^3 surface water or porewater)

In addition to an assessment of the available fraction of mercury using thermodynamics, there are 3 constants for each of the processes which need to be assessed: r, Const, and Monod.

Estimation of "r"

It is assumed for initial purposes that the methylating and demethylating bacteria operate on the same carbon fraction, and have similar capacities to degrade carbon. The value of "r" is therefore common to methylation and demethylation. It is also assumed that carbon in the water column is more readily degraded than in sediment particles, such that "r" in the water column will be higher than in sediments. Initial values of "r" were 10^{-3} and 10^{-4} day^{-1} in the water column and sediments respectively.

Estimation of "Monod"

The monod coefficient is a half-saturation constant, equal to the mercury concentration at which the rate of methylation or demethylation is reduced to 50% of its maximum asymptotic value. Estimates for this coefficient are as follows:

Table A1
Initial Estimates of Monod Constants
(ug Hg_{avail} m^{-3})

	Methylation	Demethylation
Water	400	25
Sediment	400	25

Xun et al. (1987) found that methylation in the water column was greater than linear with the addition of Hg(II) up to 66,600 ug m^{-3}. The greater than linear rate may have been due to saturation of binding sites and an increase in the bioavailable fraction of Hg(II) at higher concentrations. These results indicate that the half saturation constant is orders of magnitude above natural levels. Thus it was assumed that water column methylation is linear up to at least 40,000 ug m^{-3} in terms of total Hg(II) in solution. In terms of available Hg(II), thermodynamic calculations in a solution with typical levels of DOC (10^{-5} M) for surface waters and an assumed 1:1 DOC/Hg^{++} complexation constant of $10^{22.1}$ resulted in about 0.1% to 0.2% of Hg(II) being available for methylation. A monod constant of 400 ug m^{-3} of available Hg(II) (1% of the total) was somewhat arbitrarily selected for the water column.

Due to a lack of similar data for methylation in sediments, the same monod constant was chosen for aerobic sediments, implying that bacterial populations in surface waters and sediments respond similarly to increased mercury concentrations. Due to higher DOC levels in porewater compared to surface waters, a smaller fraction of Hg(II) is likely to be available for methylation in sediments. A thermodynamic estimate for aerobic sediments was on the order of 0.05% to 0.1% of Hg(II) in porewater being available for methylation. Concentrations of total Hg(II) in porewater might therefore need to be higher than water column concentrations to generate similar bioavailable Hg(II) concentrations and associated toxic effects.

Xun et al. (1987) reported water column demethylation was linear with additions of CH_3Hg^+ (as CH_3HgI) up to 3,730 ug m^{-3} after which the rate of increase of demethylation began to decline. This value is about 4-5 orders of magnitude above typical methylmercury concentrations in natural systems, and indicates that the demethylation process may be linear in terms of methylmercury unless systems are extremely polluted with methylmercury. A value of 3,730 ug m^{-3} of total soluble methylmercury was selected and adjusted for an estimated bioavailable fraction of about 0.5% (in the water column) to provide a water column monod constant of 25 ug m^{-3} methylmercury available for demethylation.

In sediments, Ramlal et al. (1986) reported demethylation was linear up to 44 ug CH_3HgI g^{-1} dry sediment. A concentration of 140 ug CH_3HgI g^{-1} dry sediment did not inhibit methylation. These concentrations are about 4 orders of magnitude above methylmercury concentrations in natural sediments, and indicate that demethylation in sediments may be linear in terms of methylmercury unless systems are extremely polluted. As a first estimate, the same demethylation monod constant was assigned to porewater as was used in surface water (25 ug m^{-3} available methylmercury). As a rough check on this assumption, the above value of 44 ug methymercury g^{-1} dry sediment was selected and adjusted to a porewater bioavailable concentration. Assuming a solids to porewater partitioning of methylmercury in the range of 1,000 to 10,000 (dimensionless) and an estimated bioavailable fraction of about 0.1% to 0.5% in porewater, a monod constant might be in the range of about 15 - 150 ug m^{-3} methylmercury available in porewater for demethylation.

