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**New York State**
**Department of Environmental Conservation**
**50 Wolf Road**
**Albany, New York 12233-7010**

# NEW YORK STATE'S REVISION OF THE ONONDAGA LAKE MERCURY MODELING REPORT

**Onondaga Lake Project**
**Task 7: Remedial Investigation**

**Site No. 734030-002**
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Prepared by

**TAMS CONSULTANTS, Inc.**
300 Broadacres Drive
Bloomfield, New Jersey 07003

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# ACRONYMNS

| | |
|---|---|
| | Cubic feet per second |
| $g/m^2$ - day | Grams per square meter per day |
| kg/year | Kilograms ($10^3$ grams) per year |
| MERC4 | Mercury Transport and Kinetics Model |
| Metro | Metropolitan Syracuse Sewage Treatment Facility |
| | Nanograms ($10^{-9}$ grams) per liter (part-per-trillion) |
| NYSDEC | New York State Department of Environmental Conservation |
| OCDDS | Onondaga County Department of Drainage and Sanitation |
| OLMM | Onondaga Lake Mercury Model |
| | Upstate Freshwater Institute |
| USGS | United States Geological Survey |
| WASP | Water Quality Analysis Simulation Program |

# 1. INTRODUCTION

As part of the investigation of the mercury contamination in Onondaga Lake, AlliedSignal and its consultants constructed a model of mercury behavior based on several models available in the literature. The model was to provide a framework for understanding the current conditions relating to mercury in its various forms within Onondaga Lake. This was to include both internal and external loads to the lake. The model was then to serve as a tool for the assessment of potential remedial activities and their subsequent effects on lake conditions, particularly mercury levels in fish. As part of the construction of the model, AlliedSignal was to collect sufficient data to calibrate the model on an annual basis so as to provide data-based constraints to assess internal *vs* external loads of mercury.

As is discussed later in this report, the data set obtained by AlliedSignal did not provide the constraints needed to permit an accurate assessment of annual external loads nor of internal cycling of mercury As a result, the model-based assessment contained in the AlliedSignal/PTI report entitled Onondaga Lake RI/FS Mercury Modeling Report, June 1997 is without sufficient data to support its assumptions nor its conclusions concerning mercury behavior in the lake. The AlliedSignal/PTI report is attached as Appendix A. The AlliedSignal/PTI report has been disapproved by NYSDEC.

In this report, the modeling analysis prepared by AlliedSignal/PTI is reviewed and critiqued in view of the data collected by AlliedSignal/PTI as well as other sources. On the basis of this analysis, various components of the modeling analysis are shown to be either flawed or not scientifically defensible. In some instances, AlliedSignal/PTI has chosen to emphasize a particular interpretation of the data when, in fact, one or more additional interpretations are also consistent with the data and the known history of the lake. In other instances, contentions put forth by AlliedSignal/PTI are simply not consistent with the available data.

Of particular importance to this review of the AlliedSignal/PTI modeling analysis is the unavailability of sufficient data to characterize lake conditions both temporally and mechanistically. This report describes the deficiencies of the data set used by AlliedSignal/PTI in terms of its application to the model development. Specifically, lack of appropriate data to sufficiently constrain the various fluxes and parameters contained in the model on an annual basis represents a major limitation for the model and is one of the main reasons for its rejection by NYSDEC.

Constraint of a parameter or flux simply means that sufficient data exist to permit the estimation of the parameter or flux to within a reasonable level of uncertainty independent of the model calculations. A parameter is well constrained if data exists which narrows the range of possible values of that parameter. A parameter is poorly constrained if, due to a paucity of data, that parameter can potentially vary over a wide range. Typically, the needed level of uncertainty is less than a factor of two but ultimately this depends upon the overall importance of the parameter or flux to the model. A factor of two uncertainty implies that the true value for the parameter is no more than twice the parameter estimates and no less than half the parameter estimate. As an example of the different uncertainty requirements, a minor flux may need only be known to within an order-of-magnitude of its true value since it will have only a small impact on the model's prediction of the behavior of mercury. Conversely, a thermodynamic constant such as a partition coefficient must be very well known since a small error in its value propagates throughout the model calculations and can lead to large errors in the model's predictions.

