

CONCENTRATIONS AND FLUXES OF TOTAL AND METHYL MERCURY
TO ONONDAGA LAKE, SYRACUSE, NEW YORK.

by

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ABSTRACT

Clean sampling and analytical protocols were used to enhance an understanding of patterns of the concentrations and loadings of total mercury (Hg_T) and methylmercury (CH_3Hg^+) in selected input waters of Onondaga lake. The input waters included the natural tributaries, Ninemile Creek, Onondaga Creek, Harbor Brook, Ley Creek and the effluent discharged from the Metropolitan Wastewater Treatment Facility (METRO).

The natural tributaries showed temporal variations in the concentration of Hg_T and CH_3Hg^+ . In general, concentrations of both species were slightly higher in the summer than in the winter. The range of concentrations of Hg_T and CH_3Hg^+ and the fraction of Hg_T occurring as CH_3Hg^+ were 2.6-35.8 ng/L and 0.1-1.5 ng/L, and 2-13%, respectively, for the natural tributaries. Concentrations of Hg_T and CH_3Hg^+ in the effluent of METRO were highly variable and ranged from 6.63-66.7 ng/L and 0.63-3.7 ng/L respectively, and these values were significantly higher than concentrations obtained for the natural tributaries. Fractions of Hg_T occurring as CH_3Hg^+ in the effluent ranged from 2-52%.

Concentrations of Hg_T in the tributaries were well correlated with CH_3Hg^+ ($r^2 = 0.5-0.9$) and total suspended solids ($r^2 = 0.54-0.8$). Patterns of CH_3Hg^+ showed increasing concentrations upon reduction of elevated sulfate concentrations at Harbor Brook and Ley Creek during snowmelt. At Ninemile and Onondaga creeks, variations in Hg and ionic species (i.e. chloride, sodium and calcium), showed higher concentrations under low flows and lower concentrations due to dilution under high flows, suggesting localized inputs from groundwater sources.

Loading calculations showed that both METRO (41%) and Ninemile Creek (38%) were the highest contributors of Hg_T . METRO was the highest contributor of CH_3Hg^+ (44%) to the Lake and Ninemile Creek was second (26%). In general, the tributary loadings and watershed yields ranged from 67.6-4319.3 g/yr and 22.7-125.8 mg/ha-yr, respectively, for Hg_T ; 7.5-197 g/yr and 1.5-3.9 mg/ha-yr, respectively, for CH_3Hg^+ . Concentrations and loadings of the Hg species were higher downstream of Ninemile Creek at Lakeland than upstream at Amboy. This pattern implies that Ninemile Creek exhibits significant inputs of mercury between Amboy and Lakeland.

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CHAPTER 1 - INTRODUCTION

1.1 Mercury in the Environment

Contamination of soil, sediment or water with elevated mercury (Hg) is a serious environmental problem. Mercury bioaccumulates in aquatic food chains to the extent that consumption of contaminated fish may be hazardous to birds, mammals, and humans. Mercury is unique among the environmental trace metals due to its relatively high volatility and potential for gas-phase transport. Atmospheric transport of Hg occurs over a wide regional scale resulting in widespread contamination (Matheson, 1979).

Mercury (Hg) is a natural component of coal, peat and natural gas, and thus combustion of these fuels will lead to Hg emissions. In addition to fossil fuels, waste incineration, chlorine-alkali production, crematory incineration and the use of certain pesticides lead to Hg emissions (Lindqvist et al., 1991). Mercury is also emitted from natural surfaces such as forest soils, freshwater lakes (Xiao et al., 1991) and the open ocean (Fitzgerald, 1986). A major fraction of these emissions are probably re-emissions of previously deposited Hg originating from anthropogenic emissions. Mercury has accumulated in soil over a long period of time due to atmospheric deposition. This Hg leaches from soil and is a threat to aquatic ecosystems (Pleijel and Munthe, 1995).

The last decade of environmental trace metal research has seen a shift from an emphasis on total concentrations to the importance of the chemical speciation (Andraea et al., 1981; Brinckman et al., 1982; Rapsomanikis et al., 1985; Crecelius et al., 1986). This is because an element may exist in a variety of oxidation states, complexed forms, and even covalently-bound organic compounds, which vary in bioavailability, toxicity, vola-

tility and geochemical mobility. This is particularly true for Hg (Bloom and Effler, 1990). Mercury species thought to be important in the environment includes elemental Hg (Hg^0), ionic Hg (Hg(II) , Hg(I)), complexed ionic Hg (both organic and inorganic ligands), methyl Hg (CH_3Hg^+), and dimethyl Hg ($(\text{CH}_3)_2\text{Hg}$) (Brinckman et al., 1982; Lindqvist et al., 1984).

Methyl Hg is of particular importance as a water quality parameter, since this form is highly toxic and readily accumulates in fish (Westlöö, 1967; Holak, 1982; Grieb et al., 1990; Bloom, 1992). Originally, it was thought that all CH_3Hg^+ in freshwater ecosystems was produced internally and that methylating bacteria in the sediments were solely responsible for the supply of internal CH_3Hg^+ to the water column (e.g. Jensen and Jernelöv, 1969). Later, it was found that methylation may occur in the water column (Furutani and Rudd, 1980; Parks et al., 1989), in the external slime layer of fish (Jernelöv, 1972) and the intestinal contents of fish (Rudd et al., 1980). More recently, flooded terrestrial surfaces including wetlands have been shown to be important sources of CH_3Hg^+ to freshwater ecosystems (Driscoll et al., 1994; St. Louis et al., 1994) and to reservoirs (Hecky et al., 1991). While there is no doubt that methylation occurs in these sites, quantitative determinations of the rates of methylation and of the relative importance of these internal sources has eluded researchers for decades (Winfred and Rudd, 1990).

Methyl Hg can be absorbed from water by organisms and it binds strongly to organic detritus. Thus fish and other organisms accumulate CH_3Hg^+ to higher concentrations than found in surrounding waters. Methyl Hg concentrations in water are generally very low, and constitute a small fraction (<20%) of the Hg_T content of most natural waters

(Stolzenburg et al., 1986). It is generally thought that fish and shellfish selectively retain CH_3Hg^+ in preference to $\text{Hg}(\text{II})$, mostly because CH_3Hg^+ is much more lipophilic than $\text{Hg}(\text{II})$ (Stolzenburg et al., 1986). However, Mason et al. (1995) reported that this explanation is inadequate because $\text{Hg}(\text{II})$ complexes, which are not bioaccumulated, are as lipid soluble as their CH_3Hg^+ analogs. Moreover, unlike other hydrophobic compounds, CH_3Hg^+ in fish resides in protein rather than fat tissue. Up-take of lipophilic $\text{Hg}(\text{II})$ and CH_3Hg^+ in phytoplankton, results in higher concentrations of both species, but the differences in partitioning within the phytoplankton cells between $\text{Hg}(\text{II})$ which is principally membrane bound, and CH_3Hg^+ which accumulates in the cytoplasm, lead to a greater assimilation of CH_3Hg^+ during zooplankton grazing (Mason et al., 1995). Thus the discrimination of $\text{Hg}(\text{II})$ and CH_3Hg^+ occurs during trophic transfer and enrichment occurs between water and phytoplankton (Mason et al. 1995). Because of the marked bioaccumulation of CH_3Hg^+ that occurs via the aquatic food chain, the exposure of CH_3Hg^+ by humans is primarily through the consumption of fish rather than directly through drinking water (USEPA, 1980; Gloss et al., 1990).

The major human health effects of CH_3Hg^+ are neurotoxicity in adults (Bakir et al., 1973), and toxicity of the fetus of mothers exposed to this species during pregnancy (Cox et al., 1989). Clinical manifestations of neurotoxic effects are: (1) paresthesia, a numbness and tingling sensation around the mouth, lips and extremities, particularly the fingers and toes; (2) cerebellar ataxia, a staggering gait and postural imbalance; (3) neurasthenia, an abnormal condition characterized by nervous exhaustion, vague functional fatigue and inability to concentrate; (4) dysarthria, difficulty in articulating speech; (5) concentric

constriction of the visual fields and hearing loss; (6) difficulty in swallowing, and progressive intellectual deterioration; (7) distal hypaesthesia and disturbances of superficial and deep sensations; (8) spasticity and tremor; and finally, (9) coma and death (Jugo, 1979; Goyer, 1991).

Elemental Hg (Hg^0) does not generally cause illness when ingested; however, when it is inhaled at levels below 1 mg Hg/m^3 , it may produce non-specific symptoms including shyness, insomnia, anxiety and loss of appetite (Milne et al., 1970). At higher concentrations ($1\text{-}3 \text{ mg Hg/m}^3$; Milne et al., 1970), it may cause headaches, salivation, metallic taste, chills, breathing difficulties, coughs, tremors, cramps, diarrhea, nausea, vomiting, tightness in the chest, fatigue, and lung irritation. Larger doses may produce flu-like symptoms which may result in death due to pneumonia in severe cases. Methyl Hg is transported through the blood much more readily than Hg^0 and has a long retention time in biological tissues, particularly the brain (Iverson and Brinckman, 1978).

Mercury contamination is widespread among lakes in eastern Canada, the north-eastern and upper midwest United States and Scandinavia (Surma-Aho et al, 1986; Wiener, 1987; Hankanson et al., 1988; Jackson, 1988; Regenall et al., 1991). In Sweden, despite substantial reductions in Hg emissions, Hg concentrations in fish are still increasing (Nilson et al., 1989). This study is focused on Onondaga Lake and its input waters, a site of high-level anthropogenic Hg contamination (Effler, 1987). Concentrations of Hg in fish have remained elevated long after the major discharges to the system were dramatically decreased (Bloom and Effler, 1990).

1.2 History of Mercury Contamination and Current State of Onondaga Lake

Onondaga lake is a small alkaline, dimictic lake located in metropolitan Syracuse, New York. It was a major recreational resource to the region in the late 1890's and early 1900's (Lipe et al., 1983). It supported a commercial cold water fishery (Lipe et al., 1983), and salmon migrated through the lake to spawn in its tributaries until the late 1800's. The fishing and recreational resources of the lake were essentially eliminated as a result of degradation by inputs of domestic sewage and industrial wastes. Much of the industrial pollution of the lake has been associated with discharges from an adjoining chemical manufacturing facility (Effler, 1987) that closed in 1986.

A number of reclamation measures have been taken in an effort to recover the uses of the lake (Effler, 1987). Despite reductions in the concentrations of various pollutants, it remains highly polluted and hypereutrophic. Continuing manifestations of the degraded condition of Onondaga Lake, associated with wastewater discharges, include poor transparency (Devan and Effler, 1984), high standing crops of phytoplankton (Auer et al, 1990), extended periods of hypolimnetic anoxia (Effler et al, 1988), high concentrations of public health indicator bacteria following runoff events (Bloom and Effler, 1990).

The adjoining chemical manufacturing plant discharged large quantities of Hg waste to Onondaga lake, particularly in the interval 1946 to 1970. Most of the waste emanated from two Hg-electrode chlorine production cells. An estimated 75,000 kg of Hg were discharged by the facility into the lake from 1946 to 1970 (USEPA, 1973). The lake was closed to fishing in 1970 because the Hg concentration in fish tissue exceeded the U.S. Food and Drug Administration (FDA) action level of 0.5 ppm, in effect at that time

(NYSDEC, 1989). The discharge of Hg from the facility was reduced to more than 95% soon after the U.S. Department of Justice took legal action in the summer of 1970. However, the concentration of Hg in fish continues to exceed the FDA action level (1 ppm after 1979. NYSDEC, 1987). The lake has been re-opened to recreational angling (1986) but fish caught should not be consumed.

The state of New York initiated a yearly fish flesh monitoring program for Hg in 1970. Decreases in fish tissue concentrations were reported through the 1970's presumably in response to the reduction in loadings (Bloom and Effler, 1990). In the early 1980's, however, Hg concentrations increased and leveled off at a higher average than reported in the late 1970's (NYSDEC, 1987). This occurrence is still unexplained. Bloom and Effler (1990) conducted a preliminary study of Hg chemistry in the water column of the lake. The reported high concentrations of Hg, exceeding values reported for uncontaminated surface waters by about an order of magnitude. In particular, the lake contains elevated concentrations of CH_3Hg^+ (Bloom and Effler, 1990; Jacobs et al. 1995), the form that accumulates in fish tissue (Grieb et al., 1989).

It has generally been assumed that sediment contamination is the major source of Hg to fish tissue in Onondaga Lake. However, recent Hg data from sediments (Rowell 1991; Klein and Jacobs, 1995) and input waters (Bloom and Effler, 1990; Driscoll and Wang, 1996; Henry et al., 1995) suggest that continuing inputs from tributaries or precipitation, may also be an important component of continuing Hg contamination into the lake. Sediment data indicate that much of the Hg contamination (earlier higher loads) has been buried by recent deposition. It is possible that the high Hg concentrations observed

in the water column and the persistence of elevated concentrations of Hg in fish tissue, are largely a result of continuing external loading.

In 1992, two studies were conducted, finding elevated concentrations of total Hg (Hg_T) in the major tributaries and water column of Onondaga Lake (Henry et al., 1995; Driscoll and Wang, 1996). Unfortunately, these studies were limited in scope. Driscoll and Wang (1996) investigated concentrations of Hg_T for a sampling period of eight months. While Henry et al., (1995) considered both Hg_T and CH_3Hg^+ species, measurements were made for a period less than a year. The studies however showed considerable variability in Hg concentrations, with the highest concentrations at Ninemile Creek at Lakeland and at the Onondaga County wastewater treatment plant, METRO. Mass balances for Hg inputs for the lake were conducted by Driscoll and Wang (1996) and Henry et al., (1995). Both studies showed that Ninemile Creek was the major source of Hg_T to the lake in 1992. However the two studies obtained very different mass loadings. Inputs from METRO were also an important component of Hg_T budgets, although relatively few measurements were made for this site in both studies. Henry et al. (1995) also developed mass balances for CH_3Hg^+ for the lake and they found that METRO was a major source of CH_3Hg^+ for the lake.

1.3 Study Objectives and Goal

The goal of this research was to enhance understanding of the concentration of Hg species in selected input waters of Onondaga Lake. The specific objectives were: (1) to determine the seasonal patterns of Hg_T and CH_3Hg^+ concentrations in the selected natural

tributaries and METRO effluent, (2) to determine the factors affecting the species concentration through statistical correlation with other water quality parameters and (3) to calculate fluxes of both Hg_T and CH_3Hg^+ for the various input waters to the lake.

In this investigation, selected input waters of Onondaga Lake were monitored from October 1995 to September 1996 for Hg_T and CH_3Hg^+ at monthly intervals. The selected input waters include the natural tributaries, Ninemile Creek at Amboy and Lakeland, Onondaga Creek at Spencer Street, Ley Creek at Park Street and Harbor Brook at Haiwatha Boulevard. The effluent from METRO was also monitored.

CHAPTER 2 - LITERATURE REVIEW

2.1 Concentrations of Mercury in Contaminated Sites

Mercury pollution has led to severe poisoning in several countries. The most infamous epidemics occurred in Japan at Minamata and Niigata during the 1950's and 1960's (Takizawa, 1979). These incidents gave rise to the interest in the geochemical cycle of Hg, including sources and sinks, and transport through the environment. Municipal sewage treatment plants, mining operations and direct industrial discharges are major sources of Hg loadings to aquatic systems.

The chlor-alkali industry has been a major source of Hg contamination. The total amounts of Hg lost by several chlor-alkali plants in the world have been reported by Frimerite (1970), Bothner and Carpenter (1973) and Loring and Bewers (1978). These values were 9-18 tonnes over 5 years, 35-40 tonnes over 10 years and 234 tonnes over 25 years, respectively. Also it has been shown that, even if Hg emissions from chlor-alkali plants are completely stopped, pollution of waterways would continue (Airey and Jones, 1982). Studies conducted on the transport, fate and effects of Hg in contaminated sites are summarized below.

1 Scheldt Estuary

The river Scheldt which crosses France, Belgium and The Netherlands on its way to the north sea, is highly contaminated with trace metals including Hg. The river consists of three morphological zones; the upper and lower estuaries and the fluvial river.

Both the fluvial and the upstream river are heavily polluted as a result of large domestic, industrial and agricultural wastewater discharges. Industrial applications of Hg include the chlor-alkali industry, the non-ferrous industry, polyvinyl chloride production and the phosphate industry. Industrial consumption of Hg, however, has decreased significantly over the last ten years. (Leermakers et al., 1995).

Leermakers et al. (1995) sampled the surface waters of the area on various occasions between 1991-1994. Particulate Hg concentrations ranged from 0.4-1.7 $\mu\text{Hg/g}$, and were essentially controlled by physical mixing of polluted fluvial particles with relatively unpolluted marine particles. Total dissolved Hg concentrations ranged from 0.5-5.2 ng/L and were strongly influenced by removal and mobilization processes in the upper estuary, while in the lower estuary mixing processes cause a progressive decrease in total dissolved Hg towards the mouth. Dissolved CH_3Hg^+ was analyzed and significant seasonal variations were observed with concentrations ranging from 11-120 pg/L in the winter to 80-400 pg/L in summer. Oversaturation of Hg^0 was observed throughout the whole estuary resulting in an estimated evasion flux of 140-1400 $\text{ng/m}^2\text{-day}$.

2 Carson River and Lahontan Reservoir

The Carson River site is a U.S. Environmental Protection Agency superfund site in Western Nevada, USA. Mill processing of silver and gold ores in the area resulted in the release of 6.8×10^6 Kg of Hg between 1859 and 1890 (Mach et al., 1996). Contaminated tailings have since eroded from the abandoned mill sites and are redistributed along more than 100 Km of the Carson River Valley, contaminating extensive areas.

Mach et al. (1996) assessed, water and sediments collected from the Carson River system, and from uncontaminated background locations in Nevada, for Hg_T and Hg species during drought condition in September 1994, moderate flow in February 1995, and high flow in May 1995. Total Hg and CH_3Hg^+ species in water and sediments from the river were highly elevated downstream from the historic mill sites; for example, Hg_T ranged from 21-3140 ng/L in water and 0.6-3.4 $\mu g/g$ in sediment downstream from the mill sites, compared to 1.2-17 ng/L in water and 0.003-0.006 $\mu g/g$ in sediment at background locations. Transport of Hg in the system was largely associated with suspended solids, and mass transport of all Hg species was greatest during May when high flows result from snowmelt in Sierra Nevada mountains. Concentrations of CH_3Hg^+ in the water were high (0.25-19 ng/L).

3 Imandra Lake

Imandra Lake, one of the largest lakes in northwest Russia, is being intensely polluted from the effluents of various industries. Mercury is one of the principal contaminants of the lake.

Dauvalter et al. (1996) studied the concentrations of Hg in the water, suspended matter, sediments, phytoplankton from the water column and diatoms from the sediment core, of Imandra Lake. The samples were collected three times (April, August and October of 1995). Total Hg concentrations in water column from the winter thawing period (April) ranged from 0.47-3.39 ng/L (from 0.40-3.30 ng/L and from 0.07-0.63 ng/L for dissolved and suspended Hg, respectively), with an increase in concentration towards the

water-sediment interface. In the summer, dissolved Hg concentrations decreased from 9.4 to 0.6 ng/L at 5 and 25 m depth, respectively.

4 River Mersey System

The Mersey drainage system, located in Great Britain, received waste from 160 industries and about 220 sewage outfalls. One of the major sources of Hg was a chlor-alkali facility which was known to release up to 100 Kg of insoluble Hg per day. In addition, waste was discharged from industries involved in textiles, paper, oil, coal, food dyes and sewage processing (Airey and Jones, 1982).

Airey and Jones (1982) studied the extent and distribution of Hg pollution in the Mersey drainage system during 1973 and 1974. The mean Hg_T in the water column ranged from 0.3-2.0 $\mu\text{g/L}$ for the entire area. It was found that most of this Hg was associated with particulates, but the amount varied during the year.

5 Ottawa River

The Ottawa River in Ontario, Canada, drains an area dominated by glaciated highlands, but includes some lowlands previously covered by a glacial sea and now containing extensive deposits of fine clay. Historically, the Ottawa River has received substantial inputs of organic material from industrial and municipal sources, and has been used extensively for logging operations. The main source of Hg contamination was the use of phenylmercuric acetate as a slimicide in pulp processing, before its use was discontinued in 1970 (Ottawa River Project Group, 1979).

Studies conducted on the Hg concentrations in the river, showed that the Hg_T concentrations have decreased significantly: 38 ng/L in 1972, 18 ng/L in 1973, 13 ng/L in

1975-1976 and 6.6 ng/L in 1978 (Kudo et al., 1977; 1978 and 1982). The average CH_3Hg^+ concentration measured in 1978 by Kudo et al. (1982) was 2.2 ng/L and the fraction of Hg_T as CH_3Hg^+ to the Hg_T amount was 33%. The fraction of Hg_T as CH_3Hg^+ for other components of the river were 0.1-10% for bed sediments, 28% for higher aquatic plants, 40% for benthic invertebrates and 75-90% for fish (Kudo et al., 1982).

6 Holston River

The Holston River, located in Tennessee, USA, flows into the Cherokee Lake, a 12260 ha reservoir created in 1942 by the Tennessee Valley Authority. On the North Fork of the river is the site of a former chemical manufacturing complex, which included a chlor-alkali facility and an ammonia soda plant. Drainage discharges of Hg from the chlor-alkali plant which was closed in 1972, continued to cause elevated levels of Hg in the downstream water, suspended matter, and bottom sediments. The losses were attributed to leaching of soluble Hg in solid wastes located at the site.

Turner and Lindberg (1978) studied the behavior and transport of Hg in the system, collecting samples between February 1975 and January 1976. The Hg_T concentration measured in the water immediately downstream of the plant site averaged 150 ng/L, while values immediately upstream averaged 8 ng/L. Essentially all the Hg in the water upstream of the plant site was in particulate form, but about one-third of the Hg immediately downstream occurred in dissolved form. The concentration of Hg in suspended matter and bottom sediments likewise revealed sharp increases downstream relative to upstream values. Turner and Lindberg (1978) noted that although there had been no production of chlorine since 1972, the observed twenty-fold increase in Hg_T concentrations in the water

and in suspended sediment demonstrated the presence of a large continuing loss of Hg from the vicinity of the plant.

7 Suimon River

The Suimon River is a small stream or drainage creek located in Ogaki City, Japan. It is one of the most Hg contaminated rivers in Japan. (Kudo et al., 1982). Several years ago, the Suimon River received industrial effluent containing Hg from a chemical company. The maximum Hg concentration in bed sediments near the effluent of the facility was over 100 ppm (dry), the entire course of the waterway was highly contaminated and fishing was prohibited. In 1979, the chemical company ceased using Hg in its process, removed the contaminated bed sediments from the water course and completely sealed the river bed with cement. Therefore, only a Hg residue remains in the river.

Kudo et al. (1982) collected water samples on February 1979 from the river for analysis. The average Hg_T concentration was 25.9 ng/L. Methyl Hg concentration was 7.0 ng/L, a fraction of 27% of the Hg_T concentration.

8 Minamata Bay and Yatsushiro Sea

Minamata Bay is a small area of 3 km², with its inlet located on the southwestern coast of Kyushu Island of Japan. The Yatsushiro Sea is a small inland body of water surrounded by the Amakusa island. Historically, people in this region relied exclusively on fishing. In the 1950's the bay received an industrial waste discharge containing elevated concentrations of Hg which was deposited to the sediments of the bay. This led to Minamata disease over of quarter of a century ago in which more than 100 people lost their

lives and many thousands more were paralyzed from eating Hg contaminated fish (Kudo and Miyahara, 1991).

The Hg concentrations in the bay and the sea water were measured in 1985 by Kudo and Miyahara (1991). The Hg_T concentration in the bay ranged from 125.3 ng/L at the center of the bay to 22.1 ng/L at the mouth of the bay towards the sea. The amount of organic Hg ranged from 5.5 ng/L at the center of the bay to 1.8 ng/L towards to sea. The Hg content in the water of the Yatsushiro Sea ranged from 16.4-25.8 ng/L.

9 The Wabigoon/English System

The Wabigoon/English River - Lake system is located in an area of substantial clay deposits on the Canadian Shield of northwestern Ontario. The Wabigoon River flows northwestward from Wabigoon Lake to its confluence with the English River, which merges with the Winnipeg River, which in turn, empties into Lake Winnipeg. Between 1962 and 1970, approximately 10 metric tons of Hg(II) were released into the Wabigoon River from a chlor-alkali plant-paper mill complex. Although Hg outputs were reduced between 1970 and 1975, when the use of Hg in the plant was discontinued, small amounts of residual Hg continue to be discharged into the river (Jackson et al., 1982).

Parks et al. (1986) studied the system ten years after the loading from the chlor-alkali plant were sharply reduced. The average Hg_T concentration in 1978 in depth-integrated samples from the Wabigoon River was 41 ng/L, with dissolved Hg 21 ng/L. The mean annual Hg concentration at the paper mill effluent was 194 ng/L. From August 1978 to July 1979, the Hg_T concentration in the rivers and lakes of the entire system ranged from 1.5-48 ng/L. During the period July 1979-June 1980, the concentration range of

Hg_T was 2.5-46 ng/L. Methyl Hg concentrations in the water column ranged from 0.27-5 ng/L from 1978-1980, with the highest values observed around Clay Lake (Parks et al., 1989).

10 Onondaga Lake and Tributaries

Concentrations of Hg species in Onondaga Lake are high in comparison to other polluted sites (Bloom and Effler, 1990), and this is indicative of a site that received Hg discharge from a chlor-alkali facility. Bloom and Effler, (1990) studied the water column Hg concentration from spring to fall 1989. The results of this study showed Hg_T concentration increased with depth and ranged from 7-26 ng/L, with the highest values recorded in spring. These values are significantly higher than concentrations observed in the remote Lakes located in the Adirondacks, U.S.A. (0.8-5.3 ng/L). Like Hg_T, CH₃Hg⁺ concentrations also increased with depth and ranged from 0.34-9.7 ng/L. The mean Hg⁰ concentration was 0.07 ng/L and (CH₃)₂Hg concentrations were less than 1% of the Hg_T values.

Driscoll and Wang (1996) studied the Hg_T concentrations in both the lake and its tributaries. Total Hg in the tributaries ranged from 1.2-21.28 ng/L while that in the lake ranged from 2.6-19.2 ng/L. Bloom (1990) also measured the concentrations of Hg_T and CH₃Hg⁺ in the tributaries in November 1989 and reported values ranging from 3.6-18 ng/L and 0.06-1.05 ng/L respectively.

2.2 Removal of Mercury from Effluents and Wastewaters

Municipal wastewater treatment plants represent a common focusing point of the industrial, commercial and domestic liquid waste of modern society. These plants are

basically designed to remove biochemical oxygen demand, solids, nitrogen and phosphorus. However, wastewater treatment plants are facing ever more stringent expectations with respect to the removal of heavy metals and synthetic organic pollutants (Balogh and Liang, 1995). To the extent that trace metals are associated with particulate phases, removal of solids is generally good; dissolved species represent more of a problem (Oliver and Cosgrove, 1974; Lester et al., 1979; Stoveland et al., 1979). In the case of Hg, good removals of the particulate fraction are typically observed, and discharges to receiving waters are minimized (Oliver and Cosgrove, 1974; Goldstone et al., 1990). The removal of Hg from wastewater prior to discharge to receiving waters is necessary to protect those waters. Equally important is the ultimate immobilization of the Hg removed.

During wastewater collection and treatment, Hg may behave in ways similar to its behavior in natural waters, except that the rates of processes may be accelerated (Mujan, 1996). In the collection and transport of wastewater to the treatment plant, Hg(II) is likely subjected to reducing conditions (caused by anoxia) and various bacteria, resulting in some conversion to Hg⁰. Elemental Hg thus formed or present initially may be stripped off at any stage of treatment that is open to the atmosphere, but particularly those units subject to forced aeration, such as aerated grit chambers and mixed liquor aeration basins (Bisogni and Lawrence, 1975). Lindqvist et al. (1991) reported that the concentrations of Hg in air evaded from a wastewater treatment plant at Rya, Goteborg, Sweden, to be at 4 to 6 ng/m³, compared with 2 to 5 ng/m³ for ambient air.

Balogh and Liang (1995), studied the Hg pathways in a large municipal wastewater treatment plant to characterize the fate of Hg entering the facility. This plant, loca-

ted in St. Paul, Minnesota, utilizes primary and activated sludge processes, and the residual waste is dewatered and incinerated. The results of this study showed that Hg removal in primary treatment averaged 79% (since 85% of the Hg in the primary influent was associated with particulate matter), and the average removal across the entire plant was approximately 95%. However, 95% of the Hg mass entering the plant was discharged to the atmosphere via sludge incinerator emissions. It has been estimated that Hg discharged to the atmosphere has a residence time on the order of days to months and atmospheric Hg emission can result in deposition on local, regional and global scales (Lindqvist and Rodhe, 1985).

Gilmour and Bloom (1995), studied the dynamics of Hg_T and CH_3Hg^+ in a Hg contaminated treatment plant which used Hg^0 as a seal in three trickling filters. The study indicated that significant CH_3Hg^+ was produced within the plant. The Hg^0 was mobilized via oxidation to $Hg(II)$ which was subsequently methylated. The principal source of CH_3Hg^+ was the Hg contaminated trickling filters and the extent of CH_3Hg^+ formation was related to the Hg_T concentration in the system.

Ghosh and Zuger (1973) studied Hg removal in an activated sludge facility and reported about 58% removal. In a similar study, Nakamura et al. (1975) using acclimated activated sludge obtained better than 99% Hg removal. Applying shock loads of trace metals like Hg to an activated sludge process can result in a phenomenon called 'sludge deflocculation', characterized by fine, stable pinpoint flocs in the supernatant (Neufeld, 1976). Because of the poor settling of these flocs, a substantial amount of solids can be lost to the discharge stream.

Anaerobic digestion of sludges is inhibited by excessive levels of trace metals. Wide variations in the concentration of metals at which these effects become noticeable have been reported (Mosey et al., 1971). Since the presence of soluble sulfides reduces the availability of trace metals which interfere with the digestion process, the addition of a sulfur compound (ferrous sulfate for instance), can ensure the protection of the anaerobic digesters (Bezeditis, 1979). While trace metals including Hg tend to be toxic towards most microorganisms, some species are not only remarkably resistant but can actually aid in the removal of trace metals. The Hg resistant bacterium *Pseudomonas* strain K62 has the ability to assimilate and volatilize organic and Hg(II) and these cells may be reused a number of times without incurring any loss of activity (Suzuki et al., 1968).

Another treatment method that removes Hg is chemical precipitation. Since metal sulfides are generally more insoluble in water than the corresponding hydroxides, sulfide precipitation has gained increased acceptance (Bezeditis, 1979). Hannah et al. (1977) and Maruyama et al. (1975) conducted studies of Hg removed by chemical clarification using lime, ferric chloride and alum. Cumulative removals of Hg following lime treatment and activated carbon adsorption of 91% were observed. Perry (1974a) also reported about 97% of Hg removal from the treatment of a chlor-alkali effluent when conventional sulfide precipitation using sodium sulfide were installed in the treatment process. The use of ferrous sulfide, a relatively insoluble compound gives high Hg removals without the generation of undesirable hydrogen sulfide (Feigenbaum, 1977). In the presence of chelating agents, it is difficult to achieve high Hg removals (Nilson, 1970). The use of certain

polyelectrolytes has also proved useful as they are capable of complexing with considerable amounts of Hg ions (Swanson et al., 1973; Wing et al., 1974).

Ion exchange and activated carbon adsorption are other techniques that are effective in Hg removals from solutions. Methyl Hg as well as Hg(II) can be successfully removed by several chelating resins in the pH range of 1-9 (Law, 1971) and the Hg retained can be readily eluted with a slightly acidic 5% thiourea solution allowing the resin to be reused a number of times. With activated carbon, adsorptive capacity is a function of such parameters as carbon size, ambient temperature, pH and initial concentration of the wastewater treated. Netzer and Norman (1973) reported greater than 99% removal with a combination of pH adjustment between the range 3-11 and activated carbon adsorption. Altering the surfaces of the activated carbon by soaking in carbon disulfide or by chelating the Hg prior to adsorption resulted in higher Hg removals than with unmodified carbon (Humenick and Schnoor, 1974).

Some wastewater treatment facilities, required to achieve very low levels of effluent biochemical oxygen demand and suspended solids, use effluent filtration to physically remove additional suspended materials not settled out during final clarification. Removal of these fine solids can be expected to increase Hg removals. These filters are regularly backwashed, resulting in recycling of removed solids (and Hg) back to earlier stages of treatment (Mugan, 1996).

Disinfection, a chemical treatment process is used at all municipal treatment facilities. Chlorination is used widely for effluent disinfection, but the effect of chlorine disinfection on Hg removal has not been studied. Ozonation is another disinfection technique.

Although ozone has limited effect in the treatment of metal-laden effluents, it is useful for the destruction of metal-organic complexes and the liberated metal can be removed by precipitation (Shambaugh and Melnyk, 1978). Netzer et al. (1972) studied the effectiveness of ozone for removing Hg from wastewaters, and the results proved that a combination of pH adjustment and ozonation can be effective for removing Hg from wastewaters.

Removal of Hg from various treatment processes results in voluminous production of sludges and proper disposal of these sludges can be troublesome and expensive (Bezeditz, 1979). Mercury may be recovered from sludges by hypochlorite and chlorine oxidation, and roasting (Perry, 1974b). Municipal landfill sites are not suitable depositories for Hg wastes since Hg tends to become very mobile in the presence of organics (Niebla et al., 1976). Sanks and Gloyna (1977), observed that clay formations in compacted blankets maintained in a moist state in the landfill can produce suitable disposal sites for Hg wastes. Since clay is highly impermeable, exhibits a strong affinity for various pollutants and has substantial cation exchange capacity, it forms an effective barrier which protects ground and surface waters from pollution from the landfill sites.

2.3 Mercury Cycling in Lake Ecosystems

Cycling consists of inputs to and outputs from a system, and transport and transformation of Hg species within the system (Figure 2.1). The external supply of Hg to Onondaga Lake include inflowing tributaries and METRO effluent, atmospheric (wet and dry) deposition and groundwater. Groundwater may represent both a delivery and a removal mechanism (Krabbenhoft and Babiarz, 1992), and groundwater discharge into

Onondaga Lake may supply Hg from surficial materials or leached soil contamination (e.g. Allied waste beds) or Hg derived from atmospheric deposition. Each input source contributes elemental, inorganic and organic Hg species to varying degrees.

Over 80% of the Hg_T in the atmosphere consists of a volatile gaseous Hg form, presumably Hg^0 (Lindqvist and Rodhe, 1985; Slemr et al., 1985; Schoeder et al., 1991). Traces of CH_3Hg^+ are also present in air (Fitzgerald et al., 1991; Brosset and Lord, 1995), but its source is yet unknown (Hall et al, 1995), although it does not appear to be due to direct anthropogenic combustion emissions (Prestbo and Bloom, 1994). The major removal mechanisms for atmospheric Hg are washout of airborne particulate and oxidized forms, aqueous oxidation of Hg^0 to more water-soluble forms and dry deposition (Pleijel and Munthe, 1995). Elemental Hg is relatively insoluble in water and oxidation by ozone to Hg(II) is known to occur in aqueous phase (Lindqvist and Rodhe, 1985; Iverfeldt and Lindqvist, 1986; Brosset, 1987; Munthe, 1992). Mercuric ion is soluble in water and scavenging by precipitation is thought to be the major process of its removal from the air (Lindberg, 1987). Methyl Hg has been observed in rain (Bloom and Watras, 1989) and probably occurs as dissolved complexes (Ahmed et al, 1987).