Estimation of "Const"

Based on previous discussions, methylation and methylation in natural unpolluted systems may effectively be linear with respect to available mercury concentrations. Under such circumstances, the equations presented for methylation and demthylation can be reorganized to take the form:

$$M = K_m * [Hg(II)]_{av}$$

$$D = K_d * [CH_3HgX]_{av}$$

where (assuming $[Hg(II)]_{av} << Monod_m$, and $[CH_3HgX]_{av} << Monod_d$):

$$K_m = r * [TOC] * Const_m * Monod_m^{-1} \text{ (in surface water)}$$

$$K_m = r * [TOC] * Const_m * porsed^{-1} * Monod_m^{-1} \text{ (in porewater)}$$

$$K_d = r * [TOC] * Const_d * Monod_d^{-1} \text{ (in surface water)}$$

$$K_d = r * [TOC] * Const_d * porsed^{-1} * Monod_d^{-1} \text{ (in porewater)}$$

K_m has the units ug MeHg day^{-1} ug $Hg(II)_{avail\ in\ solution}^{-1}$

K_d has the units ug Hg(II) day^{-1} ug $CH_3HgX_{avail\ in\ solution}^{-1}$

In these equations, values of r, monod and the available fraction of mercury for methylation or demethylation have been addressed in the above discussions, and representative values of [TOC] can be selected. Thus the remaining unknown is "Const". The literature contains some data regarding rates of methylation and demethylation which may be used to estimate "K", and thereby allow a solution for "Const". Unfortunately, these data usually involve higher than ambient mercury concentrations (eg. radio-labelled techniques), making inferences necessary regarding rates in natural systems, and/or the data are based on analytical techniques overestimating Hg(II) and methylmercury concentrations (eg. studies in the 1970's and most of the 1980's).

Jackson (1988b) developed an operational method to determine the "methylating capability" of sediments, defined as the CH_3Hg^+ generated per unit dry weight on incubation under N_2 for 10 days in the presence of 20 ml of 10 uM $HgCl_2$ and 10 g of sediment in 125 ml flasks). Based on Jackson's methylating capability data for samples from the Churchill River Diversion area, a rate of net methylation in the range of 3% to 30% of Hg_{total} per year was estimated for this discussion. Unfortunately the fraction of total mercury which was available Hg(II) was difficult to estimate. CO_2 and CH_4 production were monitored, and all samples except one showed only CO_2 production, indicating aerobic or mildly anaerobic conditions. The data for the sample which produced methane suggest a net methylation rate of about 1 percent per day, considerably higher than other samples.

Bisogni (1979) reviewed various methylation rate studies undertaken in the 1970's, and the data were used by this author to provide net methylation rates on the order of 1.5% to 25% percent per year in sediments in terms of Hg_{total}. Unfortunately these studies in the 1970's used experimental mercury concentrations orders of magnitude above ambient concentrations in sediments, and analytical techniques to determine methylmercury concentrations may have resulted in significant errors.

Several studies have used radiolabelled mercury to quantify specific methylation and demethylation rates, including Xun et al. (1987), Ramlal et al. 1986, Ramlal et al. 1985, and Furutani and Rudd (1980). Specific methylation can be measured by adding ^{203}Hg in an inorganic complex such as $HgCl_2$, and measuring the formation of alkylated ^{203}Hg. Specific demethylation can be measured by using ^{14}C in a methyl Hg form such as $^{14}CH_3HgI$, and measuring the ^{14}C end products of demethylation (Ramlal et al. 1986). Ratios of specific methylation to specific demethylation (M/D) can be calculated as follows for:

$$\frac{\text{Specific Methylation}}{\text{Specific DeMethylation}} = \frac{\text{\% added Hg methylated per gram per hour}}{\text{\% added Hg demethylated per gram per hour}}$$

Concentrations of added Hg for both specific methylation and demethylation in both cases are above ambient levels and neither method establishes "natural" rates of reaction. The rates provided by radio-labelled experiments would be useful regarding determinations of methylation rates in natural systems if the fractions of Hg(II) and methylmercury available for methylation and demethylation could be determined, and if the linearity of these processes over a range of mercury concentrations were known.