This report is arranged in a structure similar to that of the AlliedSignal/PTI Mercury Modeling Report (PTI, 1997a). Within each section the main topics of the original report are discussed and critiqued. Each of the major issues are examined within the context of the available data, both site-specific as well as other scientific literature-based sources. Inaccurate assumptions or conclusions are discussed along with the supporting evidence for their dismissal. The biological components of the AlliedSignal/PTI model are not discussed here, simply due to their complete dependence on the inaccurate geochemical model developed. Without an accurate geochemical representation, the biological model, which calculates fish exposure based on the output from the

geochemical model, cannot provide accurate estimates of biota exposure and body burdens of mercury.

Ultimately, this report notes that while the model design chosen by AlliedSignal/PTI is basically sound, the lack of data to properly constrain the various model components along with some incorrect data interpretations render the model in its current configuration of very little value as a basis for understanding mercury behavior in Onondaga Lake. Similarly, the use of the model in its current form as a predictive tool to assess the impact of various remedial scenarios is precluded.

## 1.1 History of the Model Development

As part of the Onondaga Lake RI/FS , AlliedSignal developed a computer-based simulation (or model) of mercury behavior in Onondaga Lake. AlliedSignal initially submitted a report in April 1995. The major data collection efforts supporting the model were completed in 1992, with additional laboratory studies completed during 1992 and 1993. NYSDEC rejected this modeling effort, based on a number of problems, including lack of complete annual tributary load coverage as well as lack of support for various internal mercury cycling processes. Because of these shortcomings in the data needed to develop the model, AlliedSignal and its consultants attempted to collect additional data on tributary loads in 1996. At the same time they also attempted to characterize some of the internal cycling processes for mercury. The additional tributary sampling largely failed, and the attempts to characterize some internal cycling processes met with very limited success.

Subsequent to these events, AlliedSignal again submitted a mercury modeling report in June 1997. Comments to AlliedSignal/PTI concerning the model were provided in January 1998 and a response was received on February 26, 1998. The June 1997 report was again rejected by NYSDEC based largely on the criticisms summarized in this report.

In all, AlliedSignal completed two mercury modeling efforts. The following field and laboratory collection efforts were intended to support these efforts and portions of the data generated by these efforts are included in this report:

1992 Onondaga Lake Study: involved collection of lake and tributary water column samples, lake sediment samples and lake biota samples. *In situ* experiments were also completed using limnocorrals. The lake study obtained useful data for the period from May through November 1992. No high flow/spring runoff conditions were monitored.

1993 Laboratory Studies: attempted determination of mercury flux from sediments using sediment cores in laboratory simulation of *in situ* conditions. The study also attempted an assessment of the mercury methylation rate determined from water samples held in a controlled setting. Both efforts were essentially unsuccessful in obtaining usable estimates of internal mercury fluxes.

1996 West Flume Study: involved collection of water and sediment samples from the West Flume and Geddes Brook in an attempt to quantify loads from this area to the lake.

1996 Tributary Loading Study: involved the collection of tributary samples during high flow events. The collection effort was largely unsuccessful

1996 Suspended Matter Trap Study: involved the collection of suspended matter samples from traps deployed over various periods at the base of the epilimnion and hypolimnion of Onondaga Lake. Trap data were not completely analyzed for the 1997 modeling report.

1996 Mercury Methylation Rate Study: determined net rate of methylation in laboratory simulation utilizing radioisotopes of mercury. The study determined rates for only one set of samples representing a single day of collection. Gross rates of methylation and demethylation were not determined.

## 1.2 Description of Onondaga Lake

Onondaga Lake is located in Onondaga County, New York, next to the city of Syracuse. The lake is an alkaline, hypereutrophic, "hard water" lake which has been and continues to be the recipient of both industrial and urban discharges of wastewater and runoff. Its drainage basin covers approximately 600 $km^2$ and is part of the Oswego River watershed which drains into Lake Ontario. There are four major tributaries to the lake including, in order of decreasing drainage area: Onondaga Creek, Ninemile Creek, Ley Creek, and Harbor Brook. The Metropolitan Syracuse Sewage Treatment Plant (Metro) also contributes a substantial discharge to the lake that also varies seasonally. Outflow from the lake enters the Seneca River, a tributary to the Oswego River, at an outlet at the north end of the lake.

Onondaga Lake is a dimictic lake (*i.e.*, thermally stratified in summer and winter with vertical mixing events in spring and fall). Its stratification is enhanced by the dissolved salts it receives from AlliedSignal-related discharges and seeps around the lake. The stratification has important implications for mercury cycling in the lake, since both water residence times and dissolved oxygen levels are strongly affected by the stratification. Additional information concerning the lake can be found in Chapter 1 of Appendix A.