The predominant form of Hg entering lakes is Hg(II) and it readily adsorbs to inorganic and organic particulate matter and may settle to the sediment surfaces (Reimers and Krekel, 1974; Benes and Havlik, 1979; Rudd and Turner, 1983). This deposition of particulate matter is an important mechanism of Hg transport to sediments. However Hg can be remobilized by resuspension or complexation of Hg-laden sediments. Wang et al. (1991) showed that the presence of chloride plays a crucial role in the release of Hg from

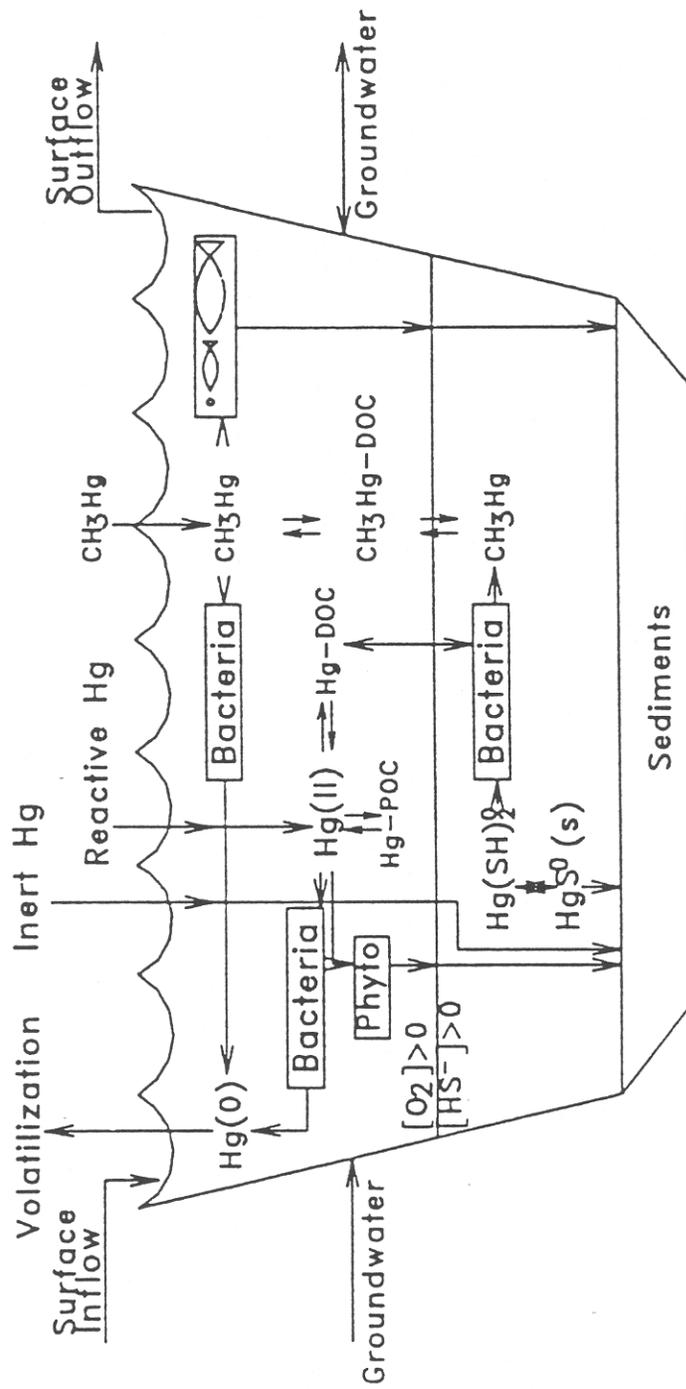


Figure 2.1. Schematic diagram summarizing the Hg cycle in lake ecosystems. (after Driscoll et al. 1994)

the freshwater sediments. It is likely that Hg is desorbed from sediments through the formation of stable chloro-Hg complexes (Sillen and Martel, 1964; Wang et al, 1991). Jackson et al. (1980) and Schindler et al. (1980) observed that a decrease in pH results in a decrease in the release of Hg from sediments.

The Hg(II) may also form complexes with dissolved organic carbon (DOC) in lakes (Miller, 1975). The nature of this bonding is poorly understood but will affect the availability of Hg for methylation (Rudd and Turner, 1983). In the presence of hydrogen sulfides, Hg(II) precipitates as HgS rendering the Hg unavailable for methylation (Bjornberg, 1988). However, mercuric sulfides occurring as polysulfide complexes may be available for methylation (Gilmour et al., 1988). In addition, if the sulfur is present as FeS, its effectiveness in reducing methylation is limited (Furutani and Rudd, 1980).

In the lake water, Hg(II) can be reduced to the volatile Hg⁰ species. This transformation may be mediated biologically by Hg resistant bacteria (Nelson and Colwell, 1975; Summers, 1985; Belliveau and Trevor, 1989; Baldi et al., 1991; Mason et al., 1995). According to Brown (1985), Hg(II) is transported into the cytoplasm where it is reduced to Hg⁰. The Hg⁰ diffuses out of the cytoplasm because of its high vapor pressure. In addition, abiotic reduction of Hg(II) can occur by photolysis in the presence of humic substances (Albert et al., 1974; Ramamoorthy et al., 1983; Allard and Arsenie, 1991; Xiao et al., 1995). Although Hg-resistant bacteria are common in aquatic systems, volatilization is primarily abiological in most freshwater systems, possibly due to the low levels of Hg present (Weiner et al., 1990). Since Onondaga Lake has such high concentrations of Hg, biological volatilization is probably significant.

Methyl Hg can be formed within the lake or in the lake catchment by the methylation of Hg(II). However, methylation of Hg is only one process in a complex cycle that involves a variety of chemical, physical and biological transformations (see Figure 2.1). The net amount of biologically available CH_3Hg^+ is a result of the rates of processes that alter the availability of Hg(II) for methylation, and rates of CH_3Hg^+ demethylation (Winfred and Rudd, 1990).

Mercuric ion can be methylated abiotically (Nagase et al., 1984; Lee et al., 1985; Webber, 1993) or microbiologically (Jensen and Jernelöv, 1969; Winfred and Rudd, 1990). Abiological methylation which can occur by the photochemical methylation of Hg(II) (Robinson and Tuovinen, 1984; Akagi and Takabatake, 1993) or by chemical transalkylation of Hg(II) in the presence of suitable methyl donors (Bertilsson and Neujahr, 1971; Imura et al., 1971; Jewett and Brinkman, 1974). Abiotic methylation appears to be insignificant in sediments (Berman and Bartha, 1986; Korthals and Winfrey, 1987), but may play a more important role in the production of CH_3Hg^+ in lake water and in streams of the lake watershed, especially at low pH (Lee et al., 1985). Biological methylation of Hg(II) in sediments is done by bacteria that excrete methylcobalamin (a vitamin B_{12} analog) which can act as a methyl donor. This process has been demonstrated by bacteria under anaerobic conditions in river and lake sediments, as well as by cell-free extracts of methanogenic bacteria (Wood et al., 1968; Jensen and Jernelöv, 1969; Olson and Cooper, 1976). Methylation under aerobic conditions has also been reported (Olson and Cooper, 1976). The efficiency of methylation is dependent on the metabolic activity of the methylating organisms, the availability of labile carbon and the total concentration of biochemi-

cally available Hg(II). The availability of Hg(II) for methylation is dependent on factors such as redox potential, pH, the presence of sulfides and organic complexing agents, and the microbial activity is dependent on organic substrate, temperature and other factors. The formation of CH_3Hg^+ will off course, not continue to increase with increasing Hg_T ad infinitum, due to the eventual toxic effects of Hg on microorganisms (Beijer and Jernelöv, 1979).

The relative importance of biological versus abiological Hg methylation in lake waters has not been determined, and warrants further study. Once formed, CH_3Hg^+ may be further methylated to $(\text{CH}_3)_2\text{Hg}$ which is volatile and readily released from lakes. This reaction however occurs at high pH (>7). Craig and Moreton (1984) established the existence of a sulfide mediated pathway for the conversion of CH_3Hg^+ in sediments to $(\text{CH}_3)_2\text{Hg}$ and this pathway may remove significant quantities annually of CH_3Hg^+ from sediments exposed to sulfide.

The net amount of CH_3Hg^+ formed in a lake is a result of the concomitant processes of methylation and demethylation (Ramal et al., 1986). The demethylation of CH_3Hg^+ is a microbial process mediated by methyl Hg-resistant bacteria (Summers, 1985) and results in the formation of Hg^0 (with Hg(II) as an intermediate) and methane (Begley et al., 1986). However, Korthals and Winfrey (1987) and Oremland et al. (1991) observed the formation of significant amounts of CO_2 as a byproduct of demethylation in anoxic freshwater sediments, suggesting the existence of an oxidative mechanism for the formation of CO_2 from CH_3Hg^+ . Demethylation appears to be primarily biological in water and sedi-

ments (Korthals and Winfrey, 1987; Ramal et al., 1986) and abiological mechanisms are unknown.

2.4 Factors Controlling Net Methylmercury Formation

The net effect of methylation and demethylation (net methylation) results in CH_3Hg^+ for bioaccumulation. Some of the environmental factors controlling these processes are discussed below.

1 Temperature

Temperature is a major factor controlling Hg methylating activity. In freshwater sediments, methylation is inhibited by low temperatures (Wright and Hamilton, 1982) and has a temperature optimum of about 35°C (Callister and Winfrey, 1986; Steffan et al., 1988). Thus an increase in the sediment temperature due to solar radiation or thermal pollution may increase the production and bioavailability of CH_3Hg^+ .

In lakes, temperature plays an important role in the seasonality of Hg methylation which often peaks in late summer and is low throughout the remainder of the year (Ramsay and Ramal, 1987). Korthals and Winfrey (1987) observed that methylation in surface sediments of Lake Clara, Wisconsin increased from spring to late summer and then decreased in the fall, while demethylation increased from early to midsummer and then decreased. In comparing sediment and water column samples from Clay Lake, Ontario, Furutani and Rudd (1980) noted coincident peaks of methylation activity throughout the summer. They suggested a common factor was controlling methylation in both compart-

ments, such as periodic resuspension of sediment or cyclic supply of substrates from phytoplankton.

2 Oxygen

Previous studies indicate that methylation of Hg predominantly occurs under anaerobic conditions, while demethylation occurs under aerobic conditions (Olson and Cooper, 1976; Compeau and Bartha, 1984). Korthals and Winfrey (1987) found the highest activity of Hg methylation in profundal surficial sediments and low but detectable methylation activity in the aerobic water column. Many other studies also reported higher gross and/or net methylation rates, or high fraction of Hg in the methylated form in reduced sediments than in oxidized sediments (Rudd et al., 1983; Compeau and Bartha, 1984; Jackson, 1989; Regnell, 1990). These observations thus suggest that episodes of anoxia in bottom waters and sediment cause an increase in net Hg methylation, and hence an increase in bioavailable Hg (Regnell and Tunlid, 1991). There are also indications that CH_3Hg^+ produced in anaerobic sediments is more stable than that produced in aerobic sediments (Olson and Cooper, 1976).

3 Discharge

Parks et al. (1989) studied the Wabigoon/English River-Lake system and observed that both low and high discharges influenced CH_3Hg^+ concentration. Under low discharges, when the river turned anoxic, higher CH_3Hg^+ concentrations were evident. The effect of high discharges on CH_3Hg^+ concentrations appeared to be site specific and dependent to some extent on the quantity of bed sediments which were resuspended.

4 Sulfate

Sulfate reducers can mineralize a large fraction of particulate organic matter entering freshwater sediments (Smith and Klug, 1981), particularly in shallow lakes and wetlands where organic substrates are abundant and sediment temperatures are relatively high in summer. Addition of either organic carbon or sulfate may stimulate sulfate reduction in sediments, potentially fertilizing Hg methylation by sulfate reducing bacteria (SRB). Several studies have demonstrated that inhibition of sulfate reduction results in a concomitant inhibition of Hg methylation in both marine (Compeau and Bartha, 1985) and freshwater sediments (Winfrey, 1985). Gilmour et al. (1992) suggested that SRB are important mediators of Hg methylation in lacustrine sediments, and provide a possible mechanism for increased CH_3Hg^+ bioaccumulation in water bodies affected by sulfate deposition. In addition, Hg methylation has been demonstrated by several strains of marine SRB (Compeau and Bartha, 1985, 1987). Based on this evidence, Compeau and Bartha (1985) concluded that SRB are the principal Hg methylators in anoxic estuarine sediments. This conclusion has spawned widespread speculation among researchers studying freshwater environments.

Gilmour and Henry (1991) speculated that the optimal sulfate concentration for Hg methylation by SBR in sediments is in the 200-500 μM (19.2-48 mg/L) range. Above this sulfate concentration, sulfide would inhibit methylation, while at lower sulfate level sulfate reduction and hence methylation would be limited by available sulfate. Gilmour and Henry (1991) further added that this optimum level would probably vary from system-to-system

and even site-to-site as a function of other factors which affect sediment sulfate reduction rates such as temperature, sediment porosity and organic carbon availability.

5 Mercury Binding, Organic Carbon and Particulates

Mercury methylation is generally thought to require soluble concentrations of Hg(II) ion (Rogers et al., 1984). However, Hg readily binds to particulates or to DOC in lakes making it less available for methylation. Although the nature of Hg binding is poorly understood, it is one of the major factors that will decrease the availability of Hg for methylation and uptake by biota (Rudd and Turner, 1983). Acidification generally enhances the solubility of metals and the release from binding sites on organic and inorganic materials (Anderson and Rubin, 1981). However, this phenomena is not evident for Hg as Ramal et al. (1985) found that the concentration of Hg(II) in sediments from Canadian Shield lakes decreased sharply when pH decreased. The reduction in Hg solubility with lower pH was attributed to the formation of insoluble mercuric sulfide, which would decrease the availability of Hg for methylation in sediments (Fagerstrom and Jernelöv, 1971).

In the water column, increased concentrations of DOC result in lower Hg methylation rates despite an increase in overall bacterial activity (Winfrey and Rudd, 1990). Presumably, ligand formation between dissolved Hg and DOC in the water column makes Hg unavailable for methylation by bacteria. Mercury is removed from the water column and deposited to sediments along with particulate organic carbon, a process which is enhanced at low pH (Jackson et al., 1980; Schindler et al., 1980). Because DOC can inhibit water-column methylation (Winfrey and Rudd, 1990), acid enhanced removal of DOC

might account for some of the observed stimulation of methylation in the water column by acidity.

Organic carbon generally has the opposite effect in sediments, enhancing both bacterial activity and methylation rate (Furutani and Rudd, 1980; Wright and Hamilton, 1982; Callister and Winfrey, 1986). Microbial processes that produce and decompose CH_3Hg^+ are dependent on the availability of biodegradable organic carbon. Numerous studies have demonstrated that Hg methylation is enhanced by increased availability of organic carbon, and increased decomposition of organic matter is a major cause of increased methylation in newly flooded reservoirs (Bodaly et al., 1984). Moreover, methylation is faster in the surface layer of sediments (Jernelöv, 1970; Callister and Winfrey, 1986; Korthals and Winfrey 1987), where microbial activity and newly sedimented, highly biodegradable organic carbon is concentrated (Winfrey, 1984). The demethylation process responds in a similar manner to organic availability. Miskimmin et al. (1992) has shown that demethylation is stimulated by additions of DOC.

Jackson (1989) showed that clay minerals, Fe and Mn oxides, and humic matter (colloids) have complex and often dramatic effects on the microbial methylation and demethylation of Hg, and other microbial activities in lake sediments. The role of clays was critically dependent on surface coatings. Clays often interfered with methylation (while in some cases strongly promoting subsequent demethylation); but iron oxide (FeOOH) often promoted methylation, and FeOOH coatings on clay tended to counter-balance the negative influence of the clay. Removal of oxide coatings depressed both methylation and demethylation. Manganese oxide (MnOOH) coatings sometimes promoted methylation,

but larger amounts of MnOOH (unlike FeOOH) strongly suppressed methylation. Upon addition of organic nutrients, oxide coatings enhanced methylation and impeded demethylation; without nutrient enrichment, the reverse tended to occur. Humic matter in solution tended to stimulate methylation; but humic coatings on clay impeded methylation and fostered demethylation. Thus, the effects of natural colloids on Hg speciation are critically important but variable, inconsistent, and not altogether predictable.

6 pH

The effect of pH on rates of CH_3Hg^+ production has been investigated, in the water column, in subsurface sediments and at the sediment-water interface. Fagerstrom and Jernelöv (1972), examining the effect of pH on Hg methylation, demonstrated that CH_3Hg^+ production was greater at low pH (5-7) and that the formation of $(\text{CH}_3)_2\text{Hg}$ was greater at high pH (>7). This experiment has often been misinterpreted to suggest that decreased pH stimulates methylation. Instead, their data demonstrated that as pH was lowered, there was a shift from the production of $(\text{CH}_3)_2\text{Hg}$ to the production of CH_3Hg^+ , but the total amount of Hg methylated remained approximately the same. However this pH shift could affect the Hg available for bioaccumulation because CH_3Hg^+ is less volatile than $(\text{CH}_3)_2\text{Hg}$ and thus retained more efficiently in lakes.

In sediments studies, however, artificially lowering the pH of sediments below 5 has resulted in both decreased Hg methylation and sulfate reduction rates (Shin and Krenkel, 1976; Furutani et al., 1984; Ramlal et al., 1985). Steffan et al., (1988) found that reduction in pH by acidification of either sulfuric, nitric or hydrochloric acid to subsurface sediments, decreased rates of CH_3Hg^+ production. The decrease is probably not a direct

effect of pH on the methylation process, nor the result of an overall decrease in microbial activity. (Furutani et al., 1984). Instead, it is likely caused by increased precipitation of Hg(II) as insoluble mercuric sulfides (Ramal et al., 1985). Thus, a pH-related effect on methylation in most subsurface sediments is unlikely (Xun et al., 1987).

In contrast to the anoxic subsurface sediments, lowering the pH at the aerobic sediment-water interface results in a two- to threefold increase in the rate of CH_3Hg^+ production (Xun et al., 1987). Winfrey and Rudd (1990) observed similar results when methylation rates at the sediment-water interface when an acidic lake was compared to a nonacidified lake in Wisconsin. Rates of methylation often peaked at or near the sediment-water interface, and decreased both in the overlying water and deeper sediments of lakes (Korthals and Winfrey, 1987). Methylation rates in buried sediments are more affected by changes in the concentration of electron acceptors than by the acidity of overlying water (Rudd et al., 1986). While the activities of both methylation and sulfate reducing bacteria are strongest at the sediment-water interface where water column acidity may affect porewater pH, sulfate gradients in sediments from acidified lakes suggest that acidification does not decrease sulfate reduction rates (Kelly and Rudd, 1984).

An additional factor affecting CH_3Hg^+ availability may be the effect of pH on the partitioning of CH_3Hg^+ at a sediment-water interface. Miller and Akagi (1979) found that release of CH_3Hg^+ from the sediment surface was enhanced at lower pH. This, along with enhanced methylation, could further increase the supply of CH_3Hg^+ to fish in acidified lakes.

In aquatic ecosystems, the concentration of CH_3Hg^+ is the net result of two opposing processes, methylation and demethylation. Thus to understand the effect of pH on net CH_3Hg^+ production in lakes, it is necessary to determine whether a change in net methylation is the result of stimulation of Hg methylation or inhibition of Hg demethylation. Ramal et al. (1985) and Steffan et al. (1988) suggested that lowering the pH of subsurface sediments resulted in little change in Hg demethylation. Hence, the observed decrease of net methylation they observed was not a result of increased demethylation, but rather a decrease in methylation. Similarly, Xun et al. (1987) found that lower pH generally resulted in little effect or only small decreases in rates of demethylation in the water column of Canadian Shield lakes, but large increases in methylation. These results show that in lake water, the ratio of methylation to demethylation is inversely correlated with pH.

7 Inorganic Mercury Concentration

Inorganic Hg can be transported to lakes from atmospheric deposition, streams or groundwater. Increases in inputs of Hg(II) usually result in increases in rates of CH_3Hg^+ production in both the water column (Xun et al., 1987) and sediments (Jensen and Jenelöv, 1969; Rudd et al., 1983). For example, Xun et al. (1987) found that rates of Hg methylation in lake water more than double for each doubling of Hg(II) concentration.

However, methylation rates are not always positively correlated to Hg(II) concentrations. Elwood et al. (1987) found that a high increase in Hg(II) concentration in the East Fork Poplar Creek near Oak Ridge, Tennessee, did not result in high CH_3Hg^+ production rates. The Hg concentrations in fish were also not exceedingly high in the

stream. The reason why Hg methylation rates and Hg concentrations are not always positively correlated to the Hg(II) concentrations is probably due to other factors that control the availability of the Hg for methylation. The proportion of the Hg_T pool that is available for methylation is unknown (Winfrey and Rudd, 1990), but this plays an important role in regulating Hg methylation than the Hg_T concentration.

8 Redox and Salinity

Compeau and Bartha (1984), studied the effects of redox potential (E_h) and salinity on the microbially mediated processes of methylation and demethylation in estuarine sediments. They reported that methylation of Hg(II) was favored at E_h -220 mV as compared to +110 mV. At -220 mV, high salinity inhibited methylation, and low salinity favored the process. At +110 mV, the salinity effect was less pronounced than at lower redox potential. Demethylation was favored at +110 mV regardless of the salinity level. Low redox potential under low salinity condition inhibited demethylation, but high salinity reversed this inhibition.

Blum and Bartha (1980), Compeau and Bartha (1983, 1984 and 1987) have demonstrated a strong negative correlation between the salinity of aerobic sediments and the ability to methylate Hg(II). These studies also lend further support to the hypothesis that H₂S produced from sulfate in low redox potential environments represents the principal mechanism by which salinity interferes with Hg(II) methylation.

CHAPTER 3 - STUDY AREA

3.1 Location and Morphometry

Onondaga Lake is located (lat. 43°06'54"N; long. 76°14'34"W) along the northern end of the city of Syracuse, in Onondaga County, in Central New York (Figure 3.1). Onondaga Lake is in the Oswego River drainage basin (see Figure 3.1, inset). The outflow from the lake exits through a single outlet at its northern end and enters the Seneca River. The Seneca River combines with the Oneida River to form the Oswego River, which flows north, entering Lake Ontario at the City of Oswego (Figure 3.1).

The lake is oriented along a northwest-southwest axis. It has a length along this axis of 7.6 km and a maximum width of 2 km. The lake covers an area of $12 \times 10^6 \text{ m}^2$, has a volume of $131 \times 10^6 \text{ m}^3$, a mean depth of 10.9 m and a maximum depth of 19.5 m. It lacks dendritic irregularities. The lake is commonly described as having two basins, the south and north, that are separated by a modest "saddle" region that is located approximately 3.6 km from the outlet. The lake flushes rapidly, an average of four times per year (Onondaga Lake Management Conference, 1993; Effler and Harnett, 1996).

3.2 Tributaries and Subbasins

The major hydrologic inputs to the lake are Ninemile Creek and Onondaga Creek which together account for about 65% of the total amount of water that flows into the lake each year, the Metropolitan Syracuse Wastewater Treatment Plant (METRO) which is the third largest source of water to the lake making up 18% of the annual inflow, Ley

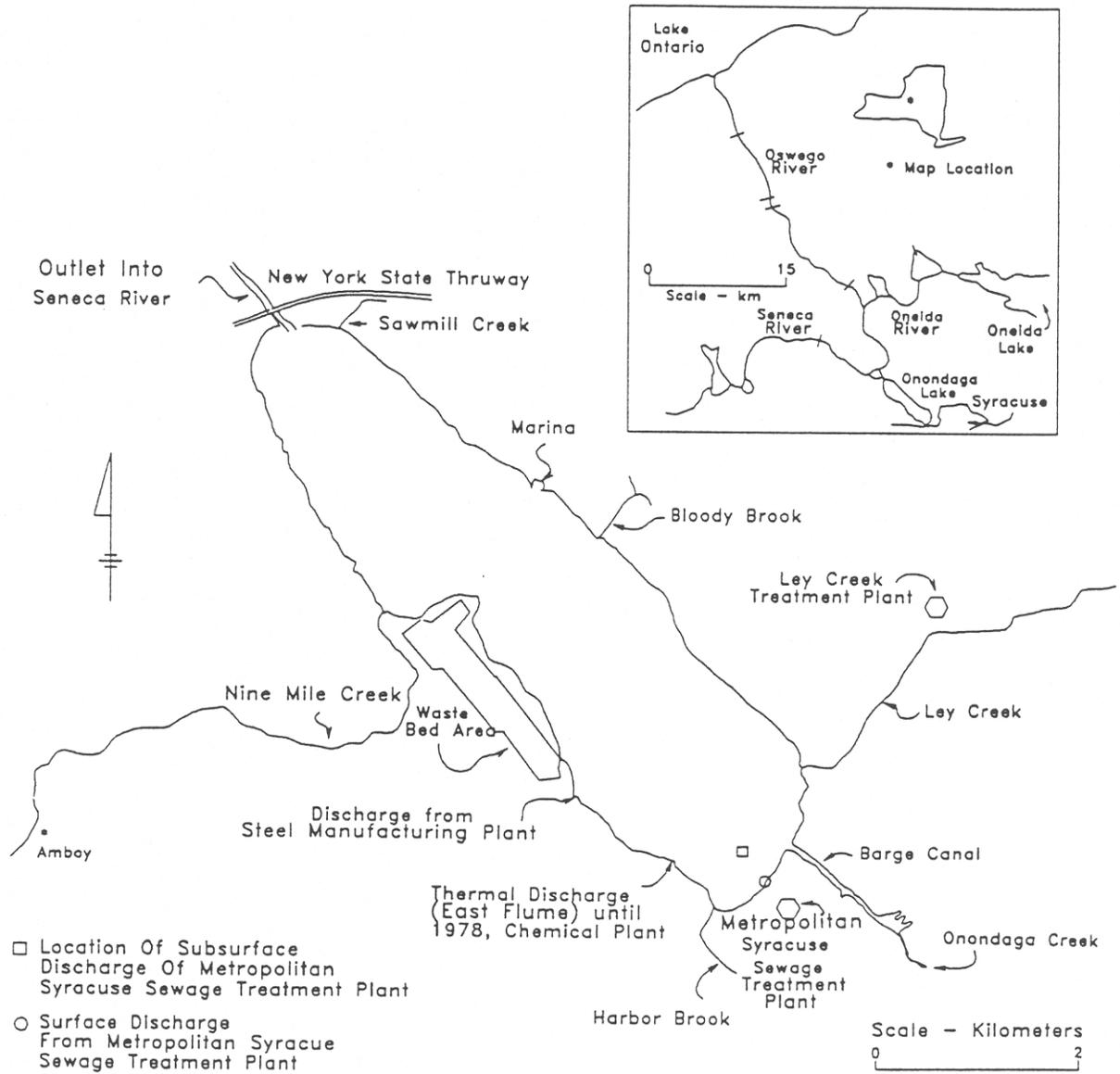


Figure 3.1. Location map for Onondaga Lake, showing the input waters. (after Effler, 1996)

Creek, Harbor Brook, Bloody Brook. This large proportion of treated wastewater is a unique feature of the lake and a leading source of its continuing water quality problems. During the summer, when the amount of water flowing into the lake from the natural tributaries is low, the discharge from METRO represents a much larger contribution of water to Onondaga Lake. Other minor tributaries include Sawmill Creek, Tributary 5A, and the East Flume. The locations of the mouths of the tributaries and the outlet are shown in Figure 3.1. A more complete map of the tributaries, including the major watershed subbasins is shown in Figure 3.2. The Onondaga Lake watershed is approximately 642 km² and lies entirely within Onondaga County, with the exception of a small portion (approximately 2 km²) in north central Cortland County.

Ninemile Creek empties into Onondaga Lake on its western shore; its watershed drains approximately 298 km² both south and west of Onondaga Lake. The Ninemile Creek watershed originates at the outlet of Otisco Lake. The total length of the Ninemile Creek mainstream is 55.2 km. From its source at the Otisco Lake outlet, the creek flows in the northern direction through the village of Marcellus, then in a more easterly direction through the village of Camillus, and eventually through the Lakeland area to Onondaga Lake. The change in configuration of the lower reaches of Ninemile Creek has been associated with the disposal of waste by a chemical manufacturer. Waste beds associated with soda ash production adjoin the lower 3 km of the stream.

Onondaga Creek drains an area of approximately 298 km² and has a mainstream length of approximately 44.2 km. The Tully mud boils, a major source of sediment to the creek and lake (Effler et al., 1992), are located about 33 km above the creek's mouth.

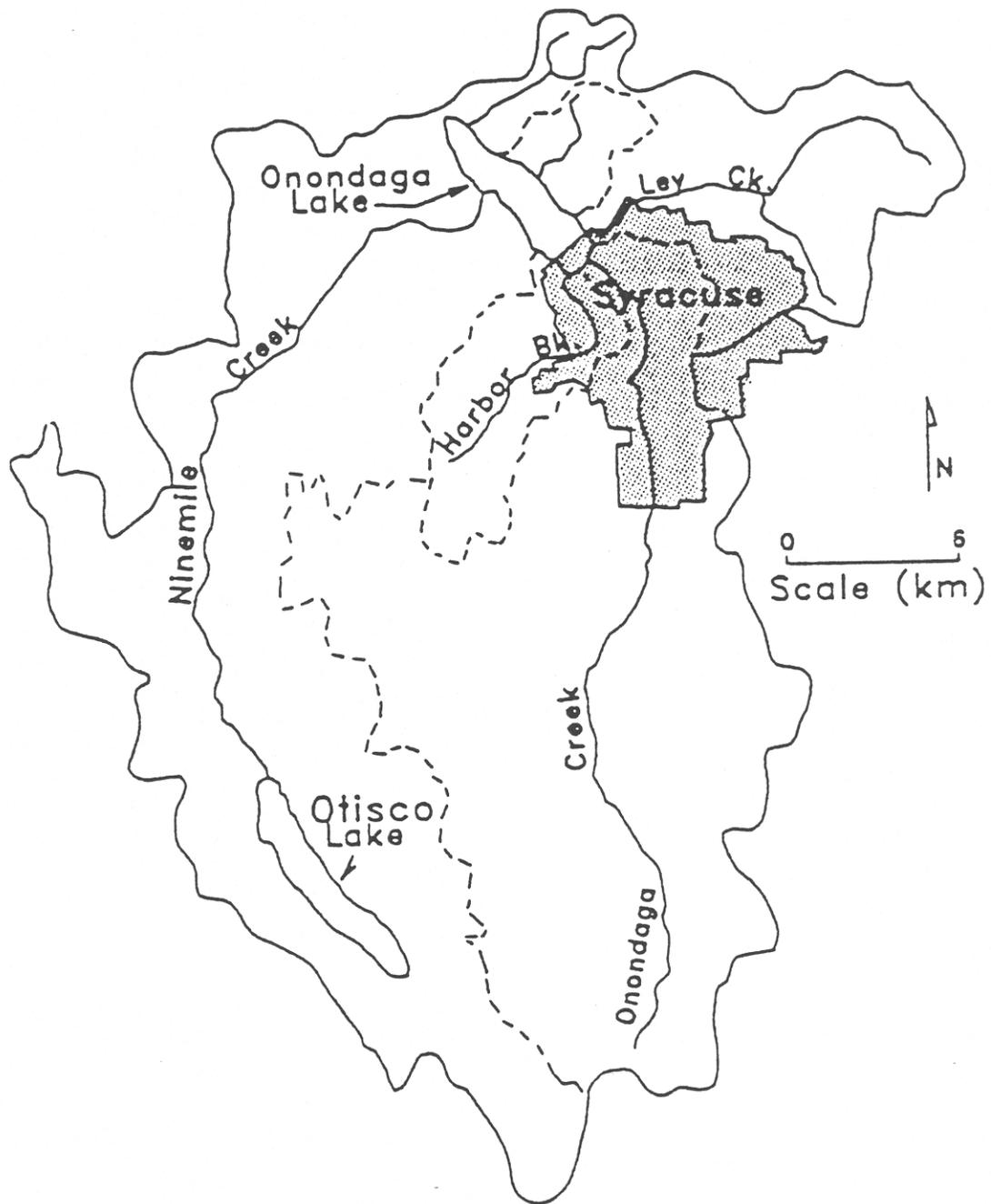


Figure 3.2. Watershed in Onondaga County, including drainage basin and subbasins for Onondaga Lake. Watershed areas: Ninemile Creek = 298 km²; Onondaga Creek = 298 km²; Ley Creek = 77.4 km²; Harbor Brook = 29.3 km². (after Effler, 1996)

Onondaga Creek empties into the southern end of the lake. The lower reaches of the creek drain a significant portion of the City of Syracuse. The watershed extends southward until just north of the Tully Valley area and westward to the drainage divide with Ninemile Creek watershed. The western branch of Onondaga Creek runs in a generally easterly direction; it joins the mainstream in the Onondaga Indian Reservation. The configuration of lower Onondaga Creek, particularly near its mouth, has been changed substantially, in part to minimize flooding.

The Ley Creek watershed is approximately 77.4 km²; it extends eastwards from the southern end of Onondaga Lake. This lake plain region is residential and industrial in character, with the exception of the headwaters that are located primarily in wetlands. This watershed has become increasingly developed in recent decades.

Harbor Brook extends to the southwest from its mouth on the southernmost end of Onondaga Lake. It has a long and narrow watershed of approximately 29.3 km². The lower reach drains a portion of the City of Syracuse while the headwaters drain a mixture of residential, agricultural, and pasture lands. This area has become more residential during the last decade.

Bloody Brook enters Onondaga Lake at roughly the midpoint of its eastern shore in Onondaga Lake Park. The watershed of approximately 29.3 km² extends to the northeast draining the lake plain area, which is heavily residential.

The setting of the lake within the Three Rivers system is illustrated as an inset in Figure 3.1. The lake outlet, located at the northwestern extreme, discharges into the Seneca

and Oneida Rivers' is known as the Three Rivers Junction. The overall river system is often referred to as the Three Rivers System.

3.3 Specific Waste Sources

Onondaga Lake has been the principal receiving water for domestic waste and much of the industrial waste from the metropolitan area from the early development of the region to the present. The most clearly manifested and pervasive industrial impacts have been associated with a chemical manufacturing facility on the west shore (Effler, 1987a).

3.3.1 Allied Signal

The chemical plant on the western shore of the lake, originally named the Solvay Process Co. (later part of Allied Chemical Co., and finally part of Allied Signal Co.), has had and continues to have major environmental impacts on the Syracuse area. The plant was originally built to produce sodium carbonate (Na_2CO_3), commonly referred to as soda ash. It was an ideal location because of the local abundance of the necessary raw materials and ample opportunity to dispose of associated wastes. The availability of these raw materials and by-products of the soda ash reactions led to an impressive diversification in chemical manufacturing at this facility. More than 30 chemicals were manufactured at this plant over its 102 years tenure. The most important processes that have impacted the lake, are the production of soda ash and chlorobenzene, and the chlor-alkali process.

1 Soda Ash.

The production of large quantities of waste accompanied the soda ash manufacturing process. A waste slurry containing CaCl_2 , excess CaO , unreacted CaCO_3 and NaCl ,

CaSO₄, and lime impurities, was pumped to waste beds where the soluble fraction (waste bed overflow) drained off and entered the lake (mostly via Ninemile Creek since the early 1940s).