Table A2 indicates a range of specific methylation rates based on radio-labelled studies.

Table A2
Representative Rates of
Specific Methylation

1)	Sediments:	% added ^{203}Hg methylated day^{-1} g^{-1} dry sed
	- Lake clay (not Clay Lake)	0.02 to 0.07
	- Granville Lake	0.10
	- Southern Indian Lake (area 4)	0.26
	- Organic floc	0.5 to 5.3
	- Notigi Reservoir	54

Source: Ramlal et al. (1987)

2)	Water Column:	% added ^{203}Hg methylated day^{-1} L^{-1}
	- ELA Lakes, Ontario (circumneutral lakes)	0.02 to 0.11

Source: Xun et al. (1987)

Based on the data in Table A2, 0.2 percent of added Hg(II) methylated per day in sediments and 0.05 percent of added Hg(II) methylated per day in the water column are taken as representative.

It is possible that elevated levels of Hg(II) result in saturation of sorption sites and higher concentrations in solution, increasing bioavailable Hg(II) relative to natural conditions. Ramlal et al. (1986) reported using 2 ug $^{203}HgCl_2$ g^{-1} dry sediment for methylation (about 2 orders of magnitude above typical Hg(II) concentrations in natural systems). Rogers et al. (1981) reported Hg(II) sorption maxima from 17,000 - 24,000 ug g^{-1} sediment, well above the concentrations used for the radio-labelled methylation technique. For preliminary purposes, it is assumed that saturation of binding sites does not occur when using radio-labelled techniques for methylation in sediments.

A further consideration is the exchangeable fraction of mercury bound to solids. Experiments carried out by Rogers et. al. (1981) suggested that Hg(II) adsorption onto solids is very fast, while desorption tends to exhibit distinct fast and very slow desorption processes (eg. desorption half-lives on the order of 5 to 25 years), ie. some adsorption could essentially be assumed irreversible as a first approximation. Although Hg(II) partitioning between solids and water is typically on the order of 10^4 to 10^5 L kg^{-1}, Ramlal et al. (1987) reported considerably lower partitioning coefficients of 345 L kg^{-1} (13:1 water to solids ratio in sample) and 145 L kg^{-1} (25:1 water to solids ratio in sample) in terms of added radio-labelled mercury. This would indicate that the ^{203}Hg additions saturated binding sites and/or only a fraction (eg. 0.1 - 1 percent) of the mercury in solids is exchangeable.

Table A3 indicates a range of specific demethylation rates based on radiolabelled studies.

Table A3
Representative Rates of
Specific Demethylation

1)	Sediments:	% added $^{14}CH_3HgI$ methylated day^{-1} g^{-1} dry sed	
	- Lake clay (Southern Indian Lake)		0.5 to 1.6
	- Flooded samples (Southern Indian Lake)		3.2 to 6.4
	Source: Ramlal et al. (1987)		
2)	Water Column:	% added ^{203}Hg methylated day^{-1} L^{-1}	
	- ELA Lakes, Ontario (circumneutral lakes)		0.6 to 2.0
	Source: Xun et al. (1987)		

Based on the data in Table A3, 0.6 percent of added methylmercury demethylated in the water column per day and 1.0 percent of added methylmercury demethylated per day in sediments are taken as representative values.

Ramlal et al. (1986) reported using 0.2 ug $^{14}CH_3HgI$ g^{-1} dry sediment for demethylation (about 3 orders of magnitude above typical methylmercury concentrations in natural systems). Sorption maxima for methylmercury were not found in the literature. For preliminary purposes, it is assumed that saturation of sites does not occur when using radio-labelled techniques for demethylation.

To use the rates of methylation or demethylation of added mercury in a modelling context, it is necessary to relate the above rates to the model rate coefficients K_m and K_d. A sample calculation for methylation in sediments follows.