## 1.3 Description of the Major Components of the Model

The shortcomings in the mercury modeling effort may be grouped along mass balance considerations. Specifically, three mass balances or budgets form the framework of the AlliedSignal/PTI model as follows:

1 A hydrologic (water) balance;

2. A suspended solids balance; and

3. A mercury balance.

The ability of the existing data set to satisfy all three balances is essential if an accurate representation of mercury behavior in the lake is to be made. A complete mass balance or budget for any component is a simple estimation of all important inputs and outputs from the lake as well as the internal processes which affect the lake. In simplest terms a mass balance can be likened to a checkbook where deposits (inputs) less withdrawals (outputs) should yield a positive balance. Month-to-month changes in the rate of deposits and withdrawals cause the account balance (or lake inventory) to change over time.

The emphasis placed on the three budgets listed above is based on their importance to understanding mercury behavior. Specifically, water provides the main means of mercury transport in the lake. Since incoming and outgoing flows serve to deliver, dilute or remove mercury in the lake, it is essential that a water balance or budget be established for the period of study. Similarly, suspended solids play a critical role. Mercury in the environment tends to adhere strongly to particulate matter and a large fraction of the mercury load to the lake is likely delivered in particle-bound form as part of the suspended matter load. In addition, suspended matter within the lake is responsible for the vertical movement of mercury from shallow to deeper waters when summer stratification prevents vertical mixing in the lake. Lastly, suspended solids settling to the lake bottom represent one of the major mercury outputs from the lake water column. Thus, a thorough understanding of the suspended solids budget for the lake is essential for an accurate mercury balance.

In this report, information and results obtained from the AlliedSignal/PTI model are discussed in the context of these balances. That is, numerical results as well as portions of the input data from the AlliedSignal/PTI model are discussed in terms of a mass balance for each of these components. Data sufficiency for inputs, outputs or related parameters is reviewed both on a time

and a quality basis. That is, sufficient temporal coverage as well as the uncertainty of the analytical results are both considered.

In their modeling design, AlliedSignal and its consultants attempted a very complex model which incorporated many expressions and constants to describe the many processes involved in mercury loading and cycling within Onondaga Lake. Unfortunately, many of the relationships and their associated constants are not well known and either were not or could not be measured. This yielded a poorly constrained model with many relatively unconstrained parameters.

The model as originally constructed by AlliedSignal/PTI contains three numerical simulation components and several submodels as follows:

Geochemical model of mercury loads and cycling within Onondaga Lake (MERC4; AScI Corp., 1992)

- Model is based on a WASP5 (USEPA, 1993) framework
- Model has been modified by PTI (1997) to include a "remineralization" term.

Biochemical model of mercury fish body burdens as affected by growth, depuration and assimilation of mercury from water, sediment and biota (MERC4; AScI, 1992)

- Modifications by PTI (1997) to include assimilation and depuration of mercury.

  Model uses output from Fish Bioenergetics Model 2 to define metabolic rate constants.

Bioenergetic model of fish metabolism and growth (Fish Bioenergetics Model 2 Hewett and Johnson, 1991)

- Model is used to produce estimates of fish metabolism, consumption, respiration, egestion and excretion as input for estimation of fish mercury exposure.

In preparing these models, AlliedSignal/PTI relied on various sources of site-specific information as well as literature values to estimate the various parameters contained in each model. As discussed in Section 2, much of the information is insufficient to constrain the models effectively and in many instances, wide ranges of parameter values are consistent with the level of agreement achieved by the model. The model attempts to represent each of the processes listed below by various equations with user-specified parameters. In most instances, the greatest uncertainty lies within the estimates of these parameters since most of the theoretical considerations (*e.g.*, the form of the sediment diffusion expression) are well known.

| Geochemical Processes | Biological Processes |
|---|---|
| Water Column Advection | Consumption |
| Water Column Dispersion | Respiration |
| Particle Settling in the Water Column | Egestion and Excretion |
| Porewater Advection | Reproduction |
| Porewater Diffusion | Bioaccumulation |
| Sediment Resuspension | |
| Volatilization | |
| Sediment Burial | |
| Precipitation and Evaporation | |
| Kinetics, Thermodynamics and Sorption | |

Detailed discussions of these processes are given in Appendix A. Review of the supporting data for the geochemical processes is provided in Section 2 of this report.