2 Solvay Waste

The solid phase left behind after drainage of the waste bed overflow is described as Solvay waste. The areal distribution of this material is shown in Figure 3.3. Deposits of Solvay waste surround about 30% of the lake; the most recent waste beds are located along Ninemile Creek. More than 814 ha are covered with this waste and the depth of these deposits vary greatly. No artificial impermeable material was used to line the waste beds. The mineral composition of the waste reported by Kulhawy et al. (1977) was 20% CaCO₃, 17% Ca silicate, 10% Mg(OH)₂, 8% CaO.CaCl₂, 7% SiO₂, 6% NaCl, 6% CaCl, 6% alk and Fe oxide, 4% Ca(OH)₂, 4% CaSO₄, and 12% H₂O of hydration. Other materials deposited along with Solvay waste included fly ash and clinker from the facility's coal burning plant, as well as small quantities of insoluble Hg, lead, and asbestos from the Allied sodium hydroxide and chlorine production facilities (Blasland and Bouck Engineers, 1989).

3 Chlorobenzene

Cholobenzene was also manufactured at the facility, and the waste (Semet residue) was disposed of in nearby lined ponds located within the watershed of Onondaga Lake. Ground water in the vicinity of several of these lagoons has been found to be contaminated with benzene and associated compounds (Geraghty and Miller, Inc., 1980, 1982) apparently as a result of leakage from the beds.

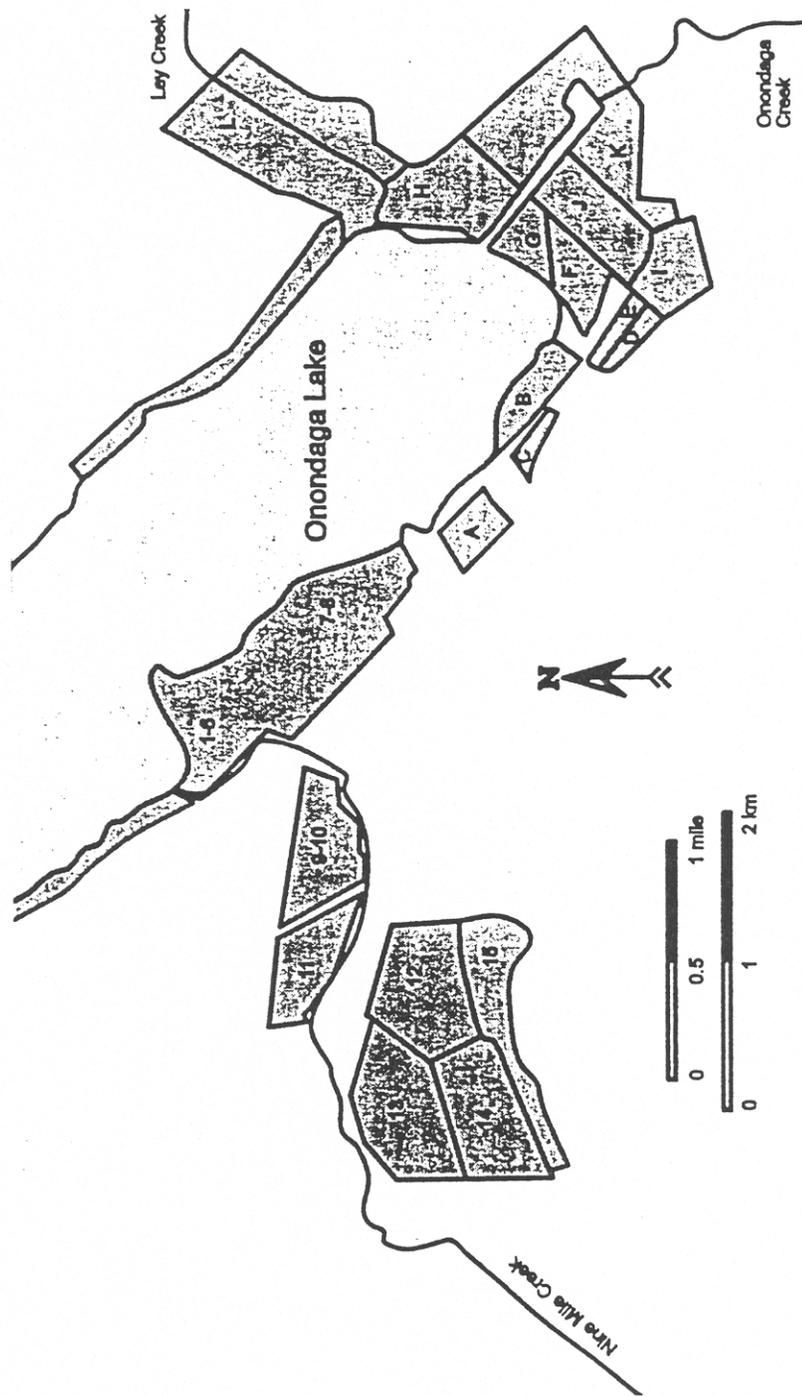


Figure 3.3. Location of Ninemile Creek and Allied waste beds around Onondaga Lake. (after Effler, 1996)

4 Cooling Water

Cooling water for the soda ash process was taken from the lake at three different intakes; one was shallow at about 3 m below the normal lake level and the other two were in deeper water. Withdrawal from the deeper intakes was preferred because of the cooler temperature; but the upper intake was used in late summer with chlorine added to oxidize the H₂S that developed in the lower waters (Effler, 1987a).

The heated (i.e. spent) process cooling water derived from the lake, was elevated in temperature and salinity and had a lower density compared to the surface waters of Onondaga Lake (Effler and Owens, 1986). Thus the water tended to enter the lake as an overflow (Effler and Owens, 1986).

4 The Chlor-Alkali Process

The availability of salt also promoted the establishment of a chlor-alkali process at the Allied facility. The products of the process are elemental Cl and an alkali, sodium hydroxide. The process involves the electrolysis of a water solution of NaCl with Hg used as the anode. An amalgam Na(Hg) was formed and was contacted with water to give an aqueous solution of NaOH. Mercury was recirculated in the process, but there were losses due to leakage and discharge, as the cells were cleaned or replaced.

3.3.2 Domestic Waste

Onondaga Lake received increasing amounts of untreated domestic waste via the tributaries of Onondaga Creek, Harbor Brook, and Ley Creek from the time of early settlement of the area through the early twentieth century. The first attempt to treat sewage involved an interceptor sewer system consisting of two sewers paralleling Onondaga

Creek and Harbor Brook, constructed in 1922. A primary sewage treatment facility was completed 1925 adjoining the southern shore to serve the interceptor, which carried 90% of the city's sewage (Effler, 1996).

Due to serious pollution of Ley Creek, a Ley Creek sewage treatment plant was constructed in 1934. This secondary facility was expanded to an average capacity of 9 million gallons per day (MGD) and an additional 11 MGD ($0.48 \text{ m}^3/\text{s}$) primary treatment was added in 1950. However this facility became overloaded due to the rapid growth of the area and in 1960 the METRO primary treatment plant was completed. According to the original plan for this facility, the METRO effluent was to be pumped around the lake, and combined with the Ley Creek effluent, and discharged to the Seneca River. A lake discharge was selected later as a cost saving measure.

The METRO plant was upgraded to secondary treatment in 1970 and tertiary treatment (phosphorus removal) in 1981. The facility was designed to treat an average flow of 80 MGD ($3.51 \text{ m}^3/\text{s}$); flows up to 120 MGD ($5.26 \text{ m}^3/\text{s}$) receive full treatment. Peak flows of 223 MGD ($9.77 \text{ m}^3/\text{s}$) can be accommodated, but flows in excess of 120 MGD ($5.26 \text{ m}^3/\text{s}$) only receive primary treatment and chlorination. The layout of the upgraded METRO facility is given in Figure 3.4.

During heavy rain storms, excess flow from the sewer system never reaches the METRO plant. Instead, untreated diluted sewage and floating debris are discharged to the tributaries of the lake through relief structure called combined sewer overflows (CSOs). There are 45 CSOs that discharge into Onondaga Creek, 19 that discharge into Harbor Brook and 2 CSOs that discharge into Ley Creek.

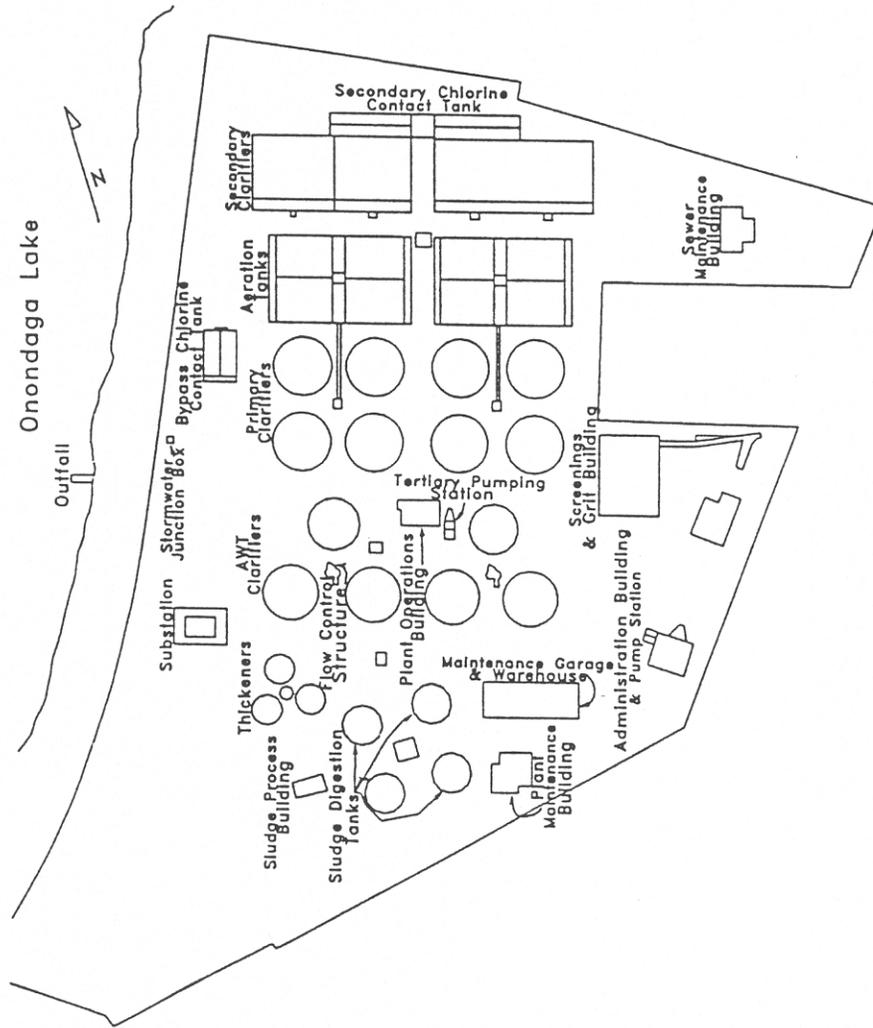


Figure 3.4. Layout of the Syracuse Metropolitan wastewater treatment plant (METRO).

3.3.3 Oil City

Oil City (Figure 3.5) is an industrial and commercial complex at the southern end of Onondaga Lake and around the mouth of Onondaga Creek. It has been used as a bulk storage and transfer facility for numerous industries since 1926. Industrial compounds utilized and stored included fuel related hydrocarbons, synthetic organic chemicals, and polychlorinated biphenyl (PCB) (NYDEC, 1989). Contaminant transport can occur through permeable sediments in the old Onondaga Creek stream bed channels, along buried sewer and utility pipeline, and through abandoned and buried drainage channels from the salt production industry. In the Oil City area, groundwater moves at a rate of 10^{-5} to 10^2 cm/s and discharges primarily to the Barge Canal and Onondaga lake (Figure 3.5) (Effler, 1996).

3.4 Hydrogeologic Setting

Onondaga Lake lies on an area that straddles two diverse physiological geologic provinces, consisting of the Ontario Lowlands to the north and the Appalachian highlands to the south (Rickard and Fisher, 1975). The Appalachian highlands are capped by the resistive Helderberg Group consisting of Devonian Hamilton Shales, Onondaga Limestone, Oriskany Sandstone and dolostones.

Brines which were associated with the lake in the past are thought to have originated in the Syracuse Formation, contained in the Salina Group, which outcrops along the base of the Helderberg Escarpment. Onondaga Lake is situated on the lowest member of the Salina Group, the Vernon Shale, which contains high concentrations of sulfate and

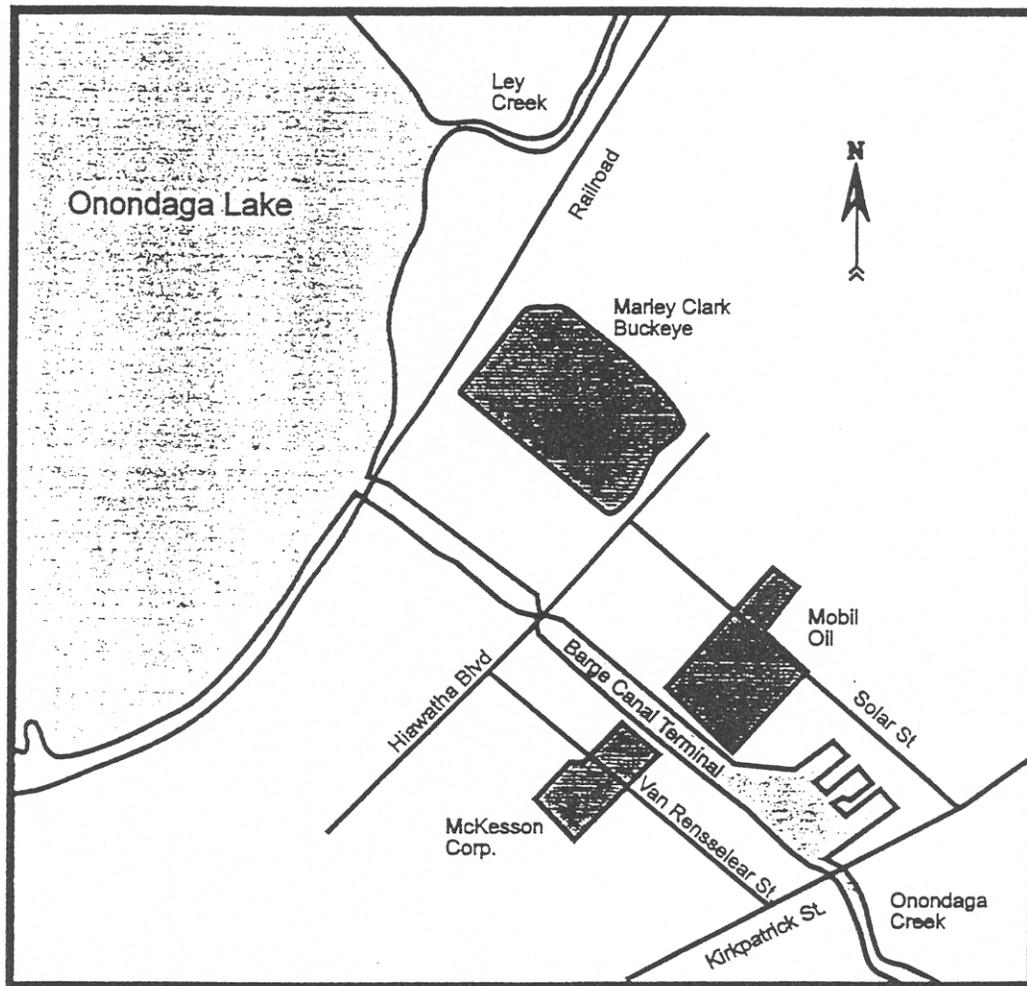


Figure 3.5. Locations of the Barge canal, and industrial complexes in the Oil City area (after Effler, 1996)

calcium concentrations in the surface waters (Winkley, 1989).

In the vicinity of the lake, two factors have been important in determining the surficial geology of the area: inundation by the Wisconsinian glaciers and the influences of human activities (Winkley, 1989). The Lake lies on a mixture of glaciolacustrine and lacustrine sands, silts, gravel, marl and clays (Winkley, 1989; Pagano et al., 1986). The surficial geology has been further changed by the creation of waste beds for the discharge of industrial by-products. Regional groundwater flow systems are topographically driven with recharge areas lying to the south in the higher elevation Appalachian highlands, with flow directed north to the Ontario lowlands (Cosner, 1984). Most of the tributaries to Onondaga Lake lie in glacial meltwater drainage channels and glacial troughs that are filled with unconsolidated interbedded sands and gravels.

Along Onondaga Creek, there are salt beds of commercial size (Salina Group), at depths averaging 366m in the Tully Valley. The dissolution of this salt gives the saline character of the groundwater in the Syracuse area (Higgins, 1995). Approximately 52 % of the annual external sediment loading to Onondaga Lake has been attributed to inputs originating from the Tully Valley mud boils and volcanoes (Figure 3.6) along Onondaga Creek (Yin and Johnson, 1984; Effler et al., 1992). These mud and sand volcanoes and boils are formed by increased groundwater pore pressures resulting in liquefaction of sediments (Shilts, 1978; Tuttle et al., 1990; Wills and Manson, 1990). Sources of increased pore pressures typically include heavy rainstorms, the onset of spring runoff, and subsidence of overlying sediments. The subsequent surficial discharge of sediments as a result of the pressure release forms a mud/sand volcano or boil (Lundqvist 1962; Dionne, 1973;

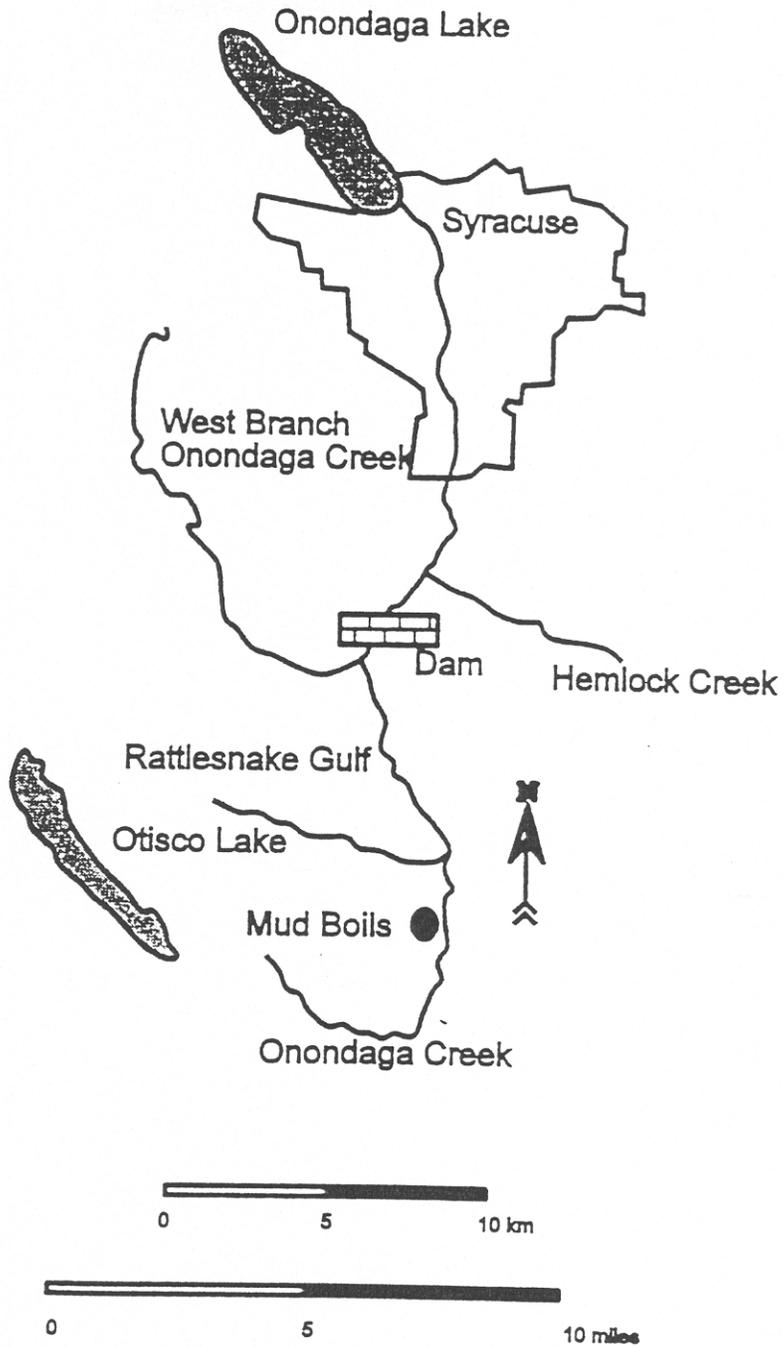


Figure 3.6. Location of the Tully Valley mud boil in relation to Onondaga Lake. (after Efler, 1996)

Washburn, 1973). The mud boils from the Tully Valley produce a mauve, tannish-colored turbid streamflow that subsequently enters Onondaga Creek and completely mixes with the creek streamflow within 1.2 km. The color is the result of the high concentrations of Otisco Valley clay found in suspension (Getchell, 1983).

Much of the land adjacent to Ley Creek from the south branch headwaters downstream to its outlet was originally marsh that was subsequently reclaimed for landfill areas and industrial parks. Reclamation was accomplished by filling in the wetland areas with municipal and industrial solid wastes along with common construction debris.

General Motors-Inland Fisher Guide Division is located along Ley Creek and Factory Ave (Figure 3.7a). Soils on the site, along with portions of Ley Creek, are known to be contaminated with PCBs as a result of the disposal and dredging of materials used in hydraulic die casting operations at the Inland Fisher Guide Facility (O'Brien and Gere Engineers 1989). The mean concentration of PCB's in the groundwater at this site is 3.62 µg/L. Mass transport of PCB's from the ground water into Ley Creek is estimated to be 0.15 gm/d (Effler, 1996).

Landfills located near the outlet of Ley Creek are shown in Figure 3.7b. The most complete set of information relates to the Crouse-Hinds Landfill which has two aquifers beneath it, with the ground water flowing towards Ley Creek, located 170 m west of the site at an average rate of 5.01×10^{-3} m/d (6 ft/yr). (Engineering Science, Inc., 1983).

Ninemile Creek flows along the Ontario Lowlands lake plain through the Allied waste beds, and presently contributes about 50% of the total chloride load to Onondaga Lake (Auer et al., 1991). Surface and groundwaters north of Warners-Amboy have high

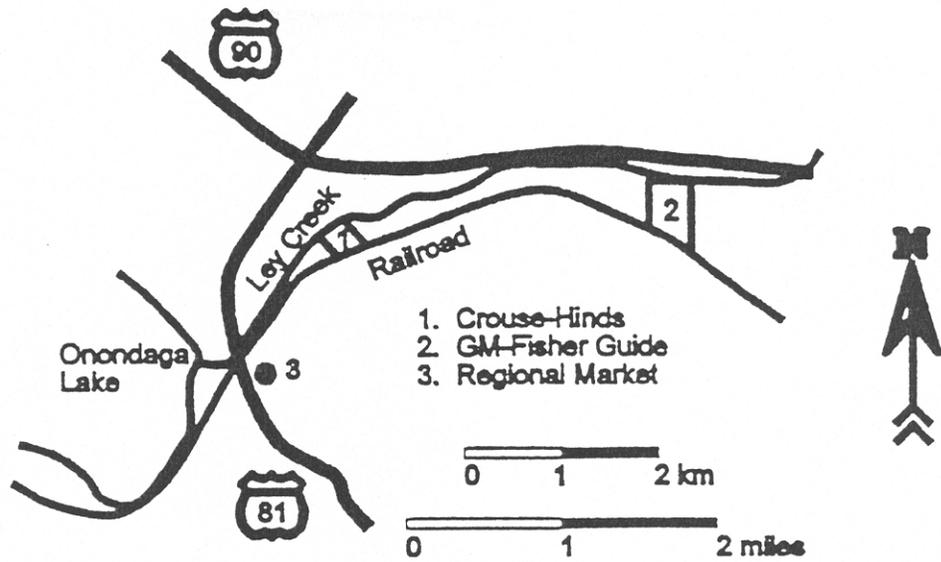


Figure 3.7(a). Location of General Motors-Inland Fisher Guide around the Ley Creek watershed. (after Effler, 1996)

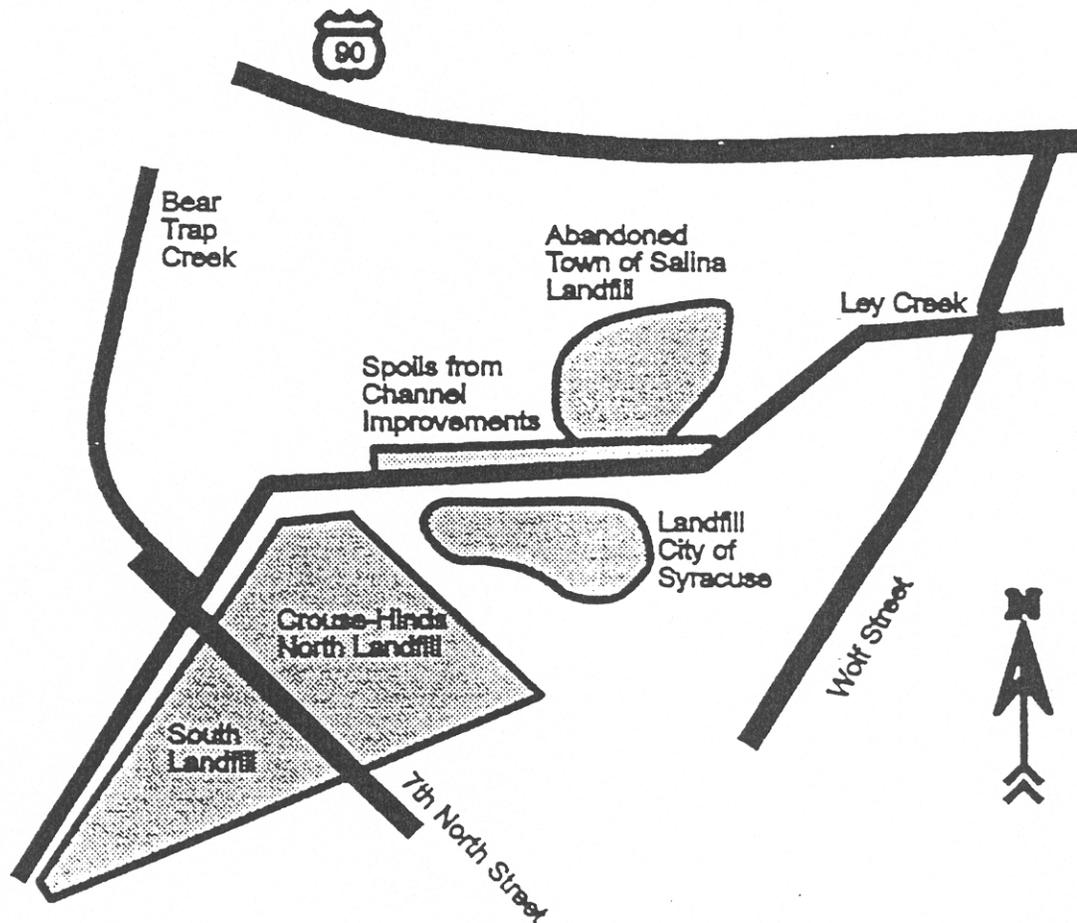


Figure 3.7(b). Locations of known landfills in the Ley Creek watershed near Onondaga Lake. (after Effler, 1996)

ionic concentrations (Kantrowitz, 1970; Winkley, 1989; Noble, 1990). Both regional and groundwater discharge and groundwater mounding under the adjacent waste beds contribute to the groundwater discharge to Ninemile Creek north of Warners-Amboy. The waste beds were built directly on the surficial sediments and much of its leachate that enters the surficial deposits ultimately discharges to Ninemile Creek (Effler et al. 1991a).

3.5 Pollution Impacts

1 Salinity

The lake is characterized by hardwater (Effler and Driscoll, 1985). It has a high ionic strength which is largely comprised of four major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and three major anions (HCO_3^- , SO_4^{2-} , and Cl^-). Four of the major ions Mg^{2+} , Na^+ , K^+ and Cl^- are largely conservative in the lake ecosystem. The dominance of Ca^{2+} , Na^+ and Cl^- reflects the very high loads of these materials received as waste from the production of soda ash. Major reductions in their concentrations occurred with the closure of the chemical facility in 1986 (Driscoll et al., 1993). The high SO_4^{2-} concentrations are largely a result of the hydrogeologic setting of the lake. Inputs of SO_4^{2-} allow for SO_4^{2-} reduction, an important anaerobic metabolic pathway in the hypolimnion following the onset of anoxia. Carbon dioxide/ HCO_3^- regulate the acid base chemistry the lake.

The high salt concentrations that have prevailed in the lake have had the following implications: (1) alteration of the biological diversity (Remane and Schleiper, 1971); (2) influence of the phytoplankton assemblage (Sonzogni et al., 1983); (3) precipitation of CaCO_3 from the upper waters during the summer months (Effler 1987b), which influences

the transparency and a number of element cycles in the lake (Effler 1987b); (4) increase water density, which alters the hydrodynamics of the lake.

2 Dissolved Oxygen (DO)

The oxygen resources of the lake are extremely limited, due to its highly eutrophic conditions. Dissolved oxygen is depleted rapidly from the hypolimnion soon after the onset of density stratification (Effler et al., 1988). The DO decreases with increasing depth, during the interval of depletion and this reflects the localization of demand at the sediment-water interface and limited vertical mixing in the hypolimnion.

The severe DO depletion causes anaerobic conditions to develop in the hypolimnion. This encourages sediment releases and subsequent hypolimnetic accumulation of nutrients (Freedman and Canale, 1977) and reduced chemical species (e.g. Fe^{2+} , H_2S , CH_4) in the hypolimnion (Murphy, 1978). The high rates of organic matter deposition facilitate the depletion of DO in the lake.

3 pH, Inorganic C, Ca_2^+ and $\text{CaCO}_3(\text{s})$

The lake water is well buffered and has pH values between 7 to 8.5 (Effler et al., 1981, 1982; Effler 1987b; Driscoll et al., 1993). Solution pH values are generally highest at the lake surface and decline with increasing depth.

The lake is oversaturated with respect to the solubility of calcite during the summer period, as a result of increased temperature (Brunskill, 1969; Strong and Eadie, 1978) and the photosynthetic process (Otsuki and Wetzel, 1974; Effler et al., 1981, 1982; Effler 1984; Effler and Driscoll, 1985). The precipitation and deposition of CaCO_3 (Effler 1987b; Kelts and Hsu 1978; Jones and Bowser, 1978) results in the following implica-

tions: (1) marked depletion of alkalinity and dissolved inorganic carbon, and the accumulation of CaCO_3 in underlying sediments (Jones and Bowser, 1978) (2) an influence on the cycling of other constituents such as phosphorus (Otsuki and Wetzel, 1972; Murphy et al., 1983; Wodker et al., 1985), dissolved organic carbon and other particles that serve as nuclei for precipitation (Johnson et al., 1991), and (3) decrease in the water clarity due to increases in light scattering (Weidemann et al., 1985; Effler et al., 1987c; Effler et al., 1991b). The closure of the soda ash/chlor-alkali facility reduced Ca^{2+} loading, but the extent of oversaturation with respect to calcite remains essentially unchanged.

4 Nitrogen Species and Phosphorous

Concentrations of total ammonia (T-NH_3), free ammonia (NH_3) and nitrates (NO_3^-) are usually high in the epilimnion in the productive months. The summer concentrations of T-NH_3 and NO_3^- in the epilimnion routinely exceed levels associated with the limitation of phytoplankton growth, and that of NH_3 and nitrite (NO_2^-) also exceed standards established to protect fish (Effler et al., 1990).

Phosphorus (P) plays a very significant role in controlling phytoplankton growth (Vollenweider, 1968; Hutchinson, 1973; Dillon, 1975; Carlson, 1977). In addition, elevated concentrations facilitate decreases in clarity and hypolimnetic oxygen depletion. The concentration of the soluble reactive phosphorus (SRP), a form immediately available to phytoplankton, generally decreases in the epilimnion during the summer, and also increases with depth in the hypolimnion clearly depicting releases from the sediments. This is the dominant form of P in the hypolimnion. The failure, or delay of the lake to recover following reduction in external P loading has been attributed to continued high rates of P

release from sediments (Ahlgren, 1977; Larsen et al., 1981; Welch et al; 1986; Driscoll et al., 1993).

6 Hydrogen Sulfide

Hydrogen sulfide accumulates to very high concentrations during summer stratification due to the high natural inputs of SO_4^{2-} coupled with elevated deposition of organic matter to the hypolimnion (Murphy, 1978; Effler, 1987a; Effler et al., 1988). Concentrations of H_2S observed in Onondaga Lake are among the highest values reported in the literature for freshwater systems.

7 Mercury

Concentrations of Hg_T and CH_3Hg^+ in Onondaga Lake are among the highest reported in the literature (Bloom and Effler, 1990). These values are indicative of a site experiencing substantial Hg contamination (see section 1.2).

CHAPTER 4 - MATERIALS AND METHODS

4.1 Cleaning Procedure for Analysis of Mercury

Contamination is one of the greatest challenges in the determination of trace metal concentrations in environmental samples. It is therefore essential to clean all apparatus to be used for sampling and analysis. The cleaning procedure employed in this research was a combination of procedures used by several investigators (Patterson and Settle, 1974; Gill and Fitzgerald, 1985).

New Teflon[®] bottles were immersed in a 20% (v/v) trace-metal grade nitric acid bath, which was heated to 70°C. The bottles were soaked for forty-eight hours. The acid bath was then turned off and the bottles were removed while still hot which ensured that the Hg released during the soaking period remained in solution and be rinsed away. The bottles were then triple rinsed with quartz-distilled, deionized water (DDIW) and filled with 1% (v/v) hydrochloric acid and leached overnight in an oven at 70°C. The bottles were then triple rinsed after leaching, filled again with 1% HCl, capped tightly, double bagged in new ziplock bags and stored in a clean room. Teflon[®] bottles that were reused were cleaned similarly, but only soaked for about ten hours.

Other laboratory supplies, including glassware and small parts made of Teflon[®] were cleaned by heating overnight in 20% (v/v) nitric acid bath, triple-rinsed, and stored in 1% HCl. They were again triple rinsed prior to use. The very high purity DDIW was produced using a quartz distillation apparatus. Water that was already distilled and deionized was fed into quartz still for polishing treatment. The DDIW was also used throughout all

analysis. The time between cleaning and use of all apparatus was minimized to reduce contamination.

4.2 Sampling Procedure and Sample Preservation

Water samples were collected monthly from October 1995 to September 1996 at various sampling sites, including Ninemile at Lakeland (NL), Ninemile at Amboy (NA), Onondaga Creek (OC), Ley Creek (LC), Harbor Book (HB) and Metro effluent (ME). In March 1996, weekly samples were collected at NL, NA and OC to fully investigate the variation in Hg concentrations during the snow melt period. The selection of a sample site was based on several factors, including potential sources of Hg and runoff discharge volumes. Additional factors such as turbulence, study objectives, stream depth and the presence of structures (bridges, dams, etc.) also impacted the selection of sampling sites. Sampling sites were selected in areas where the water was well mixed to allow for a representative sample. Sites were as far as possible from any metal supports, bridges, wires or poles and heavily traveled roads to avoid contamination (Zief and Mitchell, 1976; Bloom, 1993). The sampling activity was planned so that samples known or suspected to contain the lowest concentrations of Hg were collected first, to avoid contamination by carryover. In addition, these low Hg concentrated samples were transported to the laboratory before sampling at sites with high concentration commenced (Nriagu et al, 1993).