The units of K_m are ug MeHg produced ug $Hg(II)_{available\ in\ porewater}^{-1}$ day^{-1}. The mass of methylmercury produced can be related stoichiometrically to the mass of Hg(II) methylated by a ratio:

$$Stoich2 = (ug\ Hg(II)\ methylated) * (ug\ methylmercury\ produced)^{-1}$$

$$= 201/216\ (assumed)$$

Let:

$$zz = (ug\ Hg(II)_{avail\ added\ in\ sol'n}) * (ug\ Hg(II)_{total\ amount\ added})^{-1}$$

$$= xx * yy$$

where:

$$xx = (ug\ Hg(II)_{avail\ added\ in\ sol'n}) * (ug\ Hg(II)_{added\ amount\ in\ sol'n})^{-1}$$
$$yy = (ug\ Hg(II)_{added\ amount\ in\ sol'n}) * (ug\ Hg(II)_{total\ amount\ added})^{-1}$$

xx is the fraction of added Hg(II) in solution which is available. yy is the distribution of added Hg(II) between solids and solution. Both these variables can be estimated.

The above variables can be used to relate the model coefficient (K_m) to the radio-labelled literature rates according to:

$$K_m = K' * (stoich2 * xx * yy * 100)$$

where K'= literature rate (% added ^{203}Hg methylated g^{-1} day^{-1})

Once K_m has been estimated, "Const" can be solved for according to:

$$Const_m = (K_m * porsed * Monod_m) * (r * [TOC])^{-1}$$

A preliminary estimate of xx= 0.0005 to 0.001 was developed based on thermodynamic calculations for porewater in generic aerobic sediments. Data from Ramlal et al. (1987) would indicate that at an assumed porosity of 0.95, roughly 5-20% of *added* ^{203}Hg is in solution, based on Southern Indian Lake and Wabigoon River sediments. This range was used to represent *yy*. A value of 0.2 % of added ^{203}Hg methylated g^{-1} day^{-1} was used to represent K' based on data from Table A2. Assuming r= 10^{-4} day^{-1} in sediments, [TOC] = 10^{10} ug m^{-3} for total sediment, and Monod = 400 ug m^{-3}, K_m would be in the range of 5 to 150, with a representative value of 35 ug MeHg produced per ug $Hg(II)_{available\ in\ porewater}$ per day being used.

Using the above estimates, $Const_m$ in porewater was estimated to be in the range of 0.01 ug methylmercury per ug TOC.

Analagous estimates were undertaken for $Const_m$ in the water column, and $Const_d$ in aerobic porewater and surface waters. The estimates are presented in Table A4.

Table A4
Initial Estimates of "Const"
(ug Hg * ug TOC^{-1})

	Methylation	Demethylation
Sediment	0.01	0.0008
Water Column	0.05	0.015

It should be noted that these constants were for initial simulation purposes only. Preliminary calculations with these constants and estimates of conditions in generic aerobic natural waters and sedments resulted in about 0.8% (range 0.1% to 10%) of the total Hg(II) in sediments being methylated per year, while the corresponded rate for Hg(II) in the water column would be about 15% per year. In comparison with the sediment net methylation rates based on data from Jackson and Bisogni above (1.5% to 35% of total sediment Hg(II) methylated per year), these rates are at the low end. In terms of methylmercury, the assumed conditions resulted in 10% and 200% of methylmercury being demethylated per year in sediments and the water column respectively. These values were viewed with caution, but used for initial simulation purposes. The apparently high rate constants for transformation of the available mercury pools tended to be offset by the fact that only a small fraction of the total mercury pool was estimated to be available for transformation. Several other basic checks were performed to see if the above coeffients were feasible. In absolute terms, the rate of methylation would exceed demethylation in sediments and the water column, by factors of 3.0 and 1.3 respectively (ie. net bacterial production of methylmercury would occur in the water column and sediments). The water column would be responsible for about 10-30% of the in-situ methylmercury production for a lake with a 10 m mean depth and 3 cm of active sediments.