Manual sampling techniques (USEPA method 1669, 1995) in which the samples were collected directly into the Teflon[®] bottles was used for the surface waters. Sampling was done by a team of two people. Upon arrival at the sites, one member of the team was

designated as “dirty hands” and the other as “clean hands”. All operations involving contact with the sample bottle were handled by the individual designated as “clean hands” while “dirty hands” was responsible for all activities that do not involve direct contact with the sample.

At each sample site, the sampling personnel put on clean gloves before sample collection activity commenced, with “clean hands” donning longer length gloves. The sample storage cooler containing the clean sample bottles was opened, the double bagged sample bottle removed and the outer bag unzipped by “dirty hands”. “Clean hands” then opened the inside bag containing the sample bottle, removed the bottle, resealed and replaced the inner bag and “dirty hands” resealed the outer bag.

The cap of the bottle was unscrewed and held upside down by “clean hands” who discarded the contents from the bottle into the water body, then submerged the bottle and filled it partially with sample. The bottle was capped, shaken several times and the rinsate emptied away from the site. This was repeated two more times, after which the bottle was completely submerged and allowed to fill. When no bubbles appeared and while the bottle was still inverted so that its mouth was underwater, the cap was replaced. This was done so that contact of the sample with the air was avoided.

After collecting the sample, “dirty hands” quickly opened the outer bag while “clean hands” replaced the filled sample bottle in the inner bag and sealed it. Finally dirty hands zipped the outer bag and returned the sample to the cooler. “Dirty hands” was also responsible for documenting the sample number in the sample log together with any unusual observations concerning the sample.

The samples were then taken to the laboratory where they were preserved. In preservation, 5 ml of high purity 12N hydrochloric acid was added per liter of sample. After preservation, the samples were bagged and stored in a clean, cold room in the laboratory to await analysis.

4.3 Total Mercury Analysis

Total Hg can be defined as all bromine chloride oxidizable forms of Hg found in aqueous solution. This includes but is not limited to Hg(II), Hg⁰, strong organically complexed Hg(II) compounds, adsorbed particulate Hg, and several tested covalently bound organomercurials (i.e. CH₃HgCl, (CH₃)₂Hg and C₆H₅HgOOCCH₃) (USEPA, 1995). The determination of Hg_T in water was done by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry (CVAFS) (Fitzgerald and Gill, 1979, 1983; Bloom and Crecelius, 1983; Bloom and Fitzgerald, 1988). This method is recommended by the USEPA to gather and monitor data associated with the Clean Water Act.

4.3.1 Description of Purging System

A sample reactor or purging system was designed according to Gill and Fitzgerald (1987), Bloom and Crecelius (1983) and USEPA (1995). The function of this system was to allow for the reduction of mercuric ion in the samples to Hg⁰, and then strip the Hg⁰ to a gold collection column. A schematic diagram of the purging system is shown in Figure 4.1. The body of the purging vessel was a 250 ml borosilicate glass flat bottom flask, with standard taper 24/40 neck, fitted with a ground glass joint seal sparging-tube-cap, containing a special 4-way valve and having a glass frit that extended to within 0.2 cm of the

bubbler bottom. Nitrogen was used as the carrier or purging gas. Since it may contain organic and Hg(II) vapor which can reduce the efficiency of the gold collection columns and decrease the precision and accuracy of the analysis, a series of traps (activated carbon and a gold-coated sand column) were used to remove any contaminants before the gas stream reaches the fritted sparger and bubbling samples.

A soda lime aerosol/moisture trap was placed between the gold Hg collecting column and the outlet port of the ground glass joint seal. This trap was made 8-14 mesh soda lime in a 10 cm long x 0.9 cm inner diameter fluoropolymer tube, with the mesh packed between wads of silanized glass wool. The function of this trap was to adsorb moisture and acid fumes created during the bubbling procedure. The trap was cleaned of Hg by placing it on the output of a bubbler and purging for 1 hour with N₂ at 350 ml/min. If not taken care of, acid fumes would foul the gold collecting columns, reducing the effectiveness. The gold collecting column was located immediately after the soda lime trap. These gold collecting traps were made of a 3.4 cm long gold coated 45/60 mesh quartz sand and contained in a 10 cm x 6.5 mm outer diameter x 4 mm inner diameter quartz tubing. The ends were plugged with quartz wool. The traps were fitted with 6.5 mm inner diameter fluoropolymer friction-fit sleeves for making connection to the system. When they were not in use, fluoropolymer end plugs were inserted in trap ends to preclude contamination. A flow meter capable of controlling and measuring gas flow to the purge vessel was connected between the nitrogen gas tank and the bubblers. All the connections in this purging system, including glass-glass and glass-plastic connections, were made from Teflon[®] tubing specially washed for Hg analysis.

4.3.2 Sample Processing

Samples were oxidized prior to analysis. Each sample in the Teflon[®] bottle was thoroughly shaken and a 100 ml aliquot was poured into a 125 ml fluoropolymer bottle. The oxidizing agent, 0.2N bromine monochloride (BrCl) in concentrated HCl was added, the bottle quickly capped and allowed to react at room temperature for a minimum of 12 hours. The amount of BrCl added to the samples was 0.5 ml per 100 ml of sample water. For samples containing high concentrations of organic matter, or reduced substances, such as sulfides, more BrCl was added until a permanent 12 hr yellow color developed (USEPA, 1995).

Prior to sample analysis the following day, all traces of Hg in the bubbling system were removed. The bubblers were half filled with high purity DDIW, and 0.5 ml 20% (w/v; Gill and Fitzgerald, 1987) stannous chloride (SnCl_2) was added to each bubbler. The system was purged with nitrogen gas, for 15 min. without inserting the gold column in the analysis train. The flow rate of the purging gas was 400-600 ml/min, which was the same rate used in sample processing. This solution was then discarded and the bubblers were rinsed three times with high purity DDIW.

100 ml of 1% BrCl was then added to each bubbler, this time inserting the gold collection columns in the direction that ensures the glass frit retains the gold sand. 200 μl of 30% NH_2OH was added, the bubbler swirled and allowed to react for 5 min. 500 μl of 20% SnCl_2 was added and the bubbler capped quickly, swirled and allowed to sit for 2 min after which the system was purged with N_2 for 15 min., at a flow rate of 400-600 ml/min. The gold traps were removed after the purging period and analyzed to determine

DI/reagent blanks. With the contents still in, 500 μl of 20% SnCl_2 was again added to the bubblers allowed to react for 2 min and purged for 15 min, with blank traps. This gave the background blanks. Following this stage, with the solution in the bubblers still in place, standards of known amounts of Hg were analyzed. The standards analyzed were 100 pg, 1 ng, 5 ng, and 10 ng. In each case the required amount was pipetted into the bubblers, 500 μl of 20% SnCl_2 added, allowed to react for 2 min and purged for 15 min, with blank gold traps inserted in the analysis train. The results of these standards together with those for the DI and background blanks were used for calibration. When a high quality calibration curve was obtained, the system was then ready for water sample analysis.

The excess oxidizing reagent in the samples was pre-reduced by hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$; 30%; Bloom and Crecelius, 1983) before Hg analysis was conducted. The amount of reagent added was generally 0.2 ml per 100 ml, but it depended on the amount of BrCl consumed (CVAFS manual; PTI BR-0003) and this reagent destroyed the free halogens. The resulting mixture was allowed to react for 5 min. Further reduction was ensured by the addition of 500 μl of 20% SnCl_2 with a reaction time of 2 min. Reduction is important because any chlorine left in the sample water might destroy the gold traps (CVAFS manual).

The reduced samples were purged for 15 min, with blank gold traps used for each. During the purging period, the free Hg^0 was swept onto the gold traps where it was amalgamated. After every sample run, the bubbler content was disposed of and the bubbler rinsed thoroughly with DDIW before reused.

During the analysis, the performance of the system was assessed on a given sample matrix. One in every ten samples from a given sample site, were spiked with a 2 ng Hg_T standard in duplicate to determine the matrix spike (MS) and matrix spike duplicates (MSD). Recovery of the Hg_T was observed, and if the value was low (<75%), the procedure was checked and the analysis of the sample and MS/MSD were repeated.

4.3.3 Detection System

The Hg_T detection system consists of a two stage gold amalgamation gas train followed by a cold vapor atomic fluorescence spectrometer (CVAFS) detector connected to a computer. The gold columns in this train were each inserted within a coil consisting of 75 cm of 24-gauge nichrome wire. A schematic diagram of the detection system is shown in Figure 4.2.

The gold collection column, concentrated with Hg⁰ from water sample during purging, was set into the two-stage gold amalgamation gas train. With ultra-high purity helium gas flowing at a rate of 70 ml/min and cleaned of Hg by a gold-coated sand filter, Hg was thermally desorbed from the collection columns by heating at about 500°C (a barely visible red glow when the room was darkened), for 3 minutes. The heating was produced by the nichrome wire coil that was controlled by a variable transformer and a timing device. This Hg was subsequently adsorbed by the second analytical gold column. By using the same heating technique, the Hg was finally swept into the CVAFS detector, where the fluorescence emission of Hg was measured at 253.7 nm. This method offered two major advantages: first virtually all interferences due to organics or Cl₂ (Bothner, 1973; Fitzgerald and Gill, 1979) were eliminated; and second, all analate introduced to the

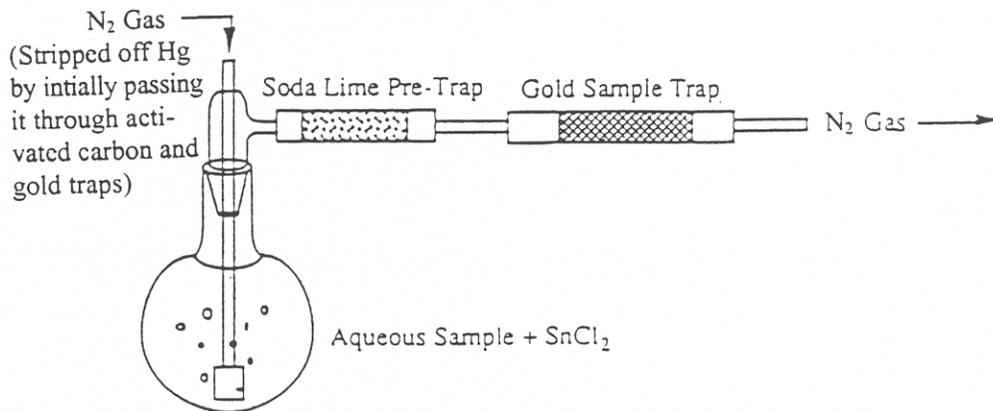


Figure 4.1. Schematic diagram of the purging system for Hg_T analysis. (after USEPA, 1995)

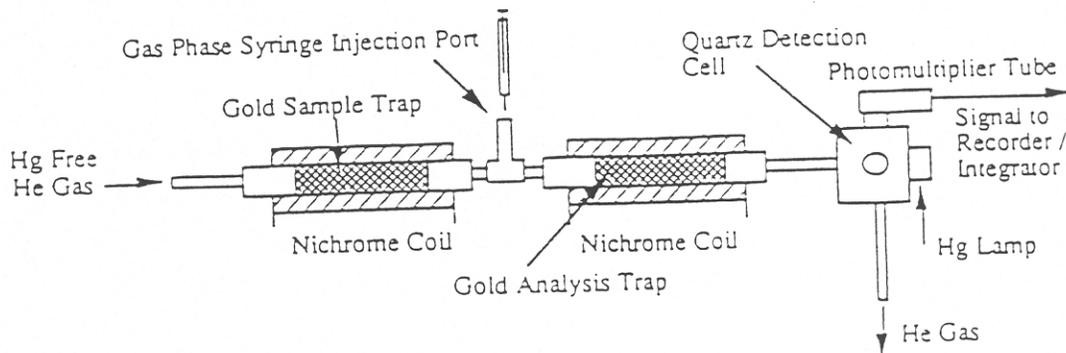


Figure 4.2. Schematic diagram of detection system for Hg_T analysis. (after USEPA, 1995)

instrument was from one gold trap, which was well characterized in terms of peak height per nanogram Hg, leading to greater analytical precision. The detection limit of the detector was ~ 0.1 picogram Hg (CVAFS manual). The output was recorded by a computer connected to the CVAFS and this contained a software package that integrated the Hg spike after the run time, giving the gross peak area.

In order to eliminate any variability in the detection of Hg caused by the characteristics of the gold coated sand traps, the analytical gold trap was generally fixed in its position unless its efficiency decreased markedly. All collection columns were blanked using the same two-stage heating process and this was done prior to inserting the traps into the purging system. However the traps were self blanked as the analysis proceeded.

4.4 Methylmercury Analysis

The analysis of CH_3Hg^+ was done in two stages. The first was an isolation procedure for the separation of the CH_3Hg^+ from the natural water sample, while the second was the aqueous phase ethylation, precollection on Tenax[®] trap, isothermal gas chromatography and CVAFS detection (Bloom, 1989; Hovart et al., 1993b; Liang et al, 1994; Bloom and VonDer Geest, 1995). Direct ethylation of natural waters without the isolation stage results in release of only reactive CH_3Hg^+ which may represent only 5-60% of total CH_3Hg^+ (Hovart et al., 1993b). Therefore the extraction step is important.

There are two isolation procedures for the separation of CH_3Hg^+ from water samples. The first is based on extraction of CH_3Hg^+ into methylene chloride and back extraction into water by solvent evaporation. The second is based on the distillation and

later condensation of CH_3Hg^+ compounds. Comparison of these two methods was done by Hovart et al., (1993) on 110 water samples of various origin. Distillation was found to be the better of the two as it gave higher recoveries (80-95%) and achieved lower detection limits. It is also less laborious and without the use of an organic solvent and provides the specific separation of CH_3Hg^+ and $(\text{CH}_3)_2\text{Hg}$, if present (Hovart et al., 1993b). Based on these research reports, the distillation method was used as the isolation technique for the analysis of CH_3Hg^+ in water samples, in this study.

4.4.1 Distillation of Samples

Up to 50 ml of eight water samples were each placed in separate 60 ml distillation acid-washed Pyrex glass tubes. One 50 ml DI blank, and one recovery test sample made by mixing a standard 2 ng CH_3Hg^+ and 50 ml of one of the samples, were also distilled along side the eight water samples. 500 μl of 50% H_2SO_4 and 200 μl of 20% KCl were injected into each of the ten glass tubes. The tubes were then set on the special heating block and the threading of each was wrapped with Teflon[®] tape (to minimize leakage) before they were tightly capped. Teflon[®] tubing (1/8 inch) was attached through each cap so that it touched the bottom of the glass tube. The other end of the Teflon[®] tubings were attached to a two gang-of-5 flowmeters connected to a N_2 gas tank. Receptor tubing also attached to the caps of the glass tubes were inserted into the matching transmitter vials consisting of ten acid-washed Teflon[®] tubes of 60 ml in volume. About 5 ml of DDIW was injected into these receiving vials and their weights recorded. The receptor Teflon[®] tubing was extended down into the water contained in the receiving vials and the vials were set in a cooler with ice and cold water to promote condensation of distillates.

Insulating the glass tubes containing the samples were several uncapped glass tubes filled with laboratory DI water and set around the distilling glass tubes on the heating block. The gas flow was turned on at a rate of 60 ml/min and the heating temperature adjusted to 145°C. This temperature was selected in order to maintain a distillation rate of 6-8 ml/hr. Therefore 5-7 hours was needed to distill 80-85% of the 50 ml water samples. This distillation isolation procedure enables CH₃HgCl to be purged from the sample together with water vapor due to the increased partial pressure of the aqueous solution at the elevated temperature (Hovart et al., 1993b).

When the receptor vials were filled to about 1 cm from the cap, the Teflon[®] tubing was removed from the transmitter vial. The body of the receptor vials were dried with clean paper towel, the caps quickly removed and the final weight of each recorded. They were then capped tightly, stored in a clean cold room for further analysis the following day. The heat and gas flow were turned off and all glassware and Teflon[®] materials were cleaned for distillation the next day.

4.4.2 Aqueous Phase Ethylation and Purging

The purging system was designed according to Bloom (1989; Figure 4.3a). The reaction/purge vessels were 250 ml flat bottom Pyrex glass flasks with 24/40 tapering fitting and a special 4-way valve sparging-tube-cap. This valve assembly allows the water sample to react initially with the ethylating agent, without bubbling, then to be purged on to the trapping column, and finally to be bypassed, so that water vapor adsorbed onto the column may be evaporated by direct flow of dry carrier gas (Bloom, 1989). The sparging-tube-cap was connected to a N₂ gas tank via a flow-meter. In addition, an activated car-

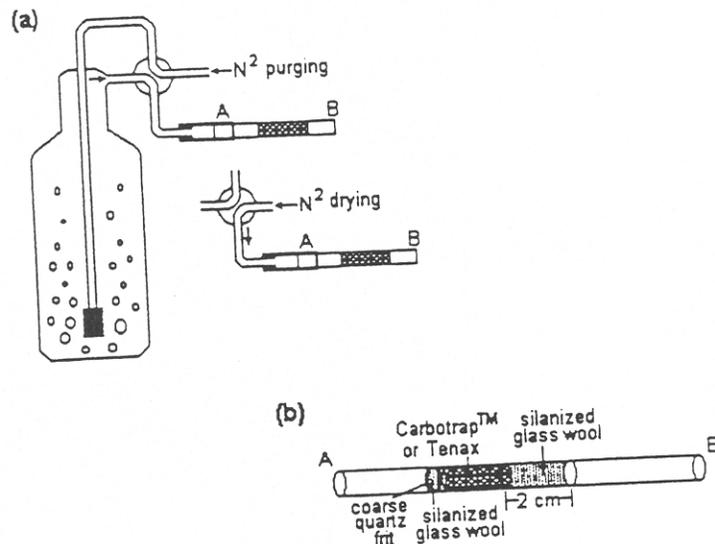


Figure 4.3. (a) Schematic diagram of purging system for CH_3Hg^+ analysis. (b) Schematic diagram for trapping column. (after Bloom, 1989)

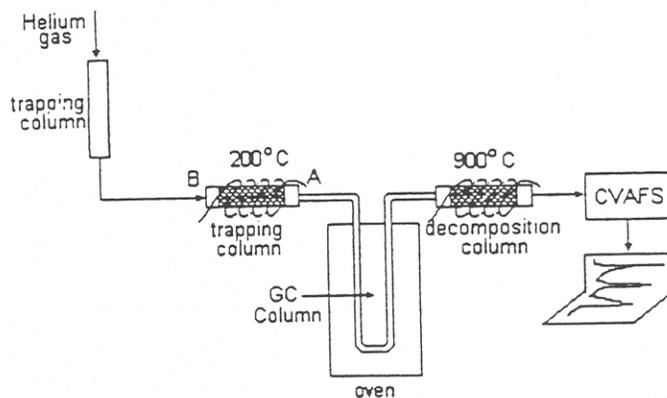


Figure 4.4. Schematic diagram of the detection system for CH_3Hg^+ analysis. (after Liang et al., 1994)

bon, and a gold coated sand trap were connected to remove any possible Hg in both the N₂ gas and laboratory air streams during purging. The trap columns for the collection of the purged organo-Hg species were constructed from quartz tubing packed with Tenax[®] (Altech, 20/35 mesh) and held in place by silanized glass wool (see Figure 4. 3b). To initially remove residual Hg from the filling, traps were heated to about 200°C for 5 min.

The reagents required for the analysis were: (1) sodium acetate buffer which was made by adding 2 moles of reagent grade sodium acetate (272 g) and 2 moles of Ultrex glacial acetic acid (118 ml) dissolved in DDIW to give a final volume of one liter; (2) 4% potassium hydroxide (KOH) and (3) 2% sodium tetraethylborate (NaE(CH₂CH₃)₄, abbreviated as NaEt₄), prepared every 2-3 days. Since the NaEt₄ reagent is extremely air sensitive, it was not weighed, but rather measured by volume and 5 ml aliquots of the solution were stored in small acid washed Teflon[®] bottles and kept in the refrigerator except during use. The ethylating agent which is a solution of 1% NaEt₄ in 2% KOH, was made on the day of analysis. The Teflon bottle with 5 ml of 2% NaEt₄ was removed from the refrigerator, thawed in a hood after which 5 ml of 4% KOH was added, then capped quickly and kept in a cooler packed with ice to insure preservation for analysis that day.

The distilled samples were analyzed two at a time. They were poured into the reaction or purge vessels and DDIW was added to bring the volume to ~100 ml. 200 µl of the acetate buffer was added to adjust the pH to 4.9±0.1 (Bloom, 1989), followed by 50 µl of the ethylating agent. The vessels were swirled to mix the contents, the 4-way valve-caps inserted and blank Tenax traps connected to the system train. The mixture was allowed to react for 10 minutes during which CH₃Hg⁺ was converted to methylethyl Hg

and Hg(II) to diethyl Hg. At the end of the reaction period, the system was purged for 20 min at a flow rate of 400-600 ml/min after which the flow was shut off, the traps removed for analysis, and the bubblers thoroughly rinsed with DDIW before processing the next set of samples. In addition to the water samples, a DI blank and standards of 50 pg, 100 pg and 200 pg of CH_3Hg^+ were also analyzed for calibration purposes. The concentration of CH_3Hg^+ in each sample was determined by dividing the concentration of CH_3Hg^+ recovered in the receptor vials by the fraction of reference standard recovery in the matrix spike.

4.4.3 Detection System

The CH_3Hg^+ detection system consisted of a thermal desorption coil, an isothermal gas chromatography (GC) column, a thermal decomposition tube and a CVAFS connected to a computer (see Figure 4.4). The trap containing the organo-Hg species after purging was inserted within the thermal desorption coil made of 24-gauge nichrome wire, extending over the length of the Tenax[®] material in the quartz tube. The helium gas flow was adjusted to a flow rate of 80 ml/min. The nichrome coil was switched on and the trap was quickly heated, reaching a peak of 200°C (internal in about 40 sec.). Heating was controlled by a timer connected in line with the system. The organo-Hg species desorbed from the trapping column were carried by the He gas through the GC column, which was held in a cylindrical oven at 100°C. The species were eluted according to their boiling points and passed through the thermal decomposition tube at a temp of ~900°C, where they were decomposed into Hg^0 and detected by CVAFS. The fluorescence signals were displayed on a computer screen with the species appearing at different retention times. All spikes

were usually observed and corresponded to Hg^0 , CH_3Hg^+ and $\text{Hg}(\text{II})$. In this analysis Hg^0 is present both as a residual from the heating of the column, and as a break-down product of the organomercurials and hence should be minimal (Liang et al., 1994). A large amount of Hg^0 would indicate major decomposition of the ethylation derivatives of CH_3Hg^+ and $\text{Hg}(\text{II})$.

4.5 Quality Assurance / Quality Control

Precision and accuracy of results are important in demonstrating laboratory capability. The quality assurance/quality control (QA/QC) program implemented for this study contained the analysis of triplicate samples, field blanks, laboratory blanks, matrix spike (MS) and matrix spike duplicates (MSD).

Triplicate samples were collected for a particular site selected at random on certain sampling dates. The Hg_T and CH_3Hg^+ results for the triplicate samples are summarized in Table 4.1. The CV for replicate analysis of samples for Hg_T ranges from 5.8-26.8% with an average of 17%. The CV range for CH_3Hg^+ was 14.5-20.5% with an average of 18.3%. These CV values satisfy the acceptable criteria for performance test (CV = 21%).

The other results of the QA/QC program are summarized in Table 4.2 above. In order to monitor matrix interferences and to further demonstrate accuracy and precision of analysis, MS and MSD were performed. Recoveries obtained were $99 \pm 7.6\%$ and $101 \pm 5.1\%$ for the analysis of Hg_T and CH_3Hg^+ , respectively. Methyl Hg recovery from the distillation procedure was $88 \pm 4.7\%$, and this value lies within the range 80-95% specified

in the literature (Hovart et al., 1993). Values obtained for the blanks are also listed in Table 4.2.

Table 4.1. Triplicate results for Hg_T (ng/L) and CH₃Hg⁺ (ng/L)

Site	Date	Species	Results	Mean	Std. Dev.	CV%
NL	Nov. '95	Hg _T	26.64, 16.93, 15.99	17.85	2.459	13.8
		CH ₃ Hg ⁺	0.48, 0.36, 0.34	0.40	0.076	19.3
LC	Jan. '96	Hg _T	3.26, 5.01, 4.24	4.17	0.877	21.0
		CH ₃ Hg ⁺	0.25, 0.39, 0.30	0.31	0.045	14.5
NA	Mar. '96	Hg _T	4.26, 4.17, 3.08	3.48	0.656	17.1
		CH ₃ Hg ⁺	0.25, 0.24, 0.17	0.22	0.044	19.8
HB	May '96	Hg _T	8.86, 9.02, 8.08	8.65	0.503	5.8
		CH ₃ Hg ⁺	0.59, 0.47, 0.69	0.58	0.111	18.8
ME	Jun. '96	Hg _T	57.91, 87.23, 54.86	66.67	17.87	26.8
		CH ₃ Hg ⁺	1.59, 2.40, 2.21	2.07	0.424	20.5
OC	Aug. '96	Hg _T	9.01, 6.32, 8.23	7.85	1.384	17.6
		CH ₃ Hg ⁺	0.59, 0.42, 0.53	0.51	0.086	16.9

NL = Ninemile at Lakeland; LC = Ley Creek; NA = Ninemile at Amboy; HB = Harbor Brook; ME = Metro effluent; OC = Onondaga Creek.

Table 4.2. Results of the QA/QC program for Hg analysis

Parameter	Hg _T (ng/L)	CH ₃ Hg ⁺
DI/Reagent blank	0.85 ± 0.09	0.06 ± 0.01
Distillation blank	N/A	0.076 ± 0.02
Background blank	1.00 ± 0.87	N/A
Field blank	1.19 ± 0.66	0.09 ± 0.04
Distillation recovery	N/A	88 ± 4.7%
MS/MDS recovery	99 ± 7.6%	101 ± 5.1%

N/A: not applicable.

4.6 Ancillary Data

Concentrations of other water quality parameters for the various sites were obtained from the Onondaga County Department of Drainage and Sanitation. Water samples from

each site were analyzed every two weeks by the County. Most of these sample dates and times did not correspond to those for the Hg analysis.

The average daily discharges for the various tributaries were obtained from the U.S. Geological Survey. There is no flow monitoring station at Amboy. Thus corresponding daily flows at Amboy were estimated according to the simple linear expression:

$$Q_{NA} = 0.80 \times Q_{NL} \quad (\text{Effler, 1996})$$

The value 0.80 equals the ratio of the upstream watershed area of Ninemile Creek for Amboy and Lakeland locations. Average daily flows at METRO were obtained from the County. The discharges for the ungauged minor tributaries including Sawmill Creek, Bloody Brook and Tributary 5A were estimated using the following expressions (Effler, 1996):

$$\text{Bloody Brook discharge (m}^3/\text{s)} = 2.86 * (\text{Harbor Brook Discharge (m}^3/\text{s)}) - 0.21$$

$$\text{Sawmill Creek discharge (m}^3/\text{s)} = 0.175 * (\text{Ley Creek Discharge (m}^3/\text{s)}) + 0.17$$

$$\text{Tributary 5A discharge (m}^3/\text{s)} = 0.341 * (\text{Harbor Brook Discharge (m}^3/\text{s)}) + 0.08.$$

The flow from the East Flume has been reported as a constant in most years since the closure of the soda ash/chlor-alkali plant; a value of 0.09 m³/s was reported for 1990 (Effler, 1996).

4.7 Calculation of Loadings

Estimates of loading depends highly on the calculation procedure used. However, the main objectives of loading estimates were to minimize biases and variances, both of which yield incorrect answers, regardless of the number of observations. Biases in loading

estimates may be due to unrepresentative sampling and the use of an inappropriate method.

An interactive user-friendly software, entitled FLUX (version 4.4) developed by Walker (1987) was used to estimate loadings for this study. This software provides several procedures to estimate loadings from intermittent grab or event sampling over a period for which complete flow data exists. Using six calculation methods, FLUX maps the flow-concentration relationship developed from the sample record onto the entire flow record to calculate total mass discharge and associated error statistics. FLUX provides an option to stratify the samples into groups based on flow or time for each method. In many cases, stratifying data increases the accuracy and precision of loading estimates. Uncertainties are characterized by error variances of the loading estimates. Flux uses a jackknife procedure to estimate error variance. This involves excluding each sampling event, one at a time, and recalculating loadings.

Method 2 was used to estimate loadings for this study because flows and concentrations were unrelated or weakly related. This method bases the loading estimate on the flow-weighted-average concentration times the mean flow over the averaging period. This amounts to a "ratio estimate" (Walker, 1987). In addition to the loading calculated, the coefficient of variation (CV) is given for each method. Values of CV (expressed as %) can be classified as good when >0.1 , fair between 0.1-0.2, and poor when >0.2 (Walker, 1987).

4.8 Statistical Analysis

Comparison of average Hg for the different sites was done at 5% significance level (i.e. 95 chances out of 100) using t-tests and setting up a two-sided hypothesis given by:

Null hypothesis, $H_0: \mu_i = \mu_j$; Alternative hypothesis, $H_1: \mu_i \neq \mu_j$.

At this significance level, the smallest difference at that would be declared significant was computed and was compared to the absolute value of each observed difference. For an α -level test against two-sided alternatives, significance will be declared when

$$|\mu_i - \mu_j| / s_{\mu_i - \mu_j} \geq t_{\alpha/2} \quad \text{or} \quad |\mu_i - \mu_j| \geq t_{\alpha/2} * s_{\mu_i - \mu_j} \quad (\text{Steel and Torrie, 1980}),$$

where μ_i and μ_j are the means tested and $s_{\mu_i - \mu_j}$ is the standard deviation appropriate to a difference between means. The test criterion for evaluating the differences between means directly is called the least significant difference, or lsd, given by

$$\text{lsd} = t_{\alpha/2} * s_{\mu_i - \mu_j} = t_{\alpha/2} * s * \sqrt{\{(n_i + n_j)/(n_i * n_j)\}},$$

where s = pooled standard deviation of all the samples at sites 1, 2, ... k. = $\sqrt{Q/(U-k)}$, and

$$Q = (x_1 - \mu_1)^2 + (x_2 - \mu_2)^2 + \dots + (x_k - \mu_k)^2, \text{ and}$$

$$U = n_1 + n_2 + \dots + n_k,$$

with $U - k$ being the degrees of freedom. If the observed difference between the means is greater than the lsd then the null hypothesis was rejected and it could be concluded that the difference was significant.

CHAPTER 5 - RESULTS

5.1 Discharge and Watershed Yield

The mean discharge, percentage contribution of inflows to the lake and the watershed yield were calculated for each gauged inflow and the sum of the ungauged inflows (Table 5.1). The discharge from ungauged input waters of Onondaga lake including Bloody Brook, Sawmill Creek and Tributary 5A were estimated using the empirical relationships given in section 4.5. A discharge of $0.09 \text{ m}^3/\text{s}$ was assumed for East Flume in the calculations. The mean total inflows to the lake during the study period was $15.67 \text{ m}^3/\text{s}$. The largest sources of water to the lake were Onondaga Creek and Ninemile Creek; together they represented about 62% of the surface discharge received by the lake during the study period.

Onondaga Creek had the highest mean discharge ($5.0 \text{ m}^3/\text{s}$) and also the highest contribution of the total inflow (32%) compared to the other input waters during the study period. Ninemile Creek showed the second highest mean discharge of $4.67 \text{ m}^3/\text{s}$ and contribution of about 30%. The ungauged tributaries were estimated to have contributed about 9% of the total inflow, approximately equal to the gauged discharge from LC. Substantial variations occurred in discharge during the study period (standard deviations ≥ 0.50). Each mean watershed yield was calculated by dividing the mean discharge by the watershed areas of the gauged tributaries. Harbor Brook had the lowest watershed yield; OC had the highest. Differences in groundwater inputs may explain the differences in the estimated yields. The contribution from METRO varied through the year based on the

input from the natural tributaries. METRO's contribution decreased in the spring and increased in the summer. Most of the water from METRO originates from outside of the Onondaga Lake watershed.

Seasonal variations in discharge at OC is depicted in the hydrograph in Figure 5.1, and this pattern represents a typical discharge pattern for the input waters to the lake. The discharges on sampling dates are shown on the hydrograph and the mean discharge for the study period plotted as a horizontal line. Strong seasonal variations in stream discharge were observed. The highest flow occurred in January, due to a mid-winter snowmelt event. Discharge was also high in March, April and May, but was low in the summer months. The discharges in winter tended to be higher than the mean discharge, with the reverse occurring in summer. The highest discharge for the Hg sampling dates occurred in snowmelt period in March.

Table 5.1. Mean discharges, % flow contributions to the lake and watershed yield for study period.

Input Water	Mean Flow (m ³ /s)	Standard Deviation	Mean % Contri- bution to Lake	Watershed yield (m/year)
Harbor Brook	0.30	0.50	1.9	0.34
Ley Creek	1.35	1.82	8.6	0.70
Onondaga Creek	5.00	4.81	31.9	0.57
Ninemile Creek	4.67	4.20	29.8	0.78
METRO	3.00	0.69	19.2	-
Others (ungauged)	1.34	1.86	8.6	-

Others = sum of Bloody Brook, Sawmill Creek, Tributary 5A, and East Flume.

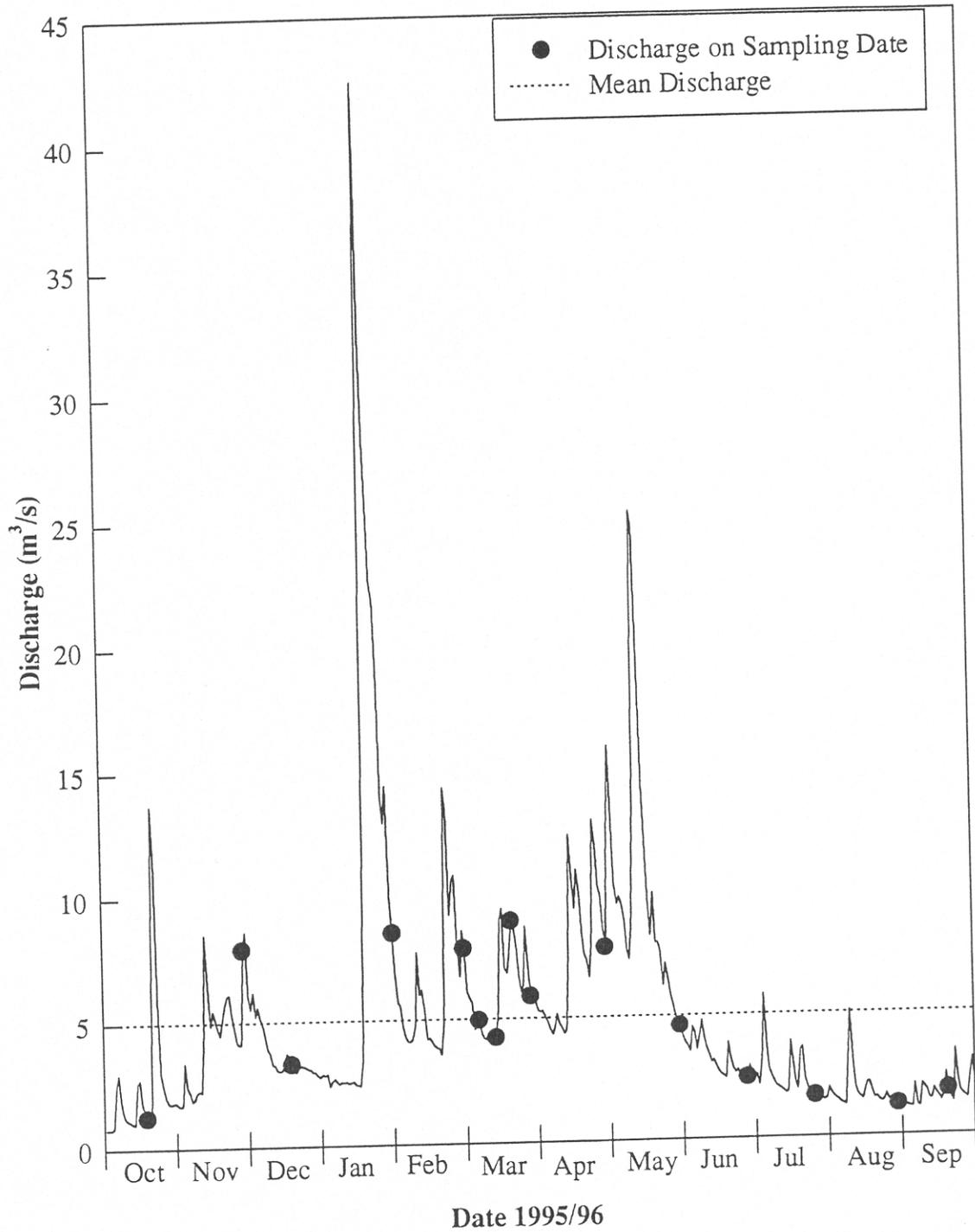


Figure 5.1. Seasonal variations in discharge (m^3/s) from October 1995 - September 1996 at Onondaga Creek.

5.2 Concentrations of Mercury Species

The natural tributaries showed temporal variations in concentration of Hg_T and CH_3Hg^+ . In general, concentrations of both species were slightly higher in summer (May - October) than in winter (November - April). Results of the monthly concentrations of both Hg_T and CH_3Hg^+ for each site are given in Appendix 1. A summary of these concentrations and the fractions of Hg_T occurring as CH_3Hg^+ (expressed as % of Hg_T) are presented in Tables 5.2, 5.3 and 5.4, and the corresponding time series plots showing seasonal patterns are given in Figures 5.2, 5.3 and 5.4, respectively. Mean concentrations of Hg_T , CH_3Hg^+ and fraction of Hg_T occurring as CH_3Hg^+ at the various sites are depicted in Figures 5.5, 5.6 and 5.7, respectively. In each figure, plots for the winter, summer and the overall means are shown and the error bars represent the standard deviations. Statistical significance tests on the difference between mean concentrations were done at 5% level and the results are presented in Appendix 2.

Ninemile Creek at Amboy showed the lowest concentrations of both Hg_T and CH_3Hg^+ of any of the study sites. The range of Hg_T concentrations observed at this site were 2.6-6.1 ng/L in winter and 5.1-7.9 ng/L in summer. The overall mean Hg_T concentration was 5.1 ng/L. The observed pattern for Hg_T concentration (Figure 5.2) showed little variation between October and January, decreased in February and March and then increased to a peak value of 7.9 ng/L in June. There was no significant difference between mean Hg_T winter and summer concentrations. Fluctuating concentrations of Hg_T with no systematic pattern were observed during the snowmelt period. Methyl Hg concentrations at NA ranged from 0.1-0.5 ng/L; the mean was 0.3 ng/L. The mean concentration in

summer (0.3 ng/L) when temperatures (Figure 5.8) were higher, was slightly higher than that in winter (0.2 ng/L) but this difference is not statistically significant. The fraction of Hg_T occurring as CH_3Hg^+ ranged from about 3 to 7% (Figure 5.4), with a mean of about 5%.

Ninemile Creek at Lakeland also showed higher concentrations of both species in summer and fluctuating concentrations with no systematic pattern during the snow melt period. Low dissolved oxygen (Figure 5.9) and higher concentrations of Cl^- , Na^+ , and Ca^{2+} (Figures 5.10, 5.11 and 5.12) mainly from groundwater inputs were observed in summer. The range of Hg_T and CH_3Hg^+ concentrations at this site were 10.6-35.8 ng/L and 0.2-1.4 ng/L, respectively. Mean concentrations of both species were 17.9 ng/L and 0.5 ng/L, respectively. Seasonal patterns for both species were similar with the concentrations decreasing between October and November, fluctuating with no systematic pattern until April, increasing to the peak values in June, and slowly decreasing in the late summer. The mean winter concentrations of Hg_T and CH_3Hg^+ were 13.2 ng/L and 0.3 ng/L respectively and the mean summer, 24.9 ng/L and 0.8 ng/L, respectively. These differences in winter and summer were statistically significant. The fraction of Hg_T occurring as CH_3Hg^+ showed no seasonal pattern and ranged from about 2-4 %, with a mean of about 3%. The peak value of the fraction of Hg_T occurring as CH_3Hg^+ was observed in June.

At OC, Hg_T concentrations initially fluctuated throughout the winter with no systematic pattern, and increased in the summer. The winter range of Hg_T concentrations observed at this site was 5.4-9.2 ng/L with summer values ranging from 7.7-14.5 ng/L.

The overall mean Hg_T concentration was 8.2 ng/L and the difference between the summer and winter mean concentrations was not statistically significant.

Table 5.2. Mean and standard deviations of Hg_T concentrations for the study sites.

Site	Winter (ng/L)	Summer (ng/L)	Overall (ng/L)
NA	4.3 ± 1.3	6.3 ± 1.1	5.1 ± 1.5
NL	13.2 ± 2.2 ^α	24.9 ± 7.6 ^α	17.9 ± 7.7
OC	7.0 ± 1.3	10.1 ± 2.7	8.3 ± 2.5
HB	6.4 ± 2.2	6.3 ± 1.7	6.3 ± 1.9
LC	4.9 ± 1.1	6.8 ± 2.5	5.8 ± 2.1
ME	40.6 ± 16.7	22.7 ± 22.9	31.7 ± 21.3 [‡]

^α Difference between mean winter and summer concentrations is statistically significant

[‡] Significantly different from other overall mean concentrations

Table 5.3. Mean and standard deviations of CH₃Hg⁺ concentrations for the study sites.

Site	Winter (ng/L)	Summer (ng/L)	Overall (ng/L)
NA	0.2 ± 0.04	0.3 ± 0.1	0.3 ± 0.1
NL	0.3 ± 0.1 ^α	0.8 ± 0.4 ^α	0.5 ± 0.3
OC	0.4 ± 0.1	0.6 ± 0.3	0.5 ± 0.2
HB	0.7 ± 0.4	0.5 ± 0.1	0.6 ± 0.3
LC	0.4 ± 0.1	0.4 ± 0.1	0.4 ± 0.1
ME	1.4 ± 0.7	1.6 ± 1.1	1.5 ± 0.9 [‡]

^α Difference between mean winter and summer concentrations is statistically significant

[‡] Significantly different from other overall mean concentrations

Table 5.4. Mean and standard deviations of fractions of Hg_T occurring as CH₃Hg⁺ (expressed as %) for the study sites.

Site	Winter %	Summer %	Overall %
NA	5.1 ± 1.0	5.0 ± 1.4	5.1 ± 1.1
NL	2.6 ± 0.7	3.2 ± 0.6	2.8 ± 0.7
OC	5.3 ± 1.5	5.6 ± 1.2	5.4 ± 1.3
HB	9.9 ± 3.2	8.5 ± 3.1	9.2 ± 3.1
LC	7.4 ± 1.5	6.8 ± 1.3	7.1 ± 1.4
ME	3.8 ± 1.9	13.8 ± 19.0	8.8 ± 13.9

Notes: NA = Ninemile Creek at Amboy; NL = Ninemile Creek at Lakeland; OC = Onondaga Creek; LC = Ley Creek; HB = Harbor Brook; ME = Metro Effluent.

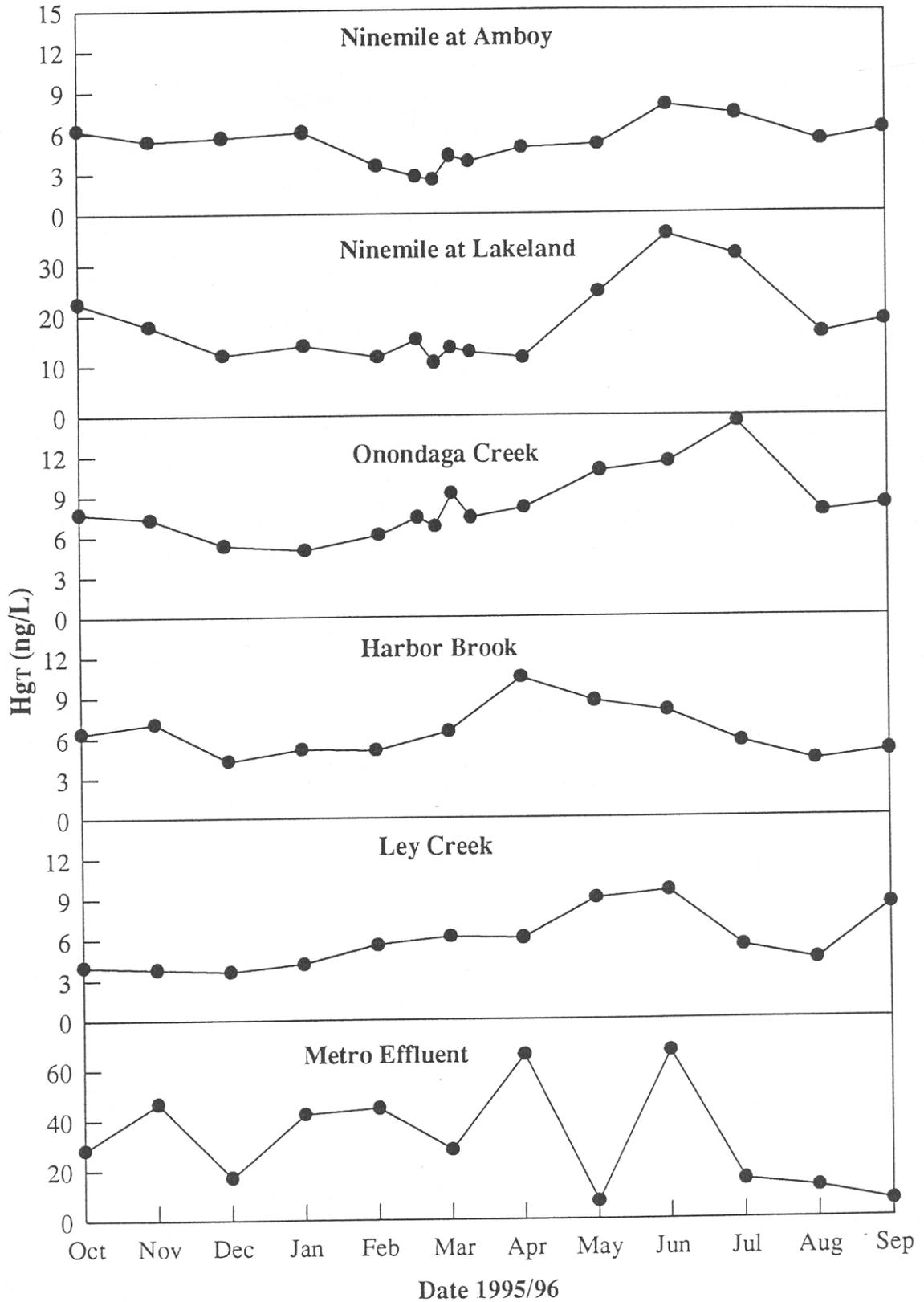


Figure 5.2. Time series of Hg_T concentrations for input waters of Onondaga Lake.

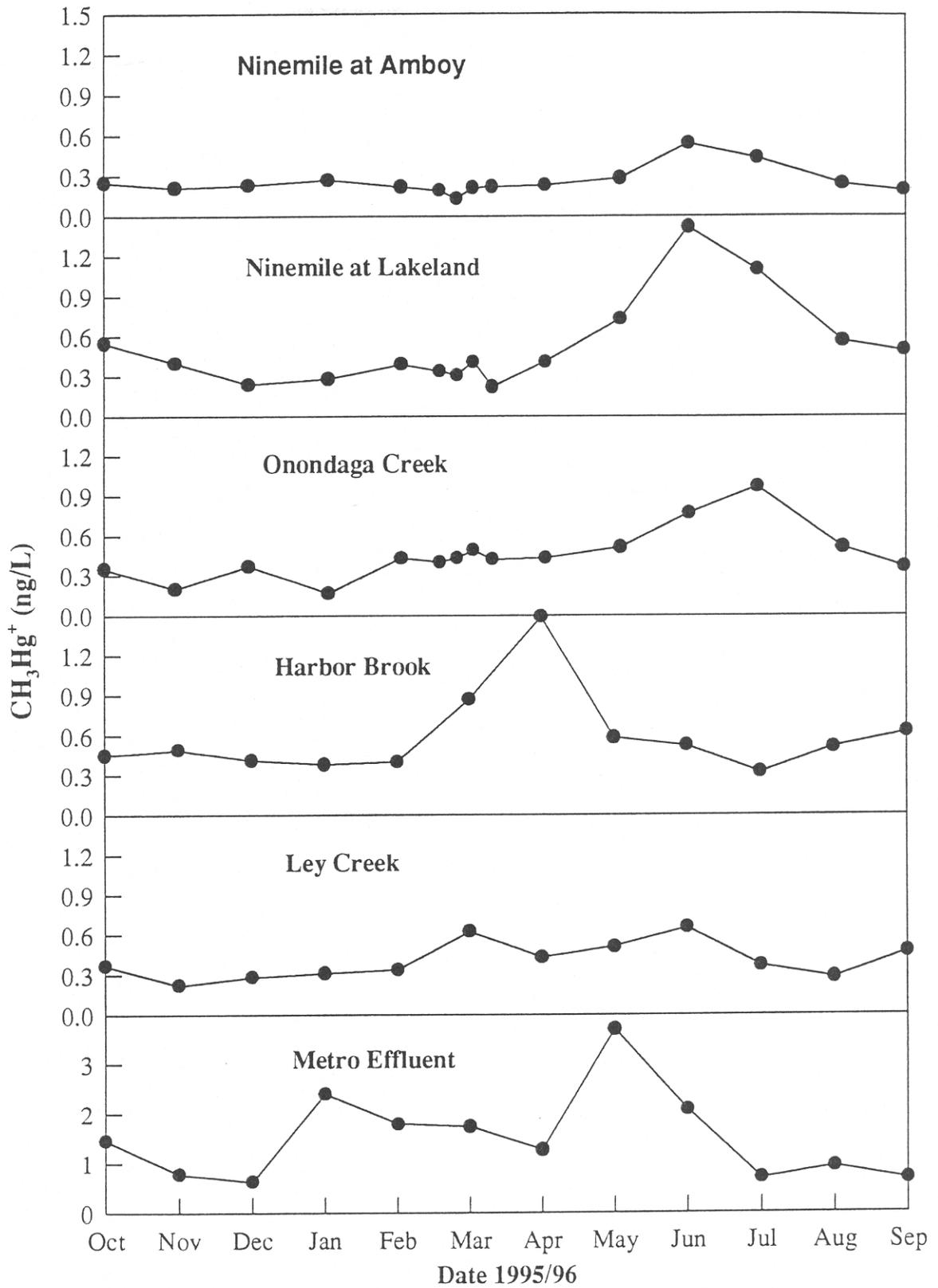


Figure 5.3. Time series of CH_3Hg^+ concentrations for input waters of Onondaga Lake.

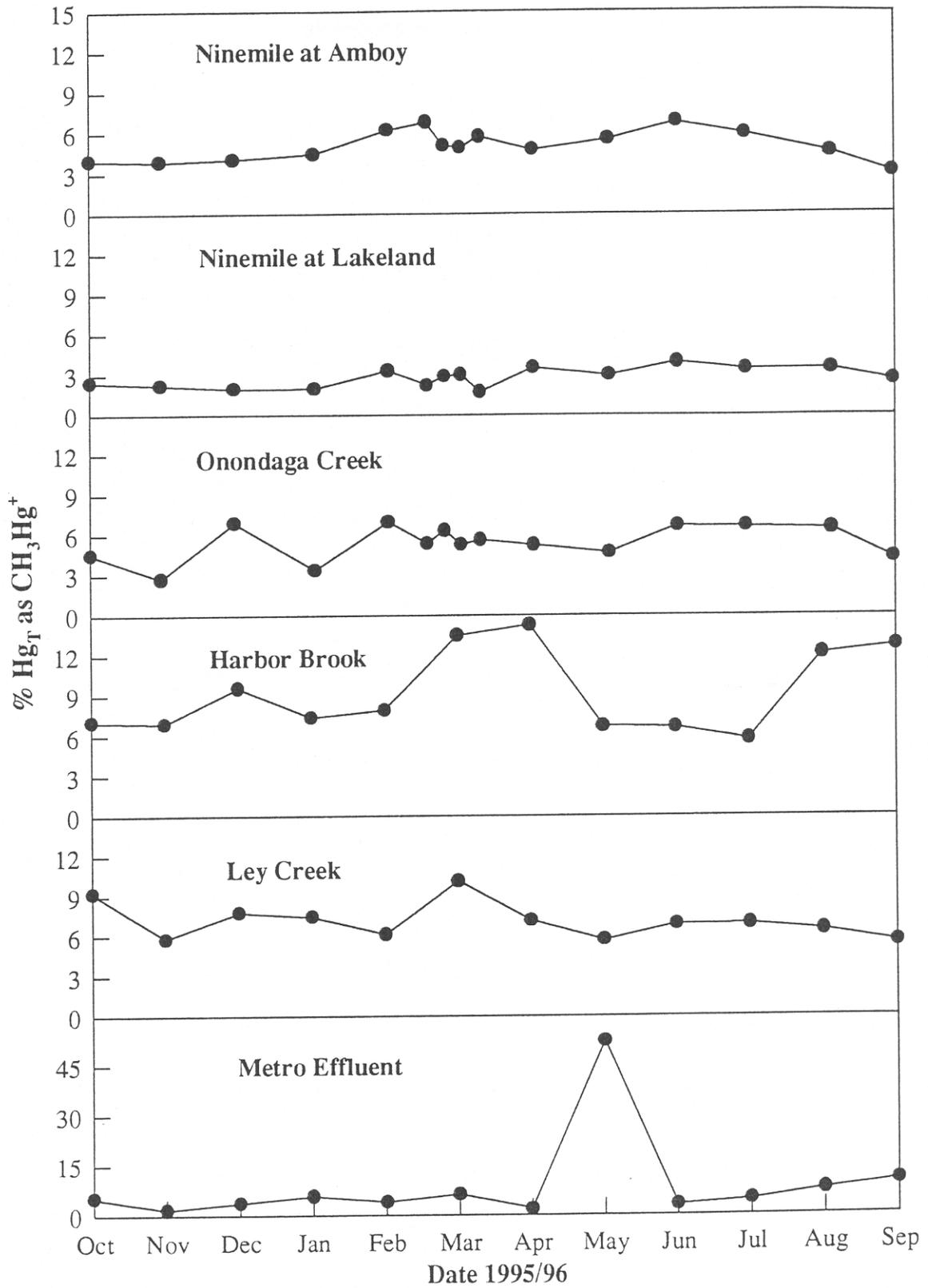


Figure 5.4. Time series of % of Hg_T occurring as CH_3Hg^+ for input waters to Onondaga Lake.

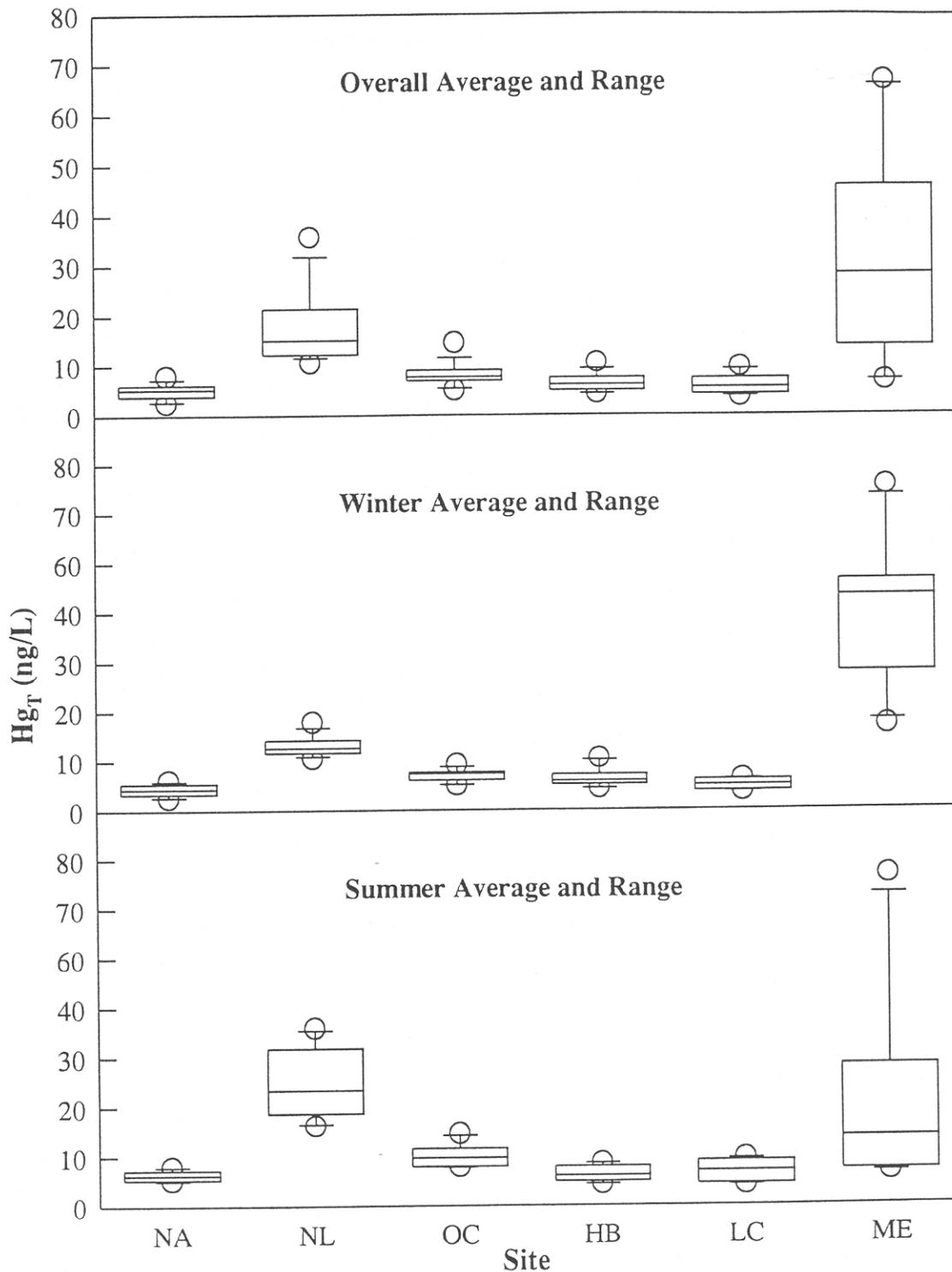


Figure 5.5. Comparison of mean Hg_T concentrations and range of concentrations for input waters of Onondaga Lake. (NA = Ninemile at Amboy; NL = Ninemile at Lakeland; OC = Onondaga Creek; HB = Harbor Brook; LC = Ley Creek; ME = Metro Effluent). Error Bars = Standard Dev.; o = Minimum and Maximum Hg_T concentrations.

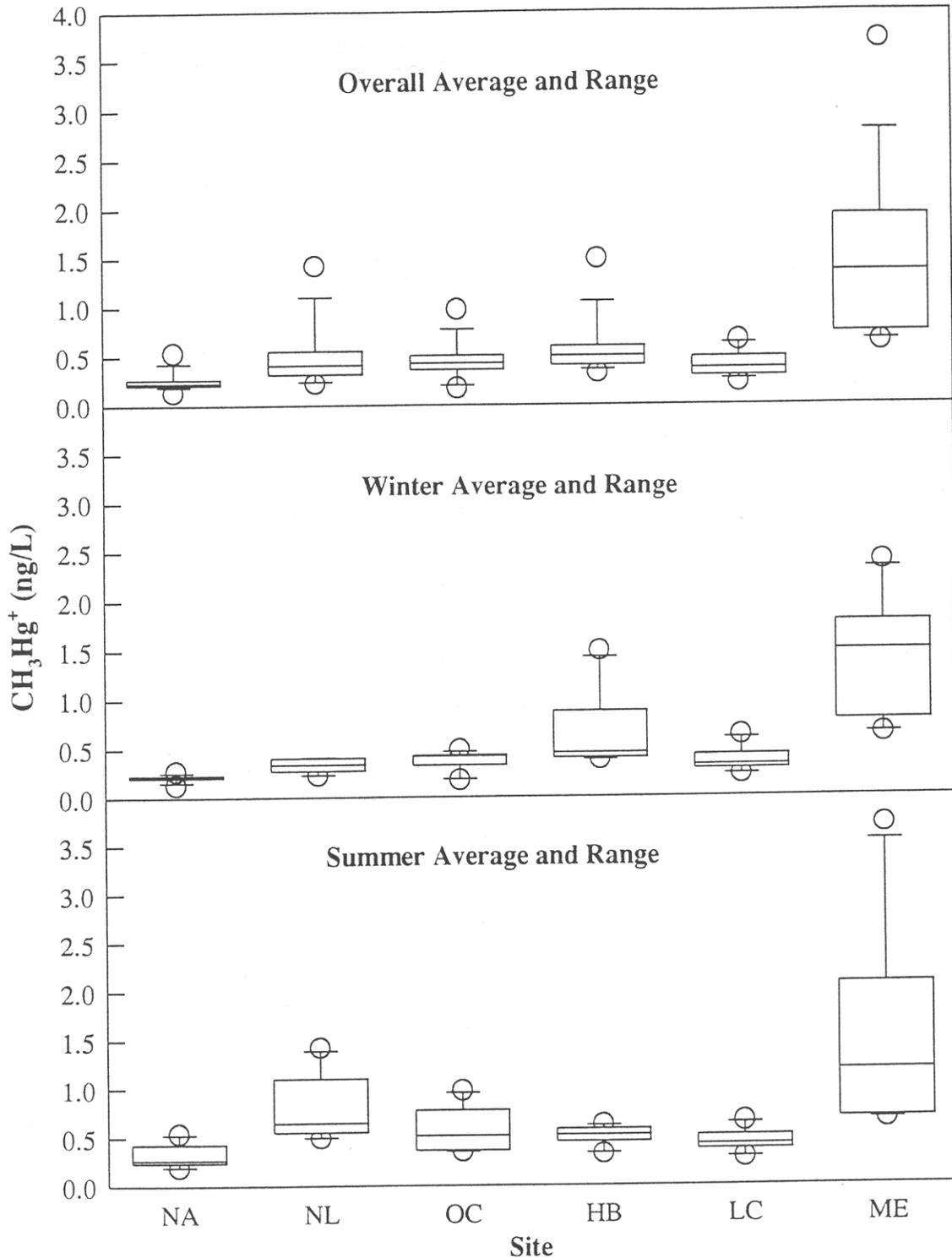


Figure 5.6. Comparison of mean CH_3Hg^+ concentrations and range of concentrations for input waters of Onondaga Lake. (NA = Ninemile at Amboy; NL = Ninemile at Lakeland; OC = Onondaga Creek; HB = Harbor Brook; LC = Ley Creek; ME = Metro Effluent). Error Bars = Standard Dev.; o = Minimum and Maximum CH_3Hg^+ concentrations.

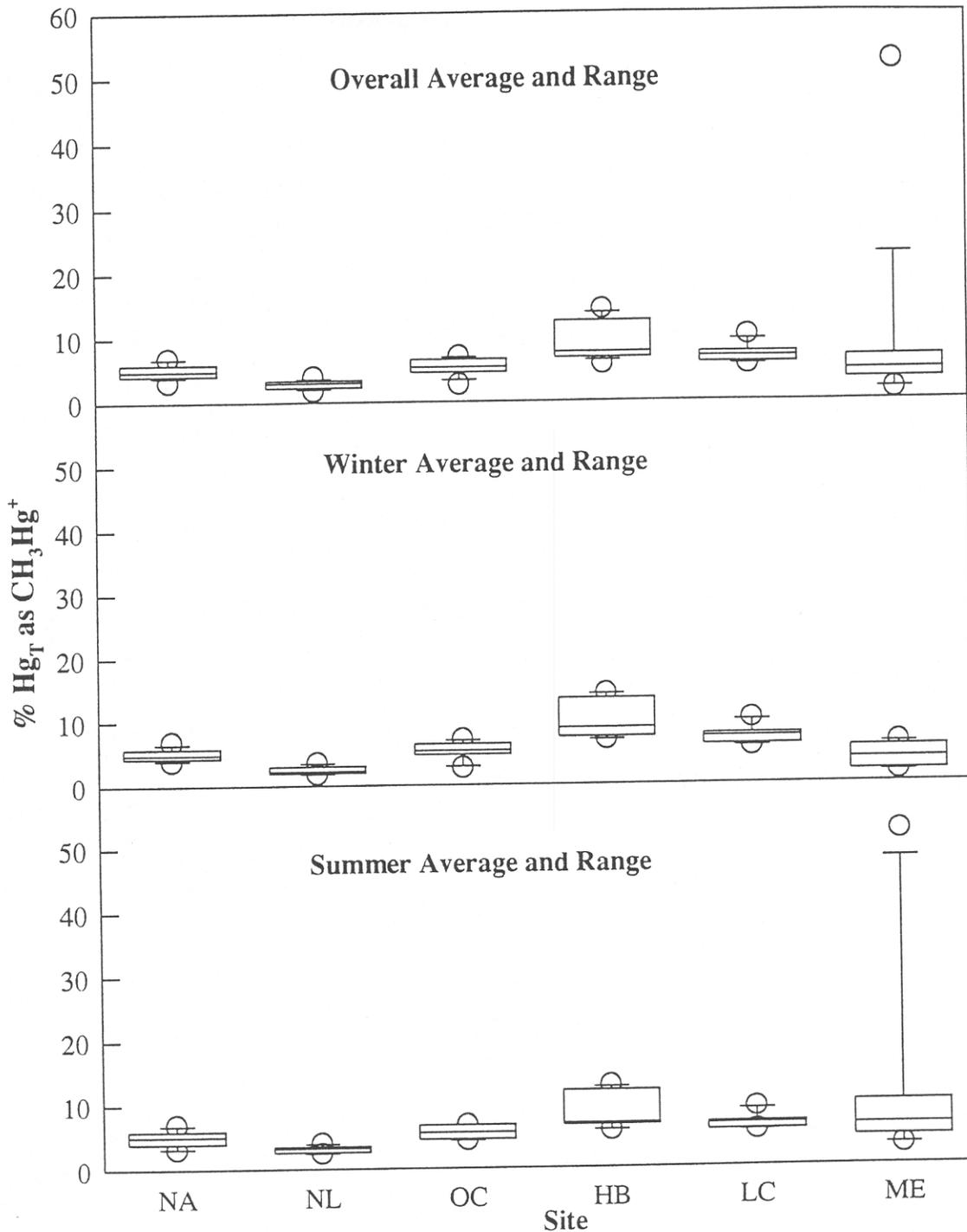


Figure 5.7. Comparison of mean % of Hg_T and % range of Hg_T occurring as CH₃Hg⁺ for input waters of Onondaga Lake. (NA = Ninemile at Amboy; NL = Ninemile at Lakeland; OC = Onondaga Creek; HB = Harbor Brook; LC = Ley Creek; ME = Metro Effluent). Error Bars = Standard Dev.; o = Minimum and Maximum % of Hg_T occurring as CH₃Hg⁺.

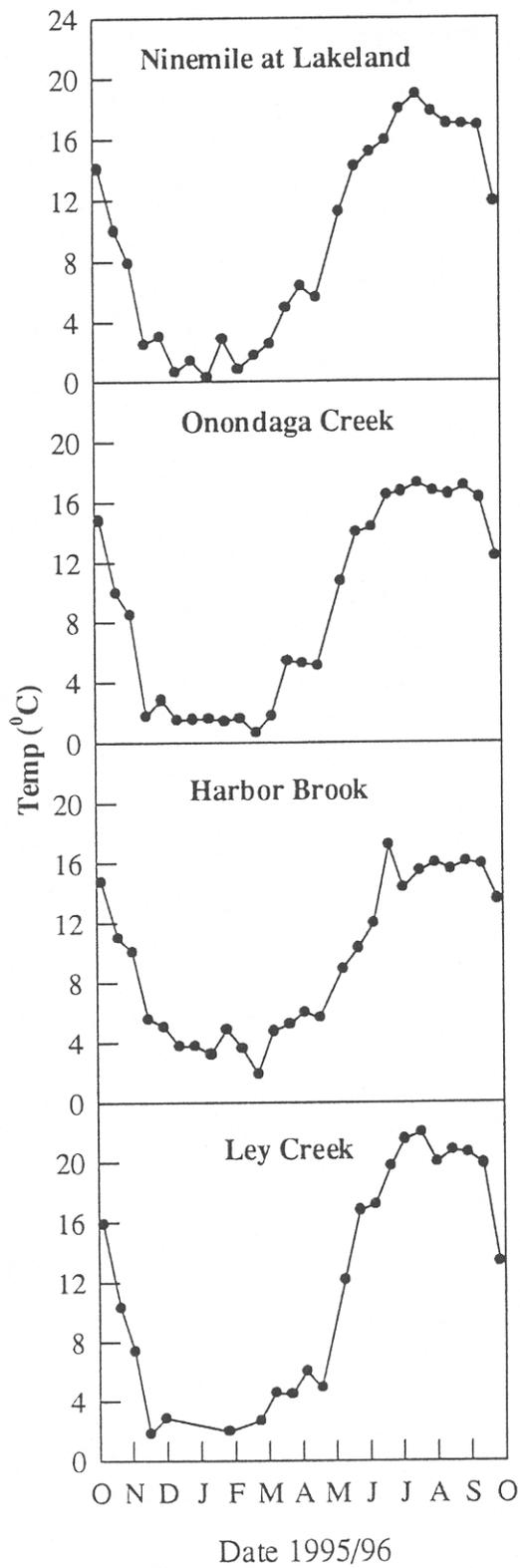


Figure 5.8. Time series of temperature (°C) for input waters of Onondaga Lake.

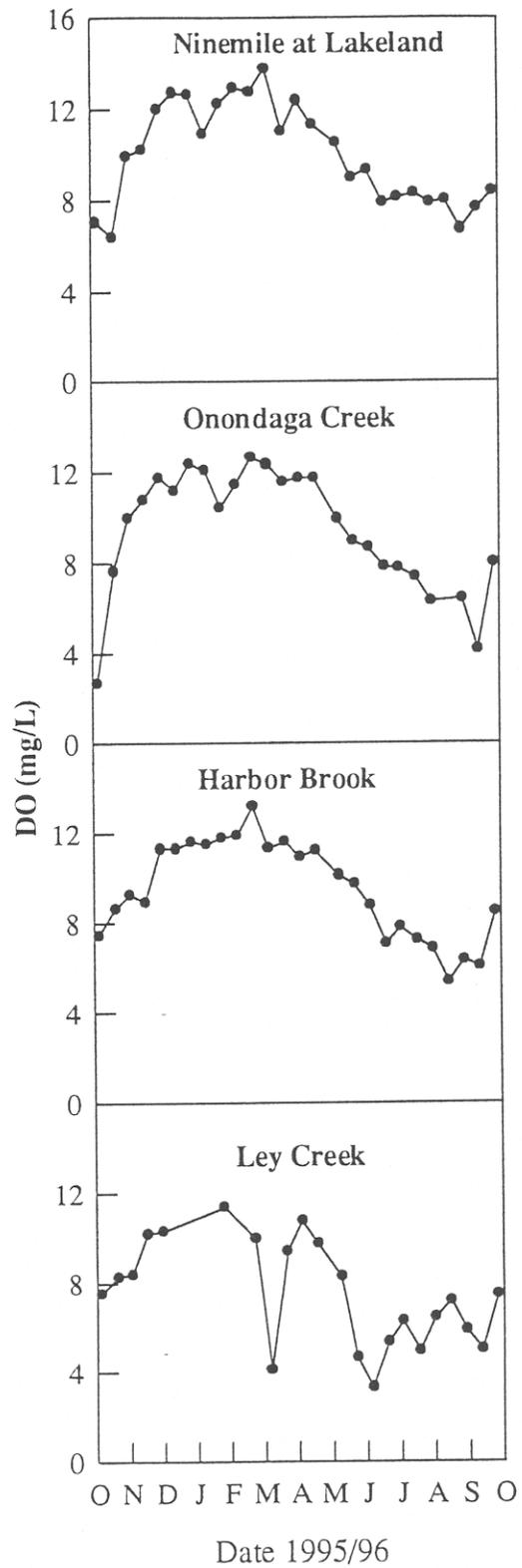


Figure 5.9. Time series of DO (mg/L) for input waters of Onondaga Lake.

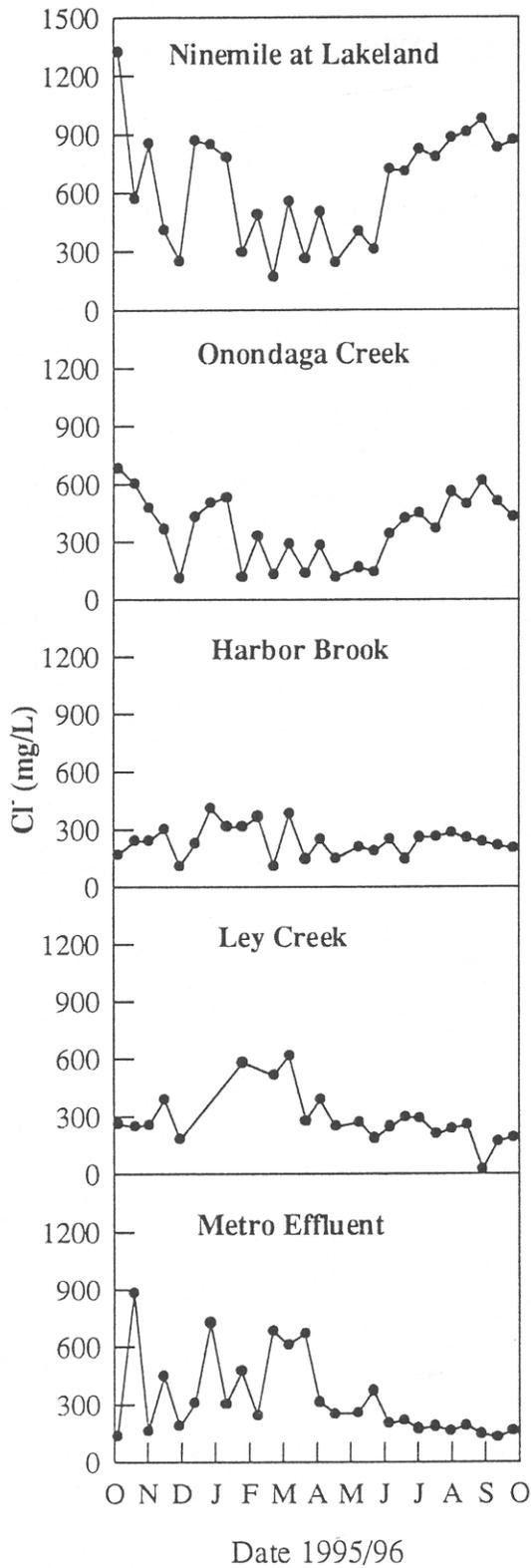


Figure 5.10. Time series of Cl⁻ (mg/L) for input waters of Onondaga Lake.

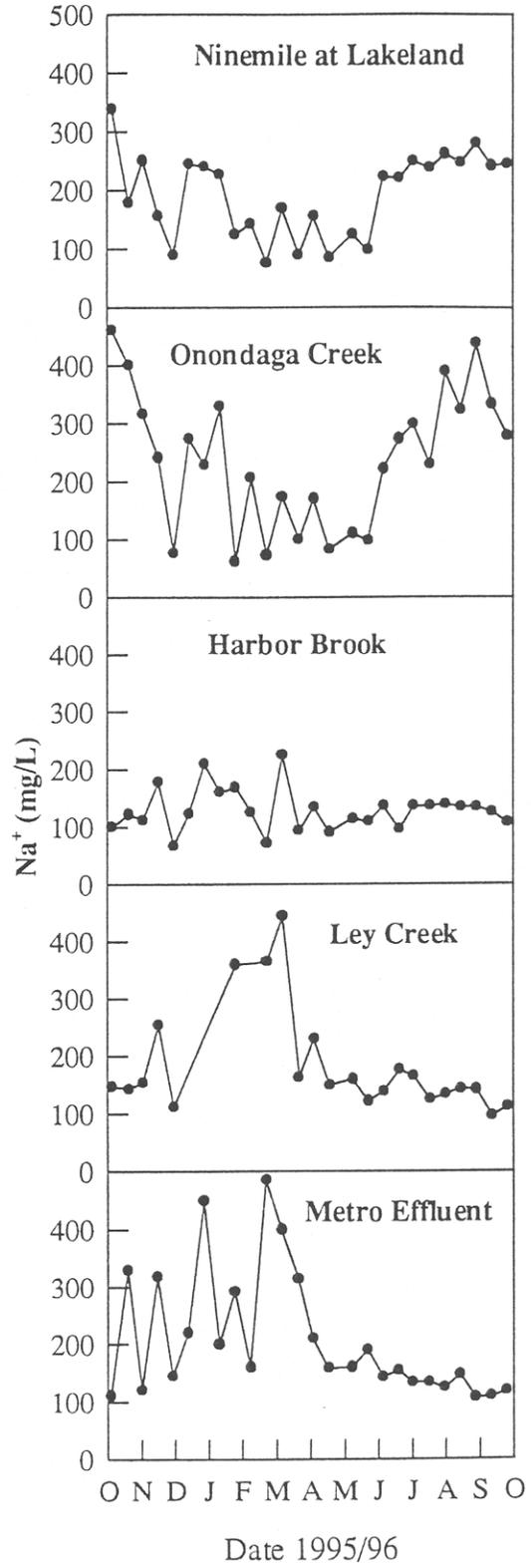


Figure 5.11. Time series of Na⁺ (mg/L) for input waters of Onondaga Lake.

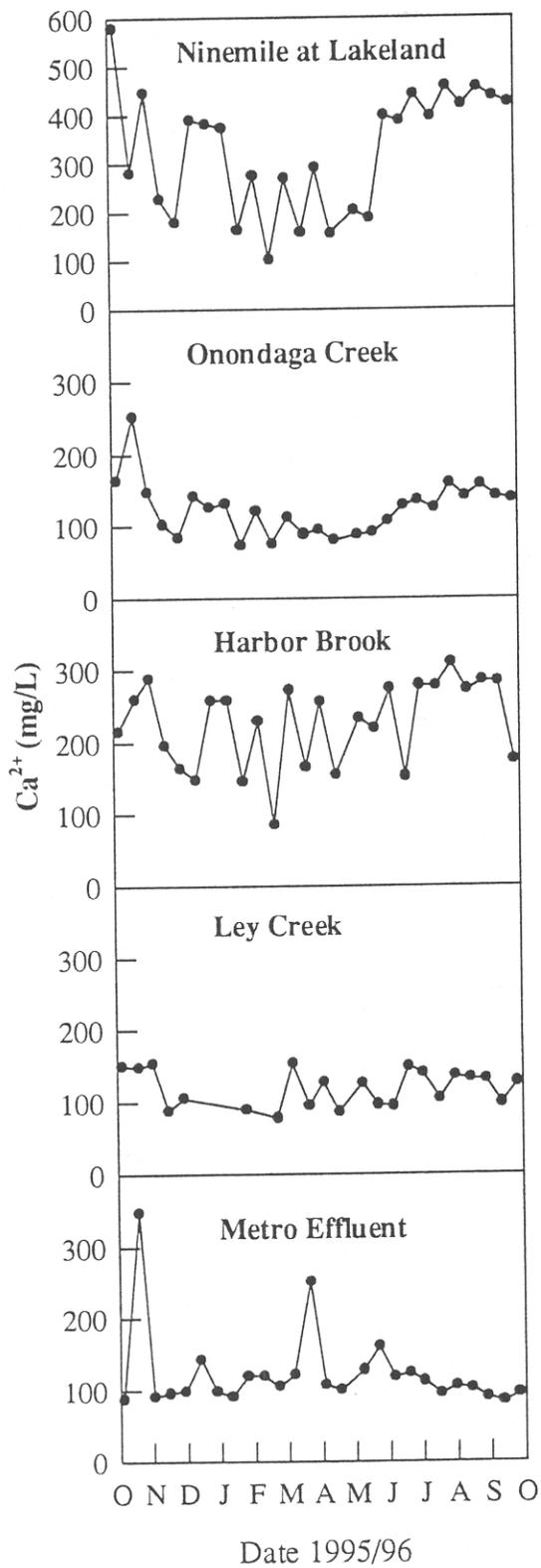


Figure 5.12. Time series of Ca^{2+} (mg/L) for input waters of Onondaga Lake.

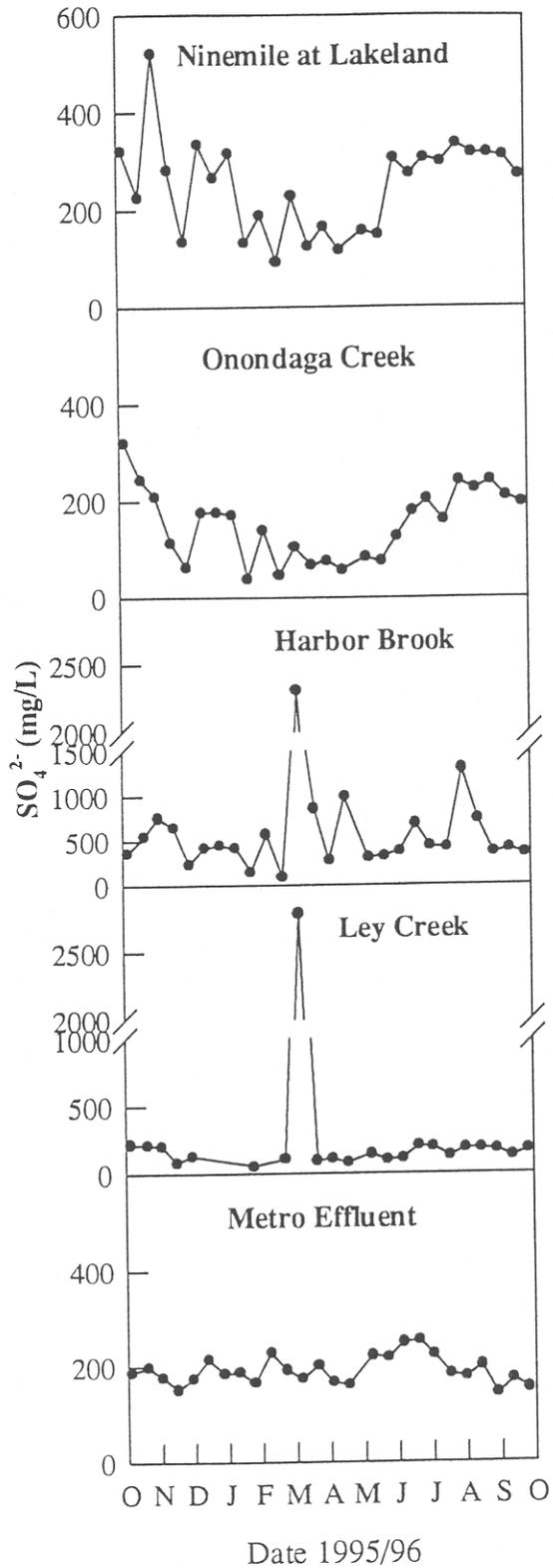


Figure 5.13. Time series of SO_4^{2-} (mg/L) for input waters of Onondaga Lake.

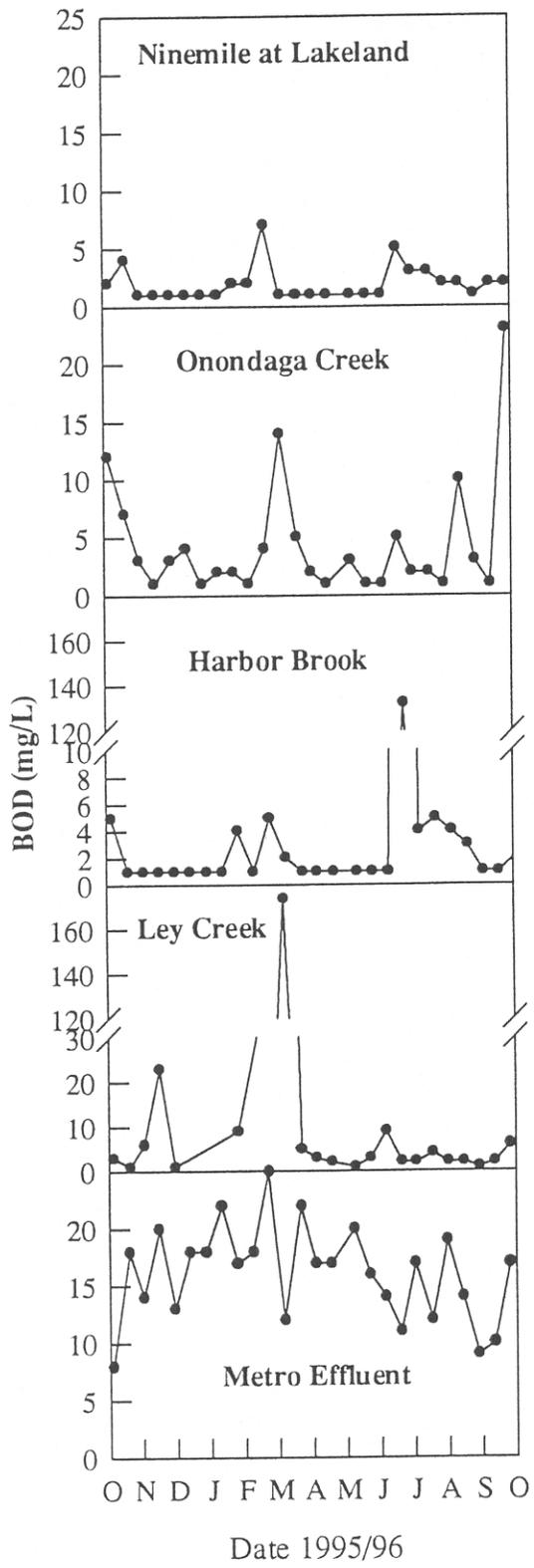


Figure 5.14. Time series of BOD (mg/L) for input waters of Onondaga Lake.

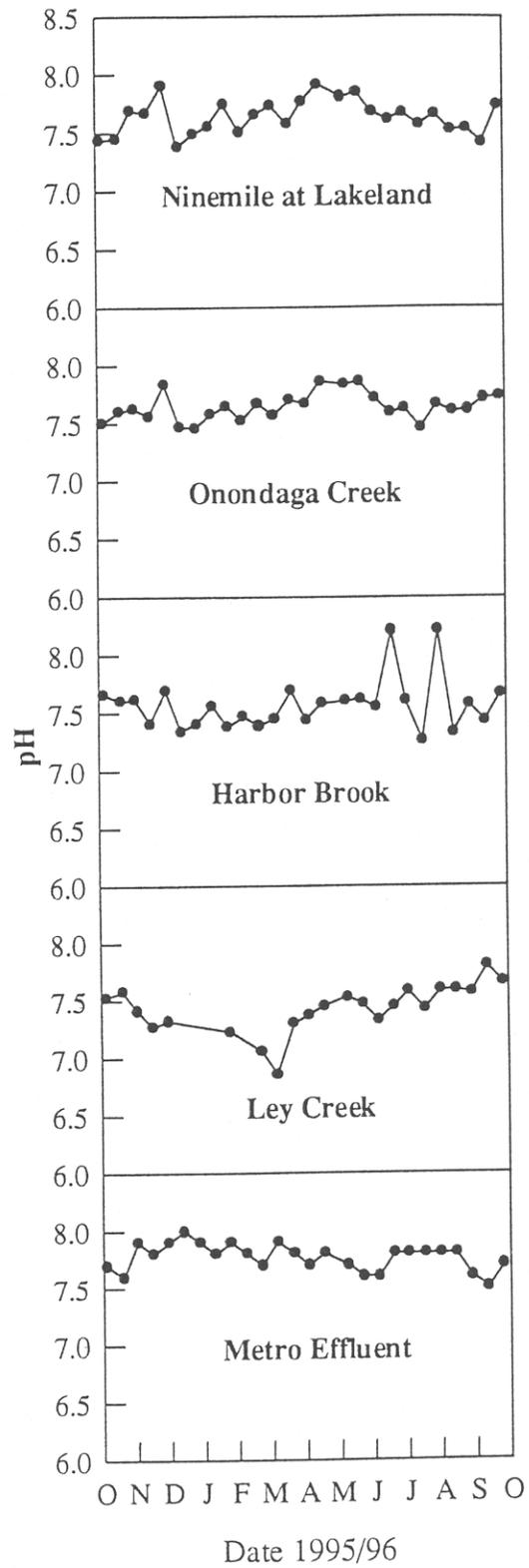


Figure 5.15. Time series of pH for input waters of Onondaga Lake. (Note: Origin at pH = 6)

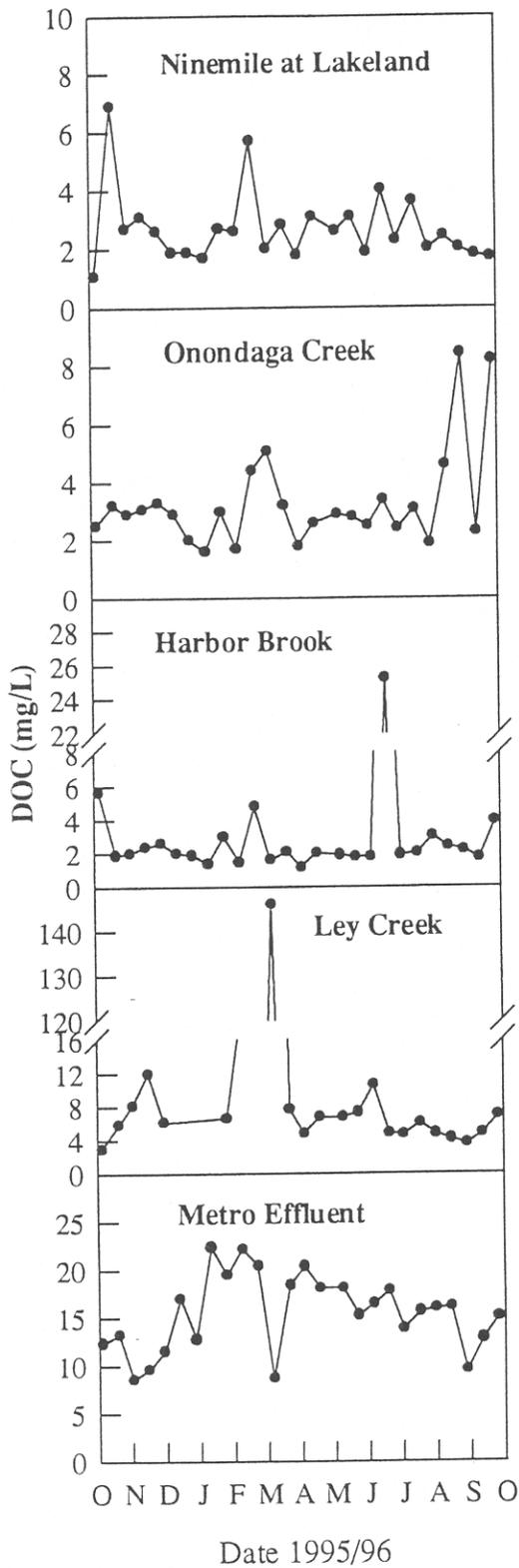


Figure 5.16. Time series of DOC (mg/L) for input waters of Onondaga Lake.

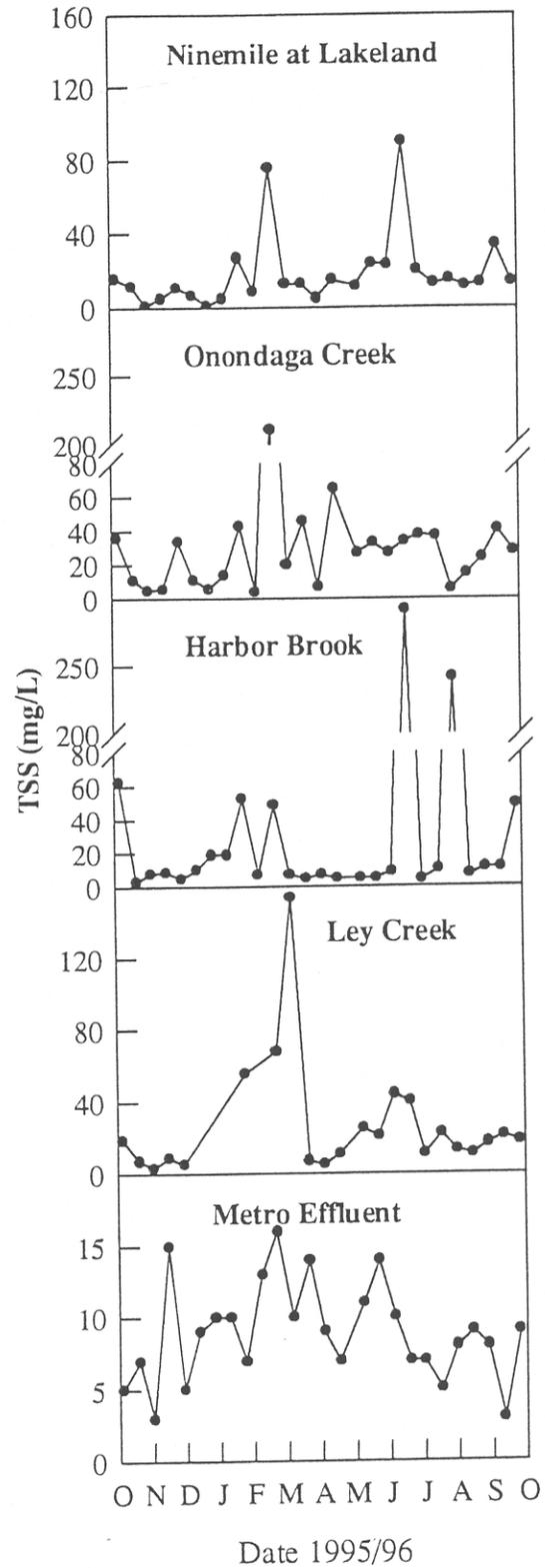


Figure 5.17. Time series of TSS (mg/L) for input waters of Onondaga Lake.

Concentrations of CH_3Hg^+ at OC increased slowly and showed little variation during the snowmelt observation period. Higher concentrations were observed in summer, when DO concentrations were low. In addition, increasing Cl^- and Na^+ concentration occurred in summer (Figures 5.10 and 5.11). The range of CH_3Hg^+ concentrations was 0.2-1.0 ng/L; the mean was 0.5 ng/L. The mean summer concentration (0.6 ng/L) was slightly higher than that in winter (0.4 ng/L), but this difference was not significant at the 5% level. The fraction of Hg_T occurring as CH_3Hg^+ showed no pattern (Figure 5.4) and ranged from about 3-7% with a mean of 5%.

Harbor Brook, showed a different seasonal pattern than the other natural tributaries, with maximum concentrations of both Hg_T and CH_3Hg^+ occurring during the snowmelt period. Patterns in Hg_T fluctuated with no systematic pattern during the initial sampling period, but increased in March to a peak concentration in April and slowly decreased later in the spring. The overall range of Hg_T concentrations was 4.2-10.4 ng/L, with no statistical difference between mean concentrations in winter (6.1 ng/L) and in summer (6.6 ng/L). The CH_3Hg^+ concentrations also initially fluctuated with no systematic pattern between 0.4-0.5 ng/L but roughly doubled in March and increased again by over 70% of the March value in April. The concentration then decreased markedly in early summer and increasing slowly again after July. The increase in the concentrations of CH_3Hg^+ occurred after very high concentrations of SO_4^{2-} were observed (Figure 5.13). The overall CH_3Hg^+ mean concentration was 0.6 ng/L. The mean winter concentration (0.7 ng/L) was slightly higher than that in summer but this difference was not statistically significant. The fraction of Hg_T occurring as CH_3Hg^+ was higher at HB than any of the other natural tributaries to

Onondaga Lake. The fraction of Hg_T occurring as CH_3Hg^+ which ranged from about 6-14% showed seasonal patterns with values higher in March and April and after July.

Concentrations of Hg_T at LC ranged from 3.6-9.5 ng/L; the mean was 5.8 ng/L. Patterns of Hg_T slightly decreased initially from October to December, but increased to higher values in summer. Maximum concentration of this species occurred in May, the concentration then decreased slowly until August, and increased in September. Winter and summer average concentrations were 4.7 ng/L and 7.0 ng/L respectively. This difference was not statistically significant.

Methyl Hg concentrations at LC were higher in both March and June. The concentration increased by over 80% in March to a value of 0.6 ng/L, decreased in April and increased to a maximum value of 0.7 ng/L in June and decreased again. The CH_3Hg^+ concentrations ranged from 0.2-0.7 ng/l; the mean was 0.4 ng/L. Like for the Hg_T concentrations, there was no significant difference between the average winter (0.4 ng/L) and summer (0.4 ng/L) concentrations at this site. The fraction of Hg_T occurring as CH_3Hg^+ ranged from about 6-10% with the peak value observed in March. Earlier in March, the creek received wastewater that was bypassed from the Ley Creek pump station resulting in high concentrations of BOD (Figure 5.14), DOC (Figure 5.16) and TSS (Figure 5.17) and a slight decrease in pH (Figure 5.15). In addition, high concentrations of SO_4^{2-} were observed (Figure 5.13), with a marked decrease in DO. This suggests that reduction of the SO_4^{2-} evidenced by the rapid decrease in the concentration with time, may be responsible for the increase in both the concentration of CH_3Hg^+ and the fraction of Hg_T occurring as CH_3Hg^+ later in the month.

Concentrations of Hg_T for ME were highly variable, ranging from 6.6-66.7 ng/L; the mean was 31.7 ng/L. The average winter Hg_T concentration (40.6 ng/L) was about twice the observed summer concentration (22.7 ng/L), but this difference was not statistically significant. The concentrations of CH_3Hg^+ observed for ME ranged from 0.6-3.7 ng/L, with the maximum concentration occurring in May. The mean CH_3Hg^+ concentration in the summer months (1.6 ng/L) was higher than that in the winter months (1.4 ng/L), but not significantly different. The fractions of Hg_T occurring as CH_3Hg^+ in the effluent ranged from 2-52%, with the peak value occurring in May.

Mean concentrations between the sites were also statistically compared (Appendix 2). Ninemile at Lakeland showed significantly higher mean concentrations of both Hg_T and CH_3Hg^+ compared to NA. For Hg_T an increase of about 250% occurred between Amboy and Lakeland, while for CH_3Hg^+ the increase was about 104%. This suggests that NL is a "gaining" stream with respect to concentrations of both Hg_T and CH_3Hg^+ in its lower reaches. For the natural tributaries, HB and NL showed the highest CH_3Hg^+ concentrations with elevated values in HB occurring in winter. METRO effluent concentrations of both species were significantly higher than the concentrations observed in the natural tributaries.

5.3 Correlation of Mercury with Other Site Measurements

Biweekly measurements of several chemical and physical parameters were determined by the Onondaga County department of Drainage and Sanitation. A statistical summary of these parameters are given in Appendix 3. Time series plots of the seasonal varia-

tions of the parameters are depicted from Figure 5.8 to 5.17. One of objectives of this research was to examine the relationship between the Hg species and other site measurements. However, the sampling dates for Hg and the observed parameters did not exactly correspond for most of the project period. This made regression analysis problematic, since concentrations of most parameters were highly variable and difficult to predict. During the snowmelt period, special investigations were conducted at NL, NA and OC, and samples were also analyzed for DO, DOC, and TSS. In September, all sites were monitored for these species. The snowmelt and September values, together with those in August and November (when sample dates were very close) were used in the correlation analysis. Therefore, the regression relationships obtained in this study may not reflect the full sampling period. A summary of the regression results are presented in Table 5.5. and the plots for the regression relationships between the Hg species and TSS, and the those between Hg_T and CH_3Hg^+ are depicted in Figures 5.18 and 5.19, respectively. Since HB and LC were not included in the weekly snowmelt analysis, and NA is not included in the County's biweekly measurements, these three streams were combined in the regression analysis of Hg with other species. They are referred to as "other" sites in the results. Due to the differences in ranges of Hg concentrations and that of the site measurements, at the various sites, it was found that the relationships were site specific.

The inlet streams showed strong positive correlations between Hg_T and TSS (Figure 5.18). The TSS concentrations were very high in OC, and TSS accounted for about 80% of the variation of Hg_T in this tributary. Variations in CH_3Hg^+ were not as strongly correlated with TSS at OC. ($r^2 = 0.39$). Ninemile Creek also showed good rela-

relationship between Hg_T and TSS ($r^2 = 0.67$). Like for OC, the r^2 obtained for CH_3Hg^+ and TSS at NL was lower ($r^2 = 0.46$) than the value for Hg_T . In the "other" sites TSS accounted for 54% of the variability in Hg_T and some of the extreme TSS values in LC may have affected the relationship.

Methyl Hg showed poor relation ($r^2 = 0.18$) with TSS in the other sites (Figure 5.18). Higher slopes were obtained in the regression relationships between the Hg species and TSS for NL than the other sites (Table 5.5, and 5.6), and this suggests that the effect of solids on Hg distribution and transport is more pronounced at NL. METRO effluent, showed no relationship between TSS and both Hg species. The r^2 values obtained for the correlation of Hg_T and CH_3Hg^+ with TSS for ME were 0.26 and 0.01 respectively, and these values were very low compared to relationships observed for the natural tributaries.

In general, the patterns observed for DO at the inlet streams and ME showed low concentrations in summer when the temperatures were higher. Concentrations of Hg_T and CH_3Hg^+ species were higher in summer when DO was low. Both species were thus negatively correlated with DO. At NL, a good relation was obtained between CH_3Hg^+ and DO (r^2 was 0.70). Dissolved oxygen accounted for only about 37% of the variability in Hg_T at NL. At OC, the relationships with DO showed were weaker for both Hg_T ($r^2 = 0.35$) and CH_3Hg^+ ($r^2 = 0.09$). In the other streams, DO accounted for 41% and 31% of the variability of CH_3Hg^+ and Hg_T respectively. The magnitude of the slope of the regression relationships for both Hg species and DO were higher at NL than at OC and at "other" sites.

Table 5.5. Results of simple linear regressions of Hg_T with other measurements.

Site	Constituent	n	r ²	Slope	P-value
NA	CH ₃ Hg ⁺	15	0.61	0.05	<0.001
NL	CH ₃ Hg ⁺	15	0.90	0.04	<0.001
OC	CH ₃ Hg ⁺	15	0.77	0.07	<0.001
HB	CH ₃ Hg ⁺	12	0.50	0.12	0.010
LC	CH ₃ Hg ⁺	12	0.67	0.05	0.001
ME	CH ₃ Hg ⁺	12	0.01	0.004	0.727
NL	TSS (mg/L)	7	0.67	0.42	0.024
OC	TSS (mg/L)	7	0.80	0.10	0.003
“Other”	TSS (mg/L)	12	0.54	0.15	0.006
ME	TSS (mg/L)	12	0.26	1.72	0.235
NL	DO (mg/L)	7	0.37	-0.58	0.149
OC	DO (mg/L)	7	0.35	-0.24	0.120
“Other”	DO (mg/L)	12	0.31	-0.33	0.060
NL	DOC (mg/L)	7	0.31	3.93	0.198
OC	DOC (mg/L)	7	0.21	0.51	0.248
“Other”	DOC (mg/L)	12	0.40	0.95	0.027
NA	Flow (m ³ /s)	15	0.10	-0.19	0.230
NL	Flow (m ³ /s)	15	0.26	-1.24	0.050
OC	Flow (m ³ /s)	15	0.04	-0.18	0.476
HB	Flow (m ³ /s)	12	0.11	3.52	0.285
LC	Flow (m ³ /s)	12	0.03	-0.61	0.606
ME	Flow (m ³ /s)	12	0.31	22.97	0.070

Table 5.6. Results of simple linear regressions of CH₃Hg⁺ with other measurements.

Site	Constituent	n	r ²	Slope	P-value
NL	TSS (mg/L)	7	0.46	0.01	0.093
OC	TSS (mg/L)	7	0.39	0.006	0.096
“Other”	TSS (mg/L)	12	0.05	0.01	0.499
ME	TSS (mg/L)	12	0.01	0.02	0.731
NL	DO (mg/L)	7	0.70	-0.03	0.019
OC	DO (mg/L)	7	0.09	-0.01	0.467
“Other”	DO (mg/L)	12	0.41	-0.04	0.024
NL	DOC (mg/L)	7	0.12	0.10	0.447
OC	DOC (mg/L)	7	0.13	0.03	0.381
“Other”	DOC (mg/L)	12	0.18	0.06	0.175
NA	Flow (m ³ /s)	15	0.08	-0.01	0.317
NL	Flow (m ³ /s)	15	0.21	-0.05	0.085
OC	Flow (m ³ /s)	15	0.09	-0.02	0.269
HB	Flow (m ³ /s)	12	0.05	0.39	0.507
LC	Flow (m ³ /s)	12	0.05	-0.05	0.470
ME	Flow (m ³ /s)	12	0.14	0.65	0.237

Note: “Other” = HB + LC + NA.

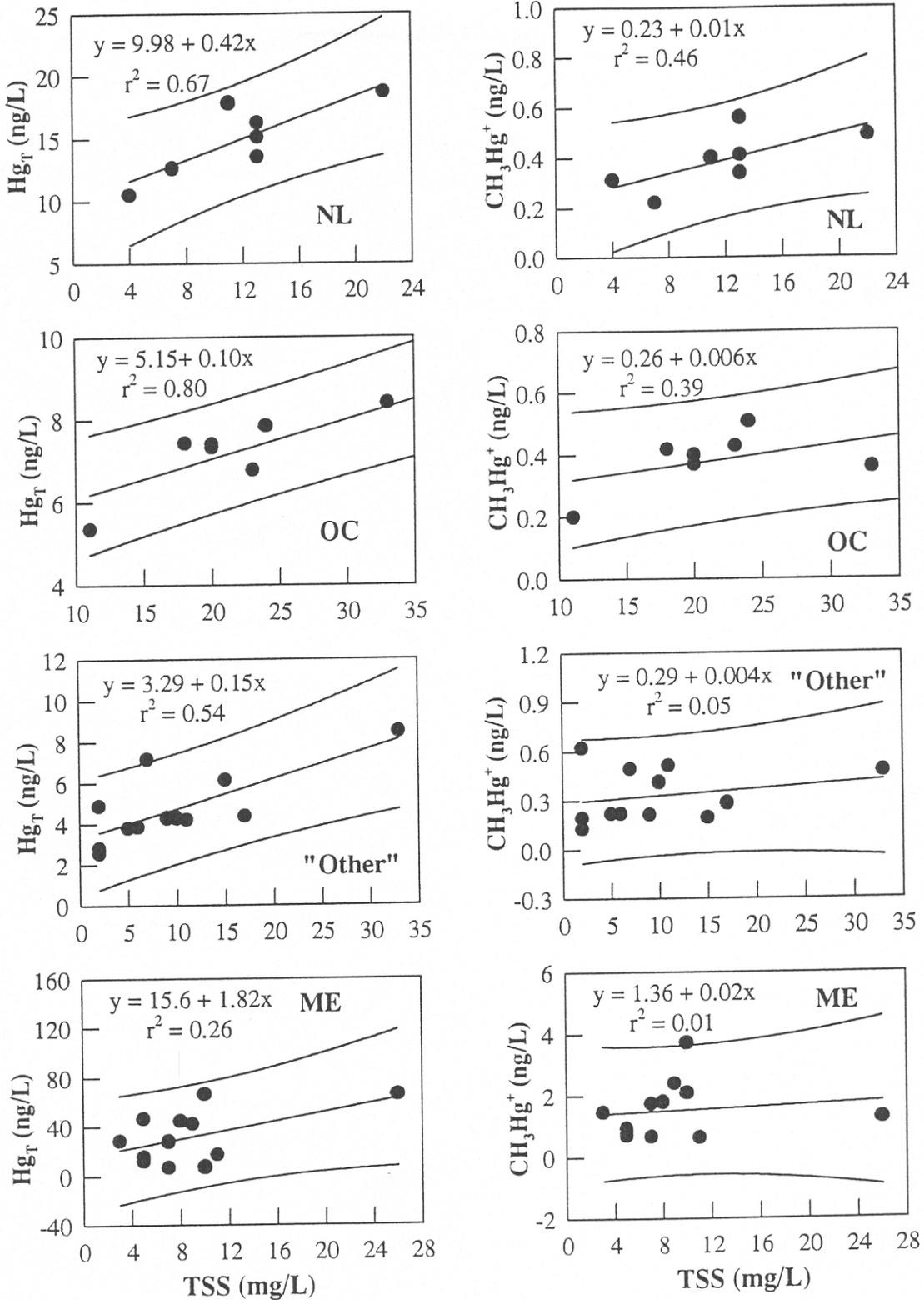


Figure 5.18. Relationships between Hg species and TSS for input waters of Onondaga Lake. (NL = Ninemile at Lakeland; OC = Onondaga Creek; "Other" = Combination of Harbor Brook, Ninemile at Amboy and Ley Creek; ME = Metro Effluent).

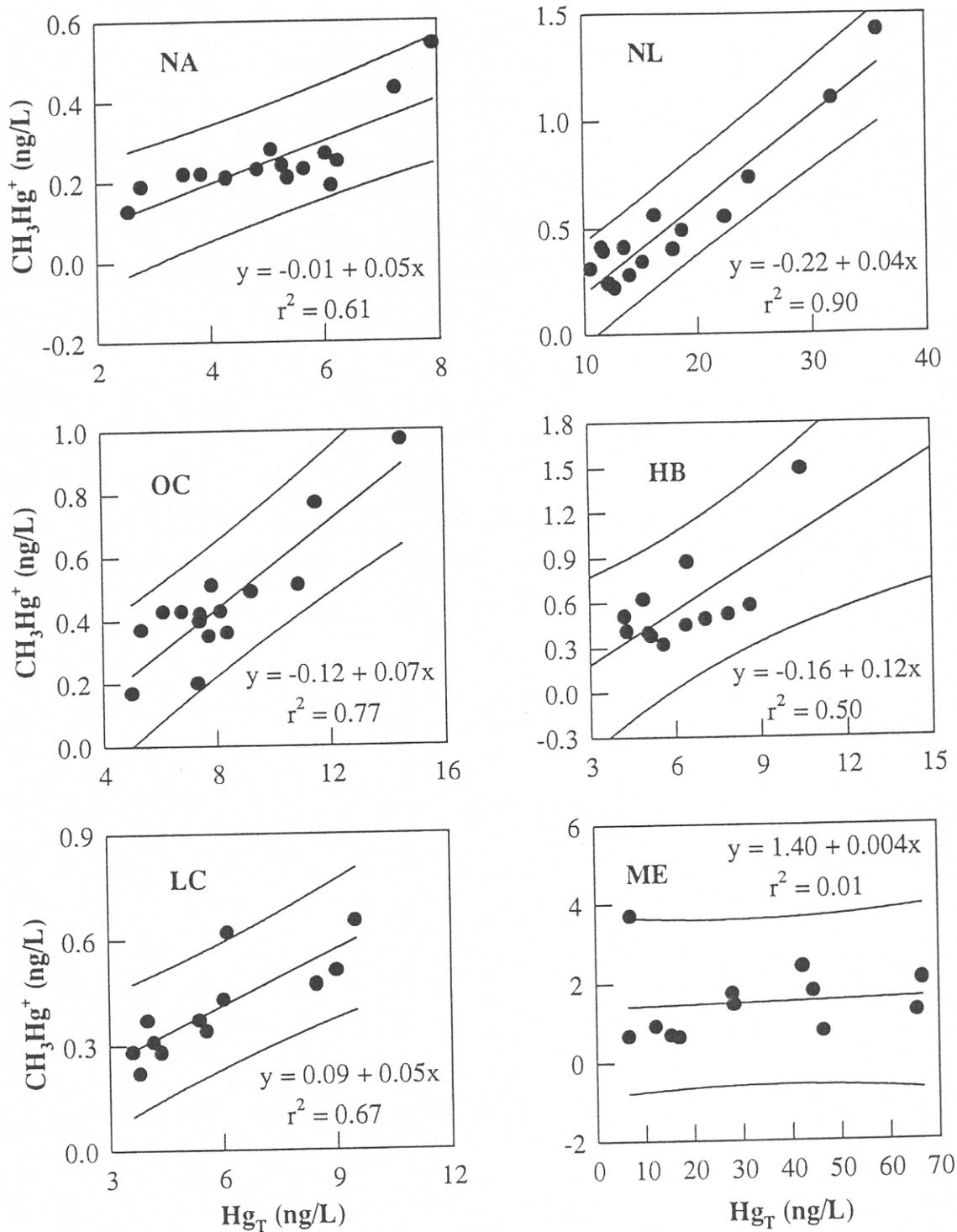


Figure 5.19. Relationships between CH_3Hg^+ and Hg_T for input waters of Onondaga Lake. (NA = Ninemile at Amboy; NL = Ninemile at Lakeland; OC = Onondaga Creek; HB = Harbor Brook; LC = Ley Creek; ME = Metro Effluent).

Positive correlations of Hg species with DOC were also observed. For NL, DOC accounted for about 31% and 12% of the variability in Hg_T and CH_3Hg^+ respectively. Corresponding r^2 values for relationships between Hg_T ($r^2 = 0.24$) and CH_3Hg^+ ($r^2 = 0.13$) and DOC were also very low at OC. At "other" sites, a higher r^2 value of 0.40 was obtained with Hg_T and DOC, but the relationship was much weaker for CH_3Hg^+ and DOC ($r^2 = 0.18$). Thus suspended solids, appears to account for most of the variability in Hg, compared to DOC.

Correlations with flow showed extremely weak relationships. At NL, OC, and LC, weak negative correlations were obtained for the correlations between flow and the Hg species, while HB and ME showed weak positive correlations. The r^2 values of the regressions ranged from 0.03-0.31 (Table 5.5 and 5.6).

Simple linear regressions between Hg_T and CH_3Hg^+ at the various sites showed strong positive correlations for the natural tributaries, and a very weak correlation for ME (Figure 5.19). At NL, OC, LC, NA and HB, Hg_T accounted for about 90%, 77%, 67%, 61% and 50%, respectively, of the variations in CH_3Hg^+ . These relatively strong relationships suggest that variability in CH_3Hg^+ can be predicted from patterns of Hg_T observed in the natural tributaries. The slopes for the regression relationships between Hg_T and CH_3Hg^+ for the streams were different at the various sites, with values of 0.05, 0.04, 0.07, 0.12, and 0.05 at NA, NL, OC, HB and LC, respectively (Table 5.5; Figure 5.19). When all the concentrations of Hg_T and CH_3Hg^+ were combined for the inlet streams the resulting correlation was: $CH_3Hg^+ = 0.21 + 0.03Hg_T$ and $r^2 = 0.38$. The low r^2 value obtained in this relationship indicates that variation in both species were site specific.

5.4 Fluxes and Specific Yields of Total and Methyl Mercury, and Total Suspended Solids

The results of the loading calculations using method 2 of the FLUX program are given in Appendix 4 and are summarized in Tables 5.7 and 5.8. The difference between mean loadings were statistically tested at 5% significant level and the results are given in Appendix 2. Figures showing the range and standard deviations of loadings, and % contribution of the loadings of both Hg_T and CH_3Hg^+ from the various input waters monitored in this study, including estimated values for ungauged minor tributaries, are given in Figures 5.20 and 5.21 respectively. The CV values for the Hg_T loading calculations were lower than that for CH_3Hg^+ , indicating higher uncertainties in the loading calculations for CH_3Hg^+ .

The average total estimated loads of Hg_T and CH_3Hg^+ to Onondaga Lake were 10,102 g/yr and 437 g/yr, respectively, with ME contributed the highest loads of both Hg_T (41%) and CH_3Hg^+ (44%) to the lake. This was due to the significantly high concentrations of both species in the ME. Ninemile Creek at Lakeland contributed the next highest loadings of both Hg_T (38%) and CH_3Hg^+ (25%). Although the total discharge during the sampling period for NL was almost about 1.6 times the discharge for ME, the flow weighted concentrations of Hg_T and CH_3Hg^+ for ME were about 2.0 and 2.9 times corresponding values at NL (Table 5.7 and 5.8). The difference between the mean loadings of Hg_T for ME and NL is not significant, while that of CH_3Hg^+ is significant. Thus both sources may be considered the major sources of Hg_T to the lake.

The mean contributions of Hg_T and CH_3Hg^+ loads to the lake from OC were 38% and 78% of the corresponding loadings from NL. Ninemile Creek showed a significant increment in loadings between Amboy and Lakeland. This incremental input could be the result of contaminated groundwater inputs to the stream. The estimated mean inputs of

Table 5.7. Fluxes and specific yields of Hg_T for input waters of Onondaga Lake.

Tributary	Drainage Area (ha)	Conc. ^α (ng/L)	Flux (g/year)	CV %	% Contribution	Specific yield (mg/ha-year)
HB	2,930	6.9	66.6±22.7	0.099	0.7±0.2	22.7
LC	7,740	6.5	282.4±106.4	0.110	2.8±0.9	36.5
OC	28,500	8.9	1,422.6±526.2	0.096	14.5±3.5	47.7
NL	29,800	22.3	3,749.8±1,978.6	0.138	38.0±8.4	125.8
ME	-	44.5	4,319.3±2,253.4	0.154	41.4±10.8	-
NA	23,840	5.6	658.2±177.7	0.070	19.2±1.3 ^β	27.6
Others ^φ	-	6.5	281.3±98.5	0.110	2.6±0.8	-

Table 5.8. Fluxes and specific yields of CH_3Hg^+ for input waters of Onondaga Lake.

Tributary	Drainage Area (ha)	Conc. ^α (ng/L)	Flux (g/year)	CV %	% Contribution	Specific yield (mg/ha-year)
HB	2,930	0.8	7.5±6.7	0.269	2.0±0.2	2.5
LC	7,740	0.5	19.3±6.7	0.102	4.7±1.6	2.5
OC	28,500	0.5	85.8±49.1	0.150	20.4±6.6	2.9
NL	29,800	0.7	110.2±96.6	0.234	24.9±9.8	3.9
ME	-	2.0	197.0±145.0	0.220	43.7±13.9	-
NA	23,840	0.3	35.2±20.5	0.153	35.1±1.6 ^β	1.5
Others ^φ	-	0.5	17.8±6.3	0.102	4.3±1.5	-

Table 5.9. Fluxes and specific yields of TSS for input waters of Onondaga lake

Tributary	Area of Drainage Basin (ha)	Mean Flux (Kg/year)	% Contribution to Lake	Specific yield (kg/ha-year)
HB	2930	1650200	7.1	563.2
LC	7740	2745100	11.7	354.7
OC	29800	11879900	50.8	398.7
NL	29800	5672300	22.3	190.3
ME	-	1434700	6.13	-
NA [#]	23840	-	-	-

[#] Not monitored biweekly. ^α Flow weighted concentrations; ^β NA expressed as % of NL loading; ^φ Others = Sum of Bloody Brook, Sawmill Creek, Tributary 5A and East Flume.

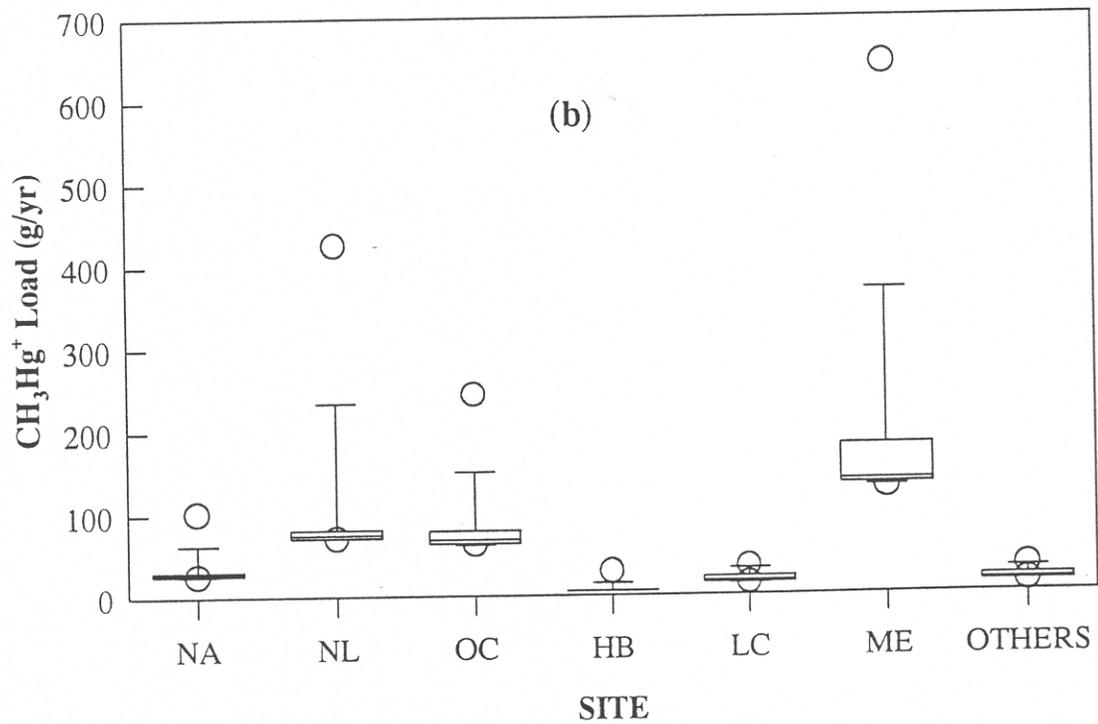
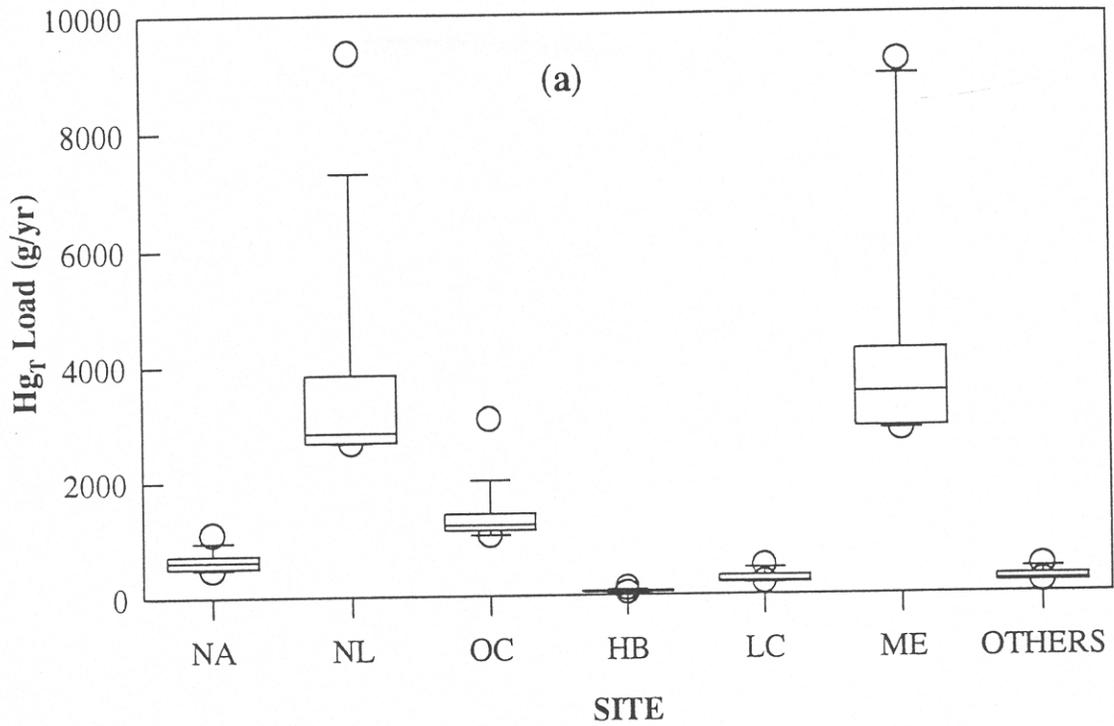


Figure 5.20(a). Loadings of Hg_T (g/yr); (b) Loading of CH_3Hg^+ (g/yr) for input waters of Onondaga Lake. (NA = Ninemile at Amboy; NL=Ninemile at Lakeland; OC = Onondaga Creek; HB = Harbor Brook; LC = Ley Creek; ME = Metro Effluent). Error Bars = Standard Dev.; o = Minimum and Maximum Loads.

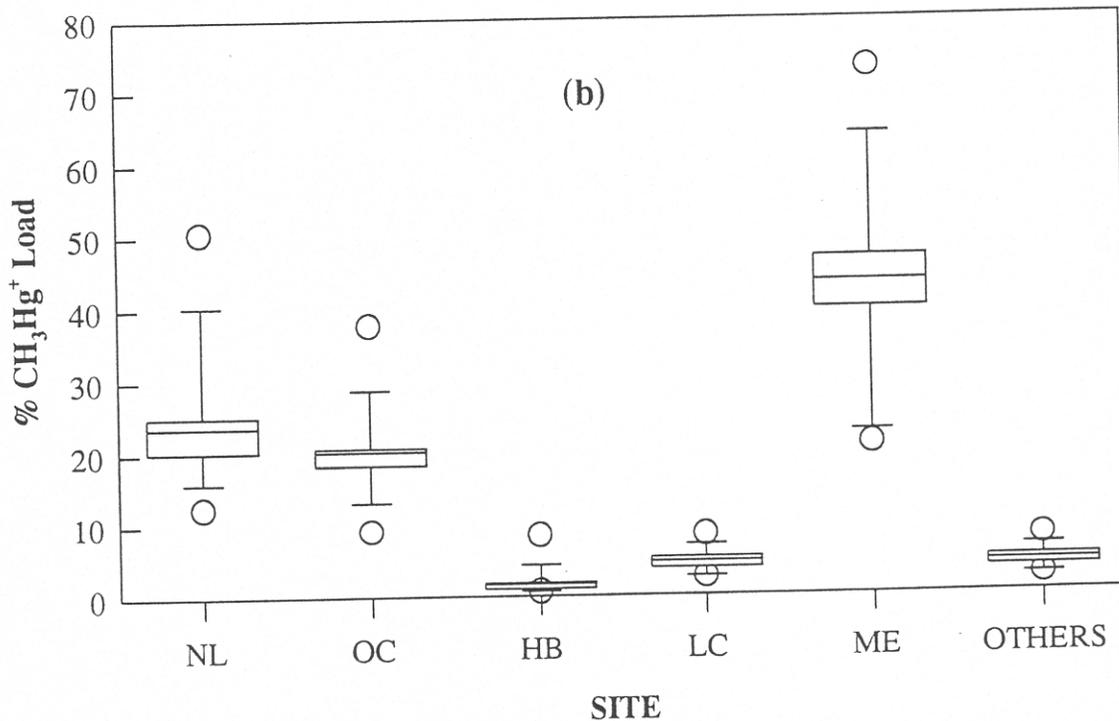
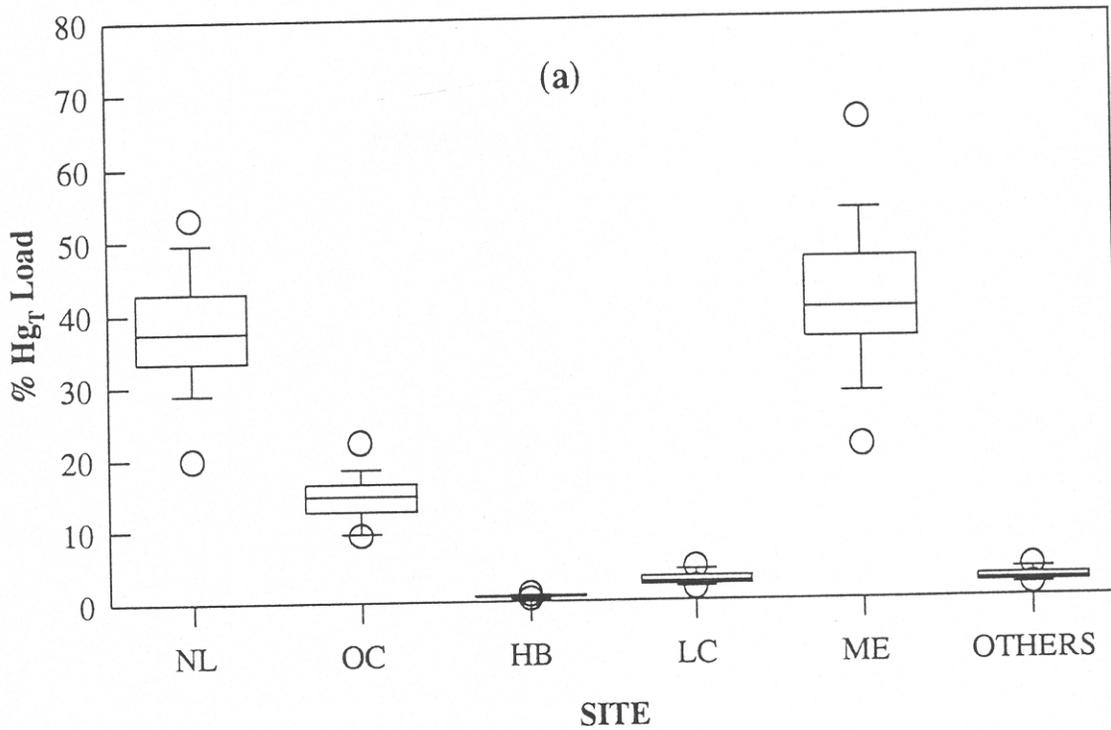


Fig5.21(a) % Contribution of Hg_T Loads; (b) % Contribution of CH_3Hg^+ Loads for input waters of Onondaga Lake. (NA = Ninemile at Amboy; NL = Ninemile at Lakeland; OC= Onondaga Creek; HB = Harbor Brook; LC = Ley Creek; ME = Metro Effluent). Error Bars = Standard Dev.; o = Minimum and Maximum % Contribution.

Hg_T to the reach between Amboy and Lakeland was 3,092 g/year or about 82% of the mean total annual load estimated at Lakeland. The corresponding mean annual inputs of CH₃Hg⁺ was 76.5 g/year or about 68% of the mean total loading at Lakeland.

The combined loading from the Bloody Brook, Sawmill Creek, Tributary 5A and East Flume, was estimated by assuming Hg concentrations similar to LC. Since the combined mean discharge from these minor tributaries was approximately equal to the mean discharge for LC, the estimated load of Hg species for these minor tributaries were similar to loads obtained for LC (Table 5.7 and 5.8). Ley Creek, HB and the combined minor tributaries accounted for less than 7% of the Hg_T load and 12% of the CH₃Hg⁺ load to the lake.

The results of the statistical analysis showed that Hg_T loads from ME and NL were significantly higher than loads from the other input waters to Onondaga Lake. These two sources produce about 80% of the Hg_T load to the Lake. The CH₃Hg⁺ load from ME was significantly higher than the loads from any of the natural tributaries. Both ME and NL accounted for approximately 70% of the total CH₃Hg⁺ load to the lake.

The specific yield of the streams was calculated by dividing the estimated flux by the drainage area. For Hg_T, the specific yield ranged from 23.1-125.8 mg/ha-year, with NL having the highest. Ninemile Creek at Lakeland also had the highest yield for CH₃Hg⁺ of any of the natural tributaries. The specific yield for CH₃Hg⁺ ranged from 1.5-3.7 mg/ha-year at the study sites.

The loadings and specific yield for TSS to Onondaga Lake for the study period were also calculated (Table 5.9). The results showed that OC contributed the highest

loading of TSS (51%) to the lake. Ninemile Creek at Lakeland was the next highest and contributed 22% of TSS to the lake. These two streams therefore accounted for about 73% of the TSS loadings to the lake. Metro effluent contributed the least TSS load (6%) to the lake. The specific yield for TSS ranged from 190.3-563.2 Kg/ha-year, with HB and NL having the highest and lowest yields, respectively.

CHAPTER 6 - DISCUSSION

6.1 Patterns of Total and Methyl Mercury and Relationship with Other Site Measurements

This study showed seasonal variations in the concentrations of Hg species in the natural tributaries of Onondaga Lake. Concentrations of both Hg_T and CH_3Hg^+ were slightly higher in summer than in winter and this pattern agrees with studies done by Parks et al. (1989) and Leermakers et al. (1995). The increase in the concentrations of the Hg species corresponded to low DO and higher temperatures. The range of Hg concentrations observed in this study was well below the New York State ambient water quality standard (Class C) for Hg (200 ng/L).

At HB and LC, the fraction of Hg_T occurring as CH_3Hg^+ increased during the snow-melt period. During this period, elevated concentrations of SO_4^{2-} were evident and the effect of SO_4^{2-} on methylation has been reported by Compeau and Bartha (1985), Gilmour and Henry (1991), and Gilmour et al. (1992). They observed that when SO_4^{2-} concentrations were elevated in aquatic systems, depletion of the SO_4^{2-} due to reducing conditions, resulted to the significant increase in Hg methylation.

At HB, it was observed that DO decreased after February and there was a marked increase in SO_4^{2-} concentration on March 6th (2310 mg SO_4^{2-} /L) (see Figure 5.13). Methyl Hg concentrations increased in samples collected on March 28th and April 29th. Thus lower DO concentrations and continued reduction of SO_4^{2-} may have facilitated the increase in CH_3Hg^+ concentrations. In addition, a high Hg(II) concentration was available

in this period for methylation due to fact that the concentration of Hg_T was high. A similar increase in CH_3Hg^+ concentration was observed after July, when another increase in SO_4^{2-} concentration was evident. The source of the SO_4^{2-} inputs or the mechanisms for DO depletion are however not clear.

Ley Creek, also showed unusually high concentrations of BOD, DOC, SO_4^{2-} and TSS on March 6th (see Figures 5.13-5.17). These unusual concentrations were due to direct discharge of wastewater from combined sewer overflow, late in February and early in March, to the tributary. At the same time, a significant decrease in DO was observed and the pH value decreased below 7. The high BOD value may be responsible for the very low DO, resulting in a condition suitable for reduction reactions. This may have enhanced SO_4^{2-} reduction and an increase in the concentration of CH_3Hg^+ and fraction of Hg_T occurring as CH_3Hg^+ in the late winter period. In addition, it is possible that the high Hg concentrations during that period may have also resulted from high Hg concentrations evident in the raw sewage discharged. In the summer, when the Hg_T increased at LC, low DO values occurred and CH_3Hg^+ showed a peak concentration in June. These observations strongly indicated that SO_4^{2-} and DO played significant roles in the patterns of CH_3Hg^+ observed for HB and LC.

The occurrence of high CH_3Hg^+ concentrations during the winter period in both HB and LC is unexpected, because temperatures were low. Temperature has been shown to be a major factor controlling Hg methylating activities. In freshwater sediments, methylation is inhibited by low temperature (Wright and Hamilton, 1982) and has a temperature optimum of about $35^{\circ}C$ (Callister and Winfrey, 1986; Steffan et al., 1988). In addition to

the effect of temperature, Gilmour and Henry (1991) reported an optimal SO_4^{2-} concentration range of 200-500 μM for Hg methylation by SO_4^{2-} reducing bacteria in sediments. Although this range may vary from site-to-site, concentrations of SO_4^{2-} above this range, would lead to inhibition of methylation due to the presence of S^{2-} . Sulfides causes Hg(II) to be precipitated thus rendering it unavailable, and it also cause CH_3Hg^+ to be transformed to $(\text{CH}_3)_2\text{Hg}$ (Craig and Moreton, 1984). The peak concentrations of SO_4^{2-} observed at both HB and LC during the snowmelt period were two orders of magnitude greater (24 mM at HB and 29 mM at LC) than this optimum range. Overall, the speculation that increased concentrations of CH_3Hg^+ may be due to the high SO_4^{2-} concentrations and the subsequent reduction of SO_4^{2-} may not be justified.

The watershed characteristics of HB and LC may also be responsible for the observed patterns of Hg. Hurley et al. (1995) has reported the importance of land use and land cover in influencing Hg concentrations, speciation and transport in rivers. The headwaters of HB drain a mixture of residential, agricultural and pasture lands. Rogers (1976) reported the production of CH_3Hg^+ in agricultural soils, and its dependence on soil texture, moisture content, temperature, and the concentration of Hg(II). Rogers (1976) also observed that an increase in moisture content increases the net loss of CH_3Hg^+ with time in the soil studied. Much of the Hg in the terrestrial environment is associated with soils, particularly in the humus-rich upper strata (Allard and Arsenie, 1991; Lindqvist et al., 1991). Once in the soil, movement of Hg is associated with movement of dissolved humic material, some of which can be transported with runoff to surface waters. Thus during the snowmelt period, high flows results and runoff from the watershed may transport the

CH_3Hg^+ that would have been formed under optimal conditions in the agricultural soil surrounding HB. This tributary showed the highest mean CH_3Hg^+ concentrations.

The headwaters of LC are located primarily in wetlands which have been reported to be important sources of CH_3Hg^+ (Driscoll et al., 1994; St. Louis et al., 1994; Hurley et al., 1995). These studies reported increasing CH_3Hg^+ concentrations in spring when flows were highest. Total Hg yields were low from the wetland catchments studied by St. Louis et al. (1994). Thus runoff in the snowmelt period to LC may also be responsible for the elevated fraction of CH_3Hg^+ observed during this period.

At NL and OC, Hg_T concentrations of Hg species were generally low during the spring snowmelt period. Concentrations of major ions including Na^+ , Ca^{2+} and Cl^- were also low in winter but increased in summer in the two streams (see Figures 5.10-5.12). Significant differences were evident between NL and NA with regard to the concentrations of Hg species and these ions. These patterns suggest that leachate and groundwater discharges from the reach between Lakeland and Amboy are probably pathways by which Hg continues to enter NL. In winter when flows are high, the input of Hg and the other ions are diluted, thus reducing their concentrations. This effect of dilution was also evident at OC, suggesting a localized input such as groundwater discharges may also be responsible for the transport of Hg to OC.

Correlation analysis between CH_3Hg^+ and Hg_T showed strong relationships for the natural tributaries. This pattern agrees with studies done in the Wabigoon/English River (Parks et al., 1989), the Adirondack Lakes (Driscoll et al 1994) and the Wisconsin lakes (Watras et al., 1995a). Also radiochemical studies done by Rudd et al. (1983) found a

linear relationship between Hg(II) concentrations and CH₃Hg⁺ production over the range of Hg_T concentrations observed in this study. The slopes of the regression equations expressing CH₃Hg⁺ as a function of Hg_T in this study, ranged from 0.05 to 0.12 and the r² ranged from 0.5 to 0.9. These results compare to corresponding values of slopes and r² obtained by Parks et al. (1989) (slope = 0.01-0.06; r² = 0.42-0.72), Driscoll et al, (1994) (slope = 0.1 and r² = 0.84) and Watras et al, (1995a) (slope = 0.49; r² = 0.95). This suggests that concentration of CH₃Hg⁺ could be predicted from concentrations of Hg_T, but the different slopes obtained for the different sites reveal that a predictive relationship determined in one site may not be useful in another. However, Kelly et al. (1995) reported that Hg_T inputs and /or concentrations are not very useful in predicting CH₃Hg⁺ concentrations especially in streams (r² = 0.01), and that other factors within ecosystems are very important in controlling CH₃Hg⁺ concentrations.

Total suspended solids was found to be a major factor controlling the concentrations of Hg_T in the natural tributaries. The association of Hg_T with solids suggest that solids may be responsible for the transport and fate of Hg_T. This observation has been reported by several investigators (Reimers and Krenkel, 1974; Beneš and Havlík, 1979; Duarte et al., 1991; Hurley et al., 1991). However the relationships estimated in this study have limitations since only a few data points were used due to the different sampling dates for Hg and TSS for most of the study period. During the dates of snowmelt monitoring of NL, NA and OC, the Hg_T and TSS concentrations exhibited little variation. Thus good correlations were obtained since 4 of the 7 points used in the analysis were from this snowmelt period. The slopes obtained for the relationship between Hg_T (ng/L) and TSS

(mg/L) varied for the different sites. Ninemile Creek at Lakeland exhibited the highest slope (0.42) and this was about three times the others (slope for OC = 0.1, slope for the others = 0.15). The high slope at NL can be attributed to the inputs of Hg from groundwater, while the low value at OC may be due to inputs of particles. Thus the degree of association varied and increment in solids concentration had the greatest impact on Hg_T concentration at NL. The relationship for OC gave the highest r² value (r² = 0.8).

Babiarz and Andren (1995), reported that concentrations of Hg_T observed in some Wisconsin rivers were weakly dependent on total suspended particles with slopes and r² values of 0.15 and 0.16 in spring; 0.14 and 0.49 in autumn. Although the slopes reported by Babiarz and Andren (1995) compare to those obtained for OC and the other sites in this study, the correlations in this study were much stronger. The regression relationships of CH₃Hg⁺ with TSS for the different sites were weaker compared to those obtained for Hg_T and this suggests that association with particulate matter is stronger for Hg_T than for CH₃Hg⁺. The highest slope (0.01) and r² (0.46) values for the regression between CH₃Hg⁺ and TSS, were obtained for NL.

Dissolved oxygen was negatively correlated with the Hg species and most of the relationships showed stronger relations with CH₃Hg⁺ than Hg_T. Several studies have reported the role of DOC in controlling Hg_T concentrations. Watras et al., (1995a,b) obtained very strong correlation between Hg_T (slope = 0.2-0.93; r² = 0.83-0.90) and CH₃Hg⁺ (slope = 0.05-0.89, r² = 0.64-0.79) species and DOC (mg/L) in temperate freshwaters in northern Wisconsin. Driscoll et al. (1994) also reported very strong relationships for both Hg_T (slope = 0.19, r² = 0.67) and CH₃Hg⁺ (slope = 0.02, r² = 0.90) for Adirondack Lakes

and DOC. The r^2 values obtained in this study are much lower ($r^2 = 0.12 - 0.40$), suggesting that suspended solids play a more important role than DOC in the fate of Hg in the tributaries of Onondaga Lake.

The relationships between Hg species and flow were poorly defined. However, negative slopes were obtained for most of the tributaries, with the exception of HB, which had peak Hg concentration in the snowmelt period and ME. Thus under low flows, when DO concentrations in the tributaries decreased, higher Hg concentrations were evident.

Concentrations of Hg_T and CH_3Hg^+ for ME were highly variable and significantly higher than values in the tributaries. Investigations done on the transformations of Hg in METRO in conjunction with this study (McAlear, 1996) showed that the Hg_T and CH_3Hg^+ concentrations in the effluent were highly variable and removal of Hg_T was closely related to solids removal efficiency. Concentrations of CH_3Hg^+ within the treatment facility did not correlate with solids.

6.2 Comparison of Mercury Concentrations to that Obtained from Other Studies done on the Onondaga Lake - Tributary System

In 1992, studies were done by on the tributaries of the lake by Driscoll and Wang (1996), and Henry et al. (1995). Bloom (1990) also measured the concentration of Hg species on November 10, 1989. The results of the mean concentrations observed in these studies and the fraction of Hg_T occurring as CH_3Hg^+ are given in Tables 6.1, 6.2 and 6.3., respectively. Mean values were also statistically compared (Appendix 2).

The results of this study, as well as the others, reveal that NL is a gaining stream since Hg concentrations downstream at Lakeland were far greater than those upstream at Amboy. The concentrations of Hg_T obtained in this study lie within the range of those of the other previous studies. However, with the exception of OC, the mean CH₃Hg⁺ concentrations in this study were significantly higher than the CH₃Hg⁺ concentrations reported by Bloom (1989). The mean concentrations of CH₃Hg⁺ for this study were also slightly higher for NL, OC, LC and ME, slightly lower for HB and significantly higher for NA, compared to values reported by Henry et al. (1995). The mean fraction of Hg_T occurring as CH₃Hg⁺ was significantly higher for LC and NA, slightly higher for NL, and OC, and slightly lower for HB compared to values obtained by Henry et al. (1995); slightly higher for NL and ME, significantly higher for NA, and significantly lower for OC, compared to Bloom (1989).

Concentrations of Hg species observed by Driscoll and Wang (1996) and Henry et al., (1995) were highly variable. A wide range of Hg_T concentrations was obtained by Henry et al. (1995), but the results showed higher concentrations of Hg in summer. The values obtained by Driscoll and Wang (1996) also displayed considerable variability in Hg_T, and sample sites were not monitored after August during the study year. The number of samples analyzed for ME by Driscoll and Wang (1996) and Henry et al. (1995) were fewer than that for the corresponding number of natural tributary samples. Regression analysis of DOC with Hg_T from the data obtained by Driscoll and Wang (1996) gave r² values of 0.34 at NA, 0.30 at NL, 0.42 at LC (Driscoll and Wang, 1996). The r² values

obtained in this study for the regression of these two species lie within similar range ($r^2=0.24-0.40$).

Table 6.1. Summary of mean concentrations (in ng/L) of Hg_T from studies done on input waters of Onondaga Lake.

Site	This Study (1996)	Bloom (1989)	Driscoll and Wang (1996)	Henry et al., (1995)
NA	5.1 ± 1.5	5.1	4.4 ± 3.3	6.4 ± 5.0
NL	17.9 ± 7.7	18	14.6 ± 6.2	26.9 ± 25.4
OC	8.3 ± 5.5	3.6	4.1 ± 2.6	12.6 ± 20.5
HB	6.3 ± 1.9	-	-	9.4 ± 10.5
LC	5.8 ± 2.1	-	4.3 ± 2.9	7.7 ± 6.8
ME	31.7 ± 21.3	35	15.0 ± 11.0	32.1 ± 15.4

Table 6.2. Summary of mean concentration (in ng/L) of CH_3Hg^+ from studies done on input waters of Onondaga Lake.

Site	This Study	Bloom ¹	Henry et al.,
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6.3 Comparison of Mercury Concentrations for the Natural Tributaries of Onondaga Lake with Other Contaminated Systems.

The concentrations of Hg in some contaminated aquatic systems were presented in section 2.1. A summary of the concentration at various Hg contaminated sites including those obtained in this study are given in the Table 6.4. The Hg concentrations of some of the sites reported in the literature are very high. Some of these values seem unreasonable and may reflect sample contamination.

Comparing the concentrations of Hg observed at the different rivers, it is evident that a wide range of values exists. At some sites, although chlor-alkali production had been terminated for quite sometime, concentrations remained elevated and were higher than those observed in this study. Ranges of concentrations observed at the Wabigoon/English system, Suimon and Ottawa Rivers are the only values that compare with the Hg_T concentrations in tributaries of Onondaga Lake. With the exception of the Carson River, ranges of CH_3Hg^+ concentrations reported for the other rivers compare to that obtained for the natural tributaries to Onondaga Lake.

6.4 Mercury Budget for Inflow Streams to Onondaga Lake

Flux calculations showed that ME contributed the highest loads of both Hg_T (41%) and CH_3Hg^+ (44%) to the lake, with NL the next highest contributor. The Hg_T load contributed by NL (38%) was about twice the combined loads for HB, LC, and OC (17%). Corresponding CH_3Hg^+ loading at NL (25%) was almost equal to the total combined CH_3Hg^+ loading for HB, LC and OC (27%). The specific yield of Hg_T (125.8 mg/ha-yr)

Table 6.4. Concentrations Hg species in waters reported for various contaminated sites.

River	Location	Cause of Contamination	Hg _T (ng/L)	CH ₃ Hg ⁺ (ng/L)	Reference
Scheldt	Europe	Industrial and Chlor-alkali	0.5 - 5.2*	0.01 - 0.4	Leermakers et al. 1995
Carson	USA	Mill Processing (Released 6.8 x 10 ⁶ Kg Hg from 1859-1890)	21-3140 1.2 - 17**	0.25 - 19	Mach et al. 1996
Mersey	Britain	Industrial and Chlor-alkali	300 - 2000	-	Airey and Jones. 1982
Ottawa	Canada	Industrial and Municipal sources	38 [#] (1972) 18 [#] (1973) 13 [#] (1975/6) 6.6 [#] (1978)	2.2 [#] (1978)	Kudo et al. 1982
Holston	USA	Chlor-alkali and Ammonia Production	150 8**	-	Turner and Lindberg. 1978
Suimon	Japan	Industrial ***	25.9 [#]	2.1 [#]	Kudo et al. 1982
Minamata	Japan	Industrial in 1950's	22.1 - 125.3	-	Kudo and Miyahara. 1991
Wabigoon/English System	Canada	Chlor-alkali and Paper mill	1.5 - 48	0.27 - 5	Parks et al. 1989
Tributaries of Onondaga Lake	USA	Chlor-alkali, domestic and industrial	2.6 - 35.8	0.13 - 1.5	This study

* Dissolved Hg concentration

** Concentration at uncontaminated upstream area (background value).

*** Contaminated sediments were removed and river bed sealed with cement in 1976.

Values represent mean concentrations.

and CH_3Hg^+ (3.9 mg/ha-yr) were also greater than yields of both species for the other natural tributaries (22.7-47.7 mg/ha-yr and 1.5-2.5 mg/ha-yr). Thus NL was the dominant contributor of both Hg species for the natural tributaries of Onondaga Lake. Significant difference in loadings of both species occurred between NL and NA and this may be attributed to inputs of contaminated groundwater between Amboy and Lakeland to the tributary.

The results of Hg fluxes and specific yields obtained in this study were compared to those estimated by previous studies (Driscoll and Wang 1996; Henry et al., 1995) (Tables 6.4 and 6.5). In addition, the discharges and TSS loadings for this study period were also compared to corresponding values for 1992, the study period for the previous studies (Tables 6.6).

Mercury budgets from previous studies showed that NL contributed significantly high loads of Hg_T to the Lake. Although the loadings of Hg_T estimated by Driscoll and Wang (1996) (2910 g/yr) and Henry et al. (1995) (7094 g/yr) were significantly different, contributions of Hg_T loads reported for NL (54%) were slightly less than twice that reported for ME (28%). The results obtained in this study however, showed both ME and NL to be the highest contributor of Hg_T , with the contribution from ME slightly higher (about 3%) than that from NL. The combined loading of Hg_T for the major input waters including NL, OC, HB, LC and ME, obtained in this study (9840.7 g/yr) were intermediate between the values reported by Driscoll and Wang (1996) (5,450 g/yr) and Henry et al. (1995) (13,154 g/yr). In all the studies, NL had the highest yield of Hg_T and the contribution of Hg_T loading from NL was more than twice the combined contribution of

Table 6.5. Comparison of Hg_T and CH₃Hg⁺ loadings for input waters of Onondaga Lake. (% contribution in parenthesis).

Site	This Study Hg _T (g/yr)	This Study CH ₃ Hg ⁺ (g/yr)	Driscoll and Wang (1996) Hg _T (g/yr)	Henry et al. (1995) Hg _T (g/yr)	Henry et al. (1995) CH ₃ Hg ⁺ (g/yr)
HB	66.6 (0.7%)	7.5 (2.0%)	40 (0.7%)	220 (1.7%)	8.7 (3.3%)
LC	282.4 (2.8%)	19.3 (4.7%)	220 (4.0%)	409 (3.1%)	5.2 (2.0%)
OC	1422.6 (14.5%)	85.7 (20.4%)	760 (14.0%)	1811 (13.8%)	49.2 (18.8%)
NL	3749.8 (38.0%)	110.7 (24.9%)	2910 (53.4%)	7094 (53.9%)	47.8 (18.3%)
NA	658.2 (19.2%) ^b	35.1 (35.1%) ^b	590 (20.3%) ^b	-	-
ME	4319.3 (41.4%)	190.6 (43.1%)	1520 (27.9%)	3620 (27.5%)	151 (57.6%)

^bNA expressed as % of NL loadings.

Table 6.6. Comparison of specific yield (mg/ha-year) for the natural tributaries of Onondaga Lake.

Tributary	This Study Hg _T	This Study CH ₃ Hg ⁺	Driscoll and Wang (1996) Hg _T	Henry et al. (1996) Hg _T	Henry et al. (1996) CH ₃ Hg ⁺
HB	23.1	2.5	13.7	75	3.0
LC	36.5	2.5	28.4	53	0.7
OC	47.7	2.8	26.7	64	1.7
NL	125.8	3.7	97.7	240	1.6
NA	27.6	2.3	2.5	-	-

Table 6.7. Comparison of discharges and TSS loadings for input waters of Onondaga Lake for this study period and 1992.

Site	This Study Discharge (m ³ /d)	1992 Discharge (m ³ /d)	This Study TSS Loading (10 ³ kg/yr)	1992 TSS loadings (10 ³ kg/yr)
HB	26,336	28,480	1,650	346
LC	116,900	120,369	2,745	1,268
OC	431,716	472,446	11,880	9,157
NL	403,166	449,577	5,673	3,713
ME	259,471	262,321	1,437	1,242
Others	115,992	123,461	N/A	N/A
TOTAL	1,353,611	1,456,654	23,385	15,726

the HB, LC and OC. In this study it was evident that Ninemile Creek is a gaining stream with respect to inputs of Hg, and this results agrees with the loadings estimated by Driscoll and Wang (1996). The percentage of Amboy's contribution to the Hg_T load at Lakeland reported by Driscoll and Wang (19%) compare to that estimated in this study (18%).

Total loadings of CH_3Hg^+ for NL, OC, HB, LC and ME, estimated in this study (420 g/yr) were higher than those reported by Henry et al. (1995) (262 g/yr). The loadings of CH_3Hg^+ estimated in this study showed that ME was the highest contributor and this agrees with the result estimated by Henry et al. (1995). Henry et al. (1995) however reported that the loading of CH_3Hg^+ for ME was 58% of the total load from the input waters and this is higher than the loading estimated in this study (44%). The yield of CH_3Hg^+ estimated in this study, revealed that NL had the highest value (3.7 mg/ha-yr) which is about 1.5 times greater than the yields estimated for HB. Henry et al., (1995) reported the opposite, with HB having the highest CH_3Hg^+ yield (3.0 mg/hg-yr), and almost twice the yield for NL (1.6 mg/ha-yr).

Differences in loadings may be due to differences in discharges, concentrations of Hg species, the period of study and/or method of flux estimation. From Table 6.6, it is evident that, discharges for the two sampling periods considered did not differ markedly, with the total discharge for this study period about 93% the discharge in 1992. Although mean concentrations of Hg_T species for the various sites reported in this study did not differ significantly from the mean concentrations reported by the two previous studies considered, the slight differences that occurred in both the concentrations and discharges

may cause differences in loadings. In addition, differences in the patterns of monthly Hg concentrations and daily discharges may be also be responsible, since the product of both quantities are considered in loading calculations. Henry et al. (1995) used very weak correlations between discharge and Hg concentrations to predict Hg concentrations for days in which samples were not collect, and also used long-term flow records for each tributary when measured flow rates were unavailable. This may be responsible for the greater differences in Hg_T loadings between Henry et al., (1995) and this study.

The investigation of concentrations and fluxes of Hg_T and CH₃Hg⁺ within METRO that was done in conjunction with this study, estimated the loadings of the Hg species for ME using the same concentrations of the Hg species reported in this study, but different load estimation methods (McAlear, 1996). For Hg_T loadings, an empirical relationship developed between Hg_T and TSS within METRO was used to estimate Hg_T concentrations for days on which water samples were not collected; while for CH₃Hg⁺ loadings, concentrations for the days samples were not collected were estimated by linear interpolation between known concentrations (McAlear, 1996). The loading results reported by McAlear (1996) for ME were 3260 g/yr and 151 g/yr for Hg_T and CH₃Hg⁺ respectively. These values are 25% and 23% lower than those estimated by the Flux program, used in this study, for Hg_T and CH₃Hg⁺ respectively. Thus the method of estimating loadings may also account for difference between values reported in the various studies.

The TSS loadings for 1992 (Table 6.6) were estimated using Flux (Method 2) and the values for the natural tributaries were significantly lower than the TSS loadings obtained for this study. In both study periods, OC was the greatest contributor. In this study, it

was evident that Hg associates with TSS, and therefore it should be expected that loadings for Hg species should be greater than those reported in the other studies. Only the loadings of CH_3Hg^+ estimated in this study were greater than the loading reported in the previous studies. For Hg_T , which showed stronger relationships with TSS, loadings estimated in this study were intermediate between the two previous studies. Therefore, in as much as solids appear be responsible for the transport of Hg species, patterns of flow may dictate Hg concentrations because of the effect of dilution or suspension.

6.5 Comparison of Specific Yields for Natural Tributaries of Onondaga Lake to Other Systems

Several investigators have reported yields of Hg for various catchment areas. Yields of Hg_T for the natural tributaries were comparable to, although on the low end of those reported for wet atmospheric deposition (70-250 mg/ha-yr) and for runoff (40-1100 mg/hg-yr) in Swedish forest lakes (Meili, 1991). With the exception of NL, yields of Hg_T for the other natural tributaries were also comparable to those reported for catchment areas in Sweden affected by atmospheric deposition Hg (8-59 mg/ha-yr) (Johnansson et al., 1991). Yields of Hg_T reported in this study were higher than those reported for pristine drainage areas in a Canadian boreal forest ecosystems (3.1- 22.8 mg/ha-yr) (St. Louis et al., 1994), in headwater streams on the Precambian Shield in Ontario, Canada (6.1-21 mg/ha-yr) (Mierle and Ingram, 1991), Svartberget catchment in northern Sweden (12-15 mg/ha-yr) (Lee et al., 1995), Gårdsjön catchment in southern Sweden (23-35 mg/ha-yr) (Lee and Hultberg, 1990) and the Allequash Creek watershed, northern Wisconsin (0.012

mg/ha-yr) (Krabbenhoft et al., 1995). Yields of CH_3Hg^+ for the natural tributaries of Onondaga Lake compare to those reported for the wetland portions of boreal forest in Canada (1.84-5.55 mg/ha-yr) but were higher than those reported for the upland portion of the boreal forest (0.07-0.96 mg/ha-yr) (St. Louis et al., 1994), Svartberget catchment in northern Sweden (0.8-1.7 mg/ha-yr) (Lee et al., 1995), Gårdsjön catchment in southern Sweden (1.2 mg/ha-yr) (Lee and Hultberg, 1990), Allequash Creek watershed, northern Wisconsin (0.006-0.015 mg/ha-yr) (Krabbenhoft et al., 1995).

CHAPTER 7 - CONCLUSIONS

Concentrations of Hg_T and CH_3Hg^+ in the natural tributaries of Onondaga Lake showed temporal variations with values slightly higher in summer than in winter. Higher concentrations occurred when discharge and DO concentrations were low. Harbor Brook however, showed different patterns of both Hg species with elevated concentrations occurring in winter. Concentrations of Hg_T and CH_3Hg^+ for ME were highly variable.

Patterns of ionic species concentrations including Cl^- , Na^+ and Ca^{2+} at NL and OC, originating mainly from groundwater sources, were higher in summer and lower in the high flow periods. These patterns coincided with patterns of Hg species concentrations in both NL and OC, suggesting that groundwater infiltration is a potential source of Hg species to the two tributaries. During winter, when high discharges occurred, the effect of groundwater was diluted, thus lowering the concentrations of Hg and ionic species.

At HB and LC, watershed characteristics may also play important role in Hg distribution patterns. Reduction of SO_4^{2-} occurred along with increased CH_3Hg^+ concentrations at HB and LC during the snowmelt period. Concentrations of Hg species for ME on the other hand, were highly variable, and dependent on the efficient removal of Hg within the treatment facility. Although CH_3Hg^+ concentrations reported in this study were slightly higher, they were comparable to those reported by previous investigators (Henry et al., 1995; Driscoll and Wang, 1996).

Concentrations of Hg_T were well correlated to CH_3Hg^+ for the natural tributaries, but the relationships varied from site-to-site. Total Hg concentrations in the natural tribu-

taries appeared to be strongly related to TSS. However, the corresponding relationships for CH_3Hg^+ were weaker. These regression relations revealed that association of Hg with TSS was site specific. Mercury species for ME were not correlated with TSS.

METRO effluent and NL were found to be highest contributors of Hg_T and ME the highest contributor of CH_3Hg^+ from the inflows streams to Onondaga Lake. However, previous investigators (Henry et al., 1995; Driscoll and Wang, 1996) have reported that NL was the greatest input of Hg_T to the lake. Loadings of both species estimated for NL were significantly higher than those of the other natural tributaries, with the exception of CH_3Hg^+ loads from OC. Significant increases in the loadings of both Hg species occurred between NA and NL, suggesting inputs from the reach between Amboy and Lakeland. The results of Hg_T loadings reported in this study were intermediate between the two previous studies (Driscoll and Wang, 1996; Henry et al., 1995). For CH_3Hg^+ , loadings reported in this study for HB, LC and ME were comparable to Henry et al. (1995), while loadings for NL and OC were higher. The highest yield of Hg_T and CH_3Hg^+ for the tributaries occurred at NL.

CHAPTER 8 - SUGGESTIONS FOR FUTURE RESEARCH

1. Unlike the natural tributaries, Hg_T for METRO was weakly correlated with CH_3Hg^+ and TSS. Thus it is important to further understand the biogeochemistry and bioavailability of Hg in the METRO effluent in comparison to natural inflows to Onondaga Lake.
2. At Harbor Brook and Ley Creek, SO_4^{2-} reduction was found to occur simultaneously with increasing CH_3Hg^+ concentrations during the snowmelt period, when temperatures were lower. Bacterial methylation activities are favorable under optimal conditions ($35^{\circ}C$). Therefore, it will be useful to further study the role of SO_4^{2-} in the methylation of Hg_T in these input waters and the effect of temperature on this process.
3. Current literature on Harbor Brook is limited. The CH_3Hg^+ concentrations in this tributary were high, compared to the other tributaries. This tributary also had the highest mean SO_4^{2-} concentration. The source(s) of SO_4^{2-} to Harbor Brook are unclear. Thus there is a need for studying the watershed characteristics and its influence on Hg inputs to the stream.
4. An important issue revealed in this study was inputs of Hg from groundwater sources at Ninemile Creek at Lakeland and Onondaga Creek. It is important to understand the concentration patterns with time at these sources in order to establish whether the Hg

concentration is decreasing or increasing with time, or is being influenced by other factors such as atmospheric deposition.

5. Future studies on Hg should be designed to monitor the concentrations of Hg at closer time intervals and during wastewater bypass events. In addition, meaningful correlations may be obtained if concentrations of auxiliary parameters are also monitored at the same time. Increasing the number of samples collected will reduce uncertainties in loading estimates. Such studies, should include monitoring other sources and sinks of Hg to Onondaga lake so that a more accurate Hg budget for the lake can be developed.

6. Analysis of water samples in future investigations, should include both the dissolved and particulate concentrations, from which partition coefficients for Hg species can be estimated. This is of importance because partitioning of Hg species between dissolved and particulate states results from the competition for Hg among ligands in solution, on colloids and abiotic particles, and in cells. Partition coefficients are directly proportional to the bioavailability of Hg to plankton, and the accumulation of Hg in fish is related to the food chain.

APPENDIX I

Monthly Concentrations of Hg_T (ng/L) for the period October 1995 - September 1996.

Month	NA	NL	OC	HB	LC	ME
18-Oct.'95	6.25	22.44	7.72	6.39	4.01	28.36
28-Nov.'95	5.37	17.85	7.33	7.07	3.80	46.53
18-Dec.'95	5.66	12.31	5.35	4.28	3.61	14.03
30-Jan.'96	6.04	13.97	5.01	5.15	4.17	42.30
29-Feb.'96	3.54	11.68	6.13	5.05	5.56	44.47
06-Mar.'96	2.79	15.11	7.41	N/A	N/A	N/A
13-Mar.'96	2.56	10.56	6.78	N/A	N/A	N/A
20-Mar.'96	4.28	13.55	9.23	N/A	N/A	N/A
28-Mar.'96	3.84	12.66	7.42	6.44	6.14	27.9
29-Apr.'96	4.84	11.55	8.16	10.44	6.03	65.57
30-May'96	5.08	24.56	10.89	8.65	9.01	7.07
27-Jun.'96	7.91	35.83	11.52	7.89	9.52	66.67
25-Jul.'96	7.26	31.83	14.52	5.60	5.38	15.3
29-Aug.'96	5.28	16.23	7.85	4.21	4.36	12.24
19-Sep.'96	6.13	18.66	8.38	4.88	8.48	6.63

Monthly Concentrations of CH₃Hg⁺ (ng/L) for the period October 1995 - September 1996.

Month	NA	NL	OC	HB	LC	ME
18-Oct.'95	0.25	0.55	0.35	0.45	0.37	1.45
28-Nov.'95	0.21	0.40	0.20	0.49	0.22	0.78
18-Dec.'95	0.23	0.24	0.37	0.41	0.28	0.63
30-Jan.'96	0.27	0.28	0.17	0.38	0.31	2.40
29-Feb.'96	0.22	0.39	0.43	0.40	0.34	1.79
06-Mar.'96	0.19	0.34	0.40	N/A	N/A	N/A
13-Mar.'96	0.13	0.31	0.43	N/A	N/A	N/A
20-Mar.'96	0.21	0.41	0.49	N/A	N/A	N/A
28-Mar.'96	0.22	0.22	0.42	0.87	0.62	1.73
29-Apr.'96	0.23	0.41	0.43	1.49	0.43	1.26
30-May'96	0.28	0.73	0.51	0.58	0.51	3.7
27-Jun.'96	0.54	1.42	0.77	0.52	0.65	2.07
25-Jul.'96	0.43	1.1	0.97	0.32	0.37	0.69
29-Aug.'96	0.24	0.56	0.51	0.51	0.28	0.92
19-Sep.'96	0.19	0.49	0.36	0.62	0.47	0.67

N/A = Sample not collected.

APPENDIX II

Result of Statistical Analysis between mean concentrations at 5% level of significance. ((+) = significant; (-) = not significant).

Comparison of overall mean Hg_T concentrations.

Site	NA	NL	OC	HB	LC	ME
NA		(+)	(-)	(-)	(-)	(+)
NL			(+)	(+)	(+)	(+)
OC				(-)	(-)	(+)
HB					(-)	(+)
LC						(+)
ME						

Comparison of overall mean CH₃Hg⁺ concentrations

Site	NA	NL	OC	HB	LC	ME
NA		(+)	(-)	(+)	(-)	(+)
NL			(-)	(-)	(-)	(+)
OC				(-)	(-)	(+)
HB					(-)	(+)
LC						(+)
ME						

Comparison of overall mean % of Hg_T occurring as CH₃Hg⁺

Site	NA	NL	OC	HB	LC	ME
NA		(-)	(-)	(-)	(-)	(+)
NL			(-)	(-)	(-)	(+)
OC				(-)	(-)	(+)
HB					(-)	(+)
LC						(+)
ME						

Comparison of mean winter Hg_T concentrations

Site	NA	NL	OC	HB	LC	ME
NA		(-)	(-)	(-)	(-)	(+)
NL			(-)	(-)	(-)	(+)
OC				(-)	(-)	(+)
HB					(-)	(+)
LC						(+)
ME						

Comparison of mean summer Hg_T concentrations

Site	NA	NL	OC	HB	LC	ME
NA		(+)	-	-	-	+
NL			(+)	(+)	(+)	-
OC				-	-	(+)
HB					-	(+)
LC						(+)
ME						

Comparison of mean winter CH₃Hg⁺ concentrations

Site	NA	NL	OC	HB	LC	ME
NA		(-)	(-)	(+)	(-)	(+)
NL			(-)	(+)	(+)	(+)
OC				(-)	(-)	(+)
HB					(+)	(+)
LC						(+)
ME						

Comparison of mean summer CH₃Hg⁺ concentrations

Site	NA	NL	OC	HB	LC	ME
NA		(-)	(-)	(-)	(-)	(+)
NL			(-)	(-)	(-)	(+)
OC				(-)	(-)	(+)
HB					(-)	(+)
LC						(+)
ME						

Comparison of mean winter % of Hg_T occurring as CH₃Hg⁺

Site	NA	NL	OC	HB	LC	ME
NA		(-)	(-)	(-)	(-)	(+)
NL			(-)	(-)	(-)	(+)
OC				(-)	(-)	(+)
HB					(-)	(+)
LC						(+)
ME						

Comparison of mean summer % of Hg_T occurring as CH₃Hg⁺

Site	NA	NL	OC	HB	LC	ME
NA		(-)	(-)	(-)	(-)	(+)
NL			(-)	(-)	(-)	(+)
OC				(-)	(-)	(+)
HB					(-)	(+)
LC						(+)
ME						

Comparison of mean winter and mean summer Hg_T concentrations for individual sites

NA	NL	OC	HB	LC	ME
(-)	(+)	(-)	(-)	(-)	(-)

Comparison of mean winter and mean summer CH₃Hg⁺ concentrations for individual sites

NA	NL	OC	HB	LC	ME
(-)	(+)	(-)	(-)	(-)	(-)

Comparison of mean winter and mean summer % of Hg_T occurring as CH₃Hg⁺ for individual sites

NA	NL	OC	HB	LC	ME
(-)	(-)	(-)	(-)	(-)	(-)

Comparison of mean concentrations of Hg_T obtained in this study with mean values reported by Driscoll and Wang (1996).

NA	NL	OC	HB	LC	ME
(-)	(-)	(-)	(-)	(-)	(-)

Comparison of mean concentrations of Hg_T and CH₃Hg⁺ and % of Hg_T occurring as CH₃Hg⁺ obtained in this study to values reported by Bloom (1989).

Parameter	NA	NL	OC	HB	LC	ME
Hg _T	(-)	(-)	(-)	(-)	(-)	(-)
CH ₃ Hg ⁺	(+)	(+)	(-)	(+)	(+)	(+)
Fraction	(+)	(-)	(+)	(-)	(-)	(-)

Comparison of mean concentrations of Hg_T and CH_3Hg^+ and % of Hg_T occurring as CH_3Hg^+ obtained in this study to values reported by Henry et al. (1995).

Parameter	NA	NL	OC	HB	LC	ME
Hg_T	(-)	(-)	(-)	(-)	(-)	(-)
CH_3Hg^+	(+)	(-)	(-)	(-)	(-)	(-)
Fraction	(+)	(-)	(-)	(-)	(+)	(-)

Comparison of mean loadings of Hg_T

Site	NA	NL	OC	HB	LC	ME
NA		(+)	(-)	(-)	(-)	(+)
NL			(+)	(+)	(+)	(-)
OC				(+)	(+)	(+)
HB					(-)	(+)
LC						(+)
ME						

Comparison of mean loadings of CH_3Hg^+

Site	NA	NL	OC	HB	LC	ME
NA		(+)	(+)	(-)	(-)	(+)
NL			(-)	(+)	(+)	(+)
OC				(+)	(+)	(+)
HB					(-)	(+)
LC						(+)
ME						

APPENDIX III

Chemical and Physical Characteristics of Tributaries to Onondaga Lake

1. Ninemile at Amboy (NA)

Variable	n	Mean	Median	Std. Dev.	Range
Discharge (m ³ /s)	366	3.73	2.26	3.36	0.63-29.44
DO (mg/L)	4	11.4	11.8	1.7	8.4-12.8
Cl ⁻ (mg/L)	4	69	64	18	54-95
Na ⁺ (mg/L)	4	62	45	46	29-130
Ca ²⁺ (mg/L)	4	116	116	21	96-135
pH	4	7.72	7.72	0.04	7.69-7.76
DOC (mg/L)	4	2.2	2.1	0.3	1.9-2.7
TSS (mg/L)	5	6.8	6.0	5.5	2-15

2. Ninemile Creek at Lakeland (NL)

Variable	n	Mean	Median	Std. Deviation	Range
Discharge (m ³ /s)	366	4.66	2.82	4.20	0.79-36.81
Temp. (°C)	26	9.2	9.0	6.7	0.3-18.9
DO (mg/L)	26	9.9	2.2	10.1	6.4-13.8
Cl ⁻ (mg/L)	28	631	640	281	169-1320
Na ⁺ (mg/L)	28	191	204	69	77-338
Ca ²⁺ (mg/L)	28	323	333	121	102-579
SO ₄ ²⁻ (mg/L)	28	246	277	96	93-522
BOD (mg/L)	28	1.9	1.0	1.4	1-7
pH	26	7.64	7.66	0.15	7.38-7.92
DOC (mg/L)	28	2.6	2.4	1.2	1.1-6.9
TSS (mg/L)	28	17.8	13.0	20.0	1-90

3. Onondaga Creek at Spencer Street (OC)

Variable	n	Mean	Median	Std. Deviation	Range
Discharge(m ³ /s)	366	5.00	3.58	4.81	0.79-42.48
Temp. (°C)	26	8.9	9.2	6.5	0.7-17.3
DO (mg/L)	25	9.5	9.9	2.7	2.7-13
Cl ⁻ (mg/L)	28	348	367	186	60-685
Na ⁺ (mg/L)	28	228	229	121	52-461
Ca ²⁺ (mg/L)	28	123	126	37	74-254
SO ₄ ²⁻ (mg/L)	26	152	166	75	39-322
BOD (mg/L)	26	4.4	2.5	5.2	1-23
pH	26	7.64	7.63	0.12	7.46-7.86
DOC (mg/L)	28	3.3	3.0	1.6	1.6-8.4
TSS (mg/L)	28	31.1	25.5	38.4	4-211

4. Harbor Brook at Haiwatha Boulevard (HB)

Variable	n	Mean	Median	Std. Deviation	Range
Discharge (m ³ /s)	366	0.30	0.21	0.50	0.08-7.84
Temp. (°C)	26	9.4	9.5	5.1	1.9-17.2
DO (mg/L)	26	9.45	9.51	2.19	5.4-13.2
Cl ⁻ (mg/L)	26	241	240	78	111-410
Na ⁺ (mg/L)	26	129	126	37	68-226
Ca ²⁺ (mg/L)	26	226	246	59	86-310
SO ₄ ²⁻ (mg/L)	26	587	422	444	95-2310
BOD(mg/L)	26	7.0	1.0	25.5	1-132
pH	26	7.57	7.67	0.23	7.26-8.22
DOC (mg/L)	26	3.2	2.0	4.6	1.2-25.2
TSS (mg/L)	26	35.1	9	70.6	3-292

4. Ley Creek at Park Street (LC)

Variable	n	Mean	Median	Std. Deviation	Range
Discharge (m ³ /s)	366	1.35	0.68	1.82	0.15-15.80
Temp. (°C)	22	12.1	12.8	7.5	1.8-22.0
DO (mg/L)	22	7.5	7.5	2.4	3.3-11.4
Cl ⁻ (mg/L)	22	289	258	137	25-617
Na ⁺ (mg/L)	22	184	149	92	97-446
Ca ²⁺ (mg/L)	22	118	126	26	78-154
SO ₄ ²⁻ (mg/L)	22	264	134	566	55-2780
BOD (mg/L)	22	13.9	3.0	37.0	1.0-174
pH	22	7.43	7.45	0.21	6.86-7.8
DOC (mg/L)	22	13.9	6.4	30.2	3.0-146
TSS (mg/L)	22	26.7	17.5	33.2	3.0-154

5. METRO Effluent (ME)

Variable	n	Mean	Median	Std. Deviation	Range
Discharge (m ³ /s)	366	3.00	2.86	0.69	1.34-5.14
Cl ⁻ (mg/L)	26	331	249	214	131-884
Na ⁺ (mg/L)	26	209	159	110	108-486
Ca ²⁺ (mg/L)	26	123	106	57	84-347
SO ₄ ²⁻ (mg/L)	26	191	186	29	142-252
BOD (mg/L)	26	16.1	17.0	4.2	8-25
pH	26	7.77	7.8	0.12	7.5-8.0
DOC (mg/L)	26	15.5	15.8	4.0	8.6-22.4
TSS (mg/L)	366	10.1	9	7.1	2.0-62.0

APPENDIX IV

Results of Hg_T Loadings Estimated by FLUX (Method 2)

Tributary	Minimum Load	Average Load	Maximum Load	Standard Dev.
NA	483.1	658.2	1102.7	177.7
NL	2645.4	3749.8	9347.1	1978.6
OC	1045.4	1422.6	3052.3	526.2
HB	49.6	66.6	126.5	22.7
LC	204.7	282.4	500.5	106.4
ME	2833.7	4319.3	9181.9	2253.5

Results of CH₃Hg⁺ Loadings Estimated by FLUX (Method 2)

Tributary	Minimum Load	Average Load	Maximum Load	Standard Dev.
NA	25.2	35.2	101.3	20.5
NL	70.6	110.2	425.2	96.6
OC	62.1	85.8	244.3	49.1
HB	5.0	7.5	28.4	6.7
LC	14.0	19.3	33.9	6.7
ME	129.7	197.0	643.0	145.0

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