## .4 Structure of the Report

This report consists of six sections which parallel the main chapters of the AlliedSignal/PTI report. Section 2, *Application of the Onondaga Lake Mercury Model*, describes the major data sets

available to constrain the model parameters. The range of the major variables and the degree of uncertainty in their estimates are presented. This section covers material presented in the report text as well as some of the material in the appendices. In Section 3, *Model Calibration*, the discussion focuses on those parameters which were selected for adjustment during calibration and supporting evidence for their adjustment. It also discusses those parameters with little or no constraint and their use in the calibration process. Section 4, *Mass Balance*, discusses the mercury mass balance obtained from the AlliedSignal/PTI model calculations. Section 5, *Model Sensitivities*, presents further sensitivity analyses of a limited number of parameters and loads whose values for this analysis of the model were allowed to vary within a range supported by the data. Typically, the parameter or load was varied beyond the very limited 20 percent range which was the extent of the range examined during AlliedSignal/PTI's sensitivity analysis. In addition, unconstrained parameters will also be discussed in terms of their potential impact on the model results. Lastly, Section 6, *Conclusions*, reviews the model conclusions presented by AlliedSignal/PTI in the context of the various issues and limitations presented in this report.

# 2. APPLICATION OF THE ONONDAGA LAKE MERCURY MODEL

In the preparation of any modeling analysis, synthesis of the available data in forms appropriate for use by the model is one of the most important tasks. For this report, the data synthesis compiled by AlliedSignal/PTI was critically examined for its representativeness of the temporal variations of lake conditions and for the degree of accuracy of its depiction of the magnitude of the various fluxes and parameters. This discussion will begin with the consideration of the three mass balances mentioned above, *i.e.*, hydrological, suspended solids and mercury.

Before beginning the discussion of these mass balances, the limnological conventions and terms used in this report relative to those of the AlliedSignal/PTI report should be noted. In this report, the lake is divided into two basic domains, a surface layer or epilimnion and a deep layer or hypolimnion. Under most circumstances, these layers are found to be internally homogeneous. These layers are separated by a transitional zone or metalimnion where lake properties rapidly change with depth. Based on AlliedSignal/PTI's model development, it appears that the metalimnion has been incorporated into the epilimnion for the purposes of modeling. The epilimnion in Onondaga Lake is partially underlain by shallow lake sediments and partially underlain by the hypolimnion. The hypolimnion is completely overlain by the epilimnion. Figure 2-1 is a sketch of the lake structure.

In constructing its model, AlliedSignal/PTI subdivided the epilimnion into two zones, a littoral zone where the epilimnion is underlain solely by sediment and a pelagic zone where the epilimnion is underlain solely by the hypolimnion. The important distinguishing features here are the availability of lake sediments to the littoral zone and the output from the pelagic zone to the hypolimnion via suspended particle settling. In reality, horizontal mixing in the epilimnion is relatively fast so that the entire epilimnion layer "sees" both conditions. As is discussed later in this report, the model has internal exchange terms which account for the rapid horizontal exchange. AlliedSignal/PTI also refers to the hypolimnion as the profundal zone. Both terms refer to the same lake layer.

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## 2.1 Hydrological Loads and Sinks

The first mass balance required for a successful mercury simulation is the hydrological or water balance. Mercury transport in the Onondaga Lake setting is inherently tied to water-borne transport either in dissolved or suspended matter form. Air-borne transport does occur but the majority of any air-borne flux is delivered via the integration of watershed deposition by the tributaries to the lake. Thus, constructing an accurate representation of the water loads to and from the lake is an essential first step in the modeling process. The water inputs and outputs for the lake for the months of May 1992 through November 1992 as compiled by AlliedSignal/PTI are summarized graphically in Figure 2-2.

### Hydrological Inputs to the Lake

Probably the most important single data set for the hydrological balance is the tributary discharge data collected by the USGS for both major tributaries to the lake (*i.e.*, Onondaga Creek and Ninemile Creek) as well as for two of the smaller tributaries (*i.e.*, Ley Creek and Harbor Brook). The USGS reports mean daily flow for each of these tributaries at locations close to the lake entry points. According to the USGS (1998), records for these discharges are generally considered good under ice-free conditions and fair when the lake is ice covered. As a result of both the extent and accuracy of this data, gauged tributary discharge to the lake is considered to be well known.

In addition to the direct discharge to the lake, there are several other important water loads to the lake. The most important discharge to the lake in terms of flow volume is the outfall from the Metropolitan Syracuse Sewage Treatment Facility (Metro). Discharge from this facility is monitored daily by the Onondaga County Department of Drainage and Sanitation (OCDDS) Thus, its discharge rate to the lake is considered well known.

The remaining inputs of water to the lake consist of minor tributaries, precipitation, groundwater, and Seneca River backflow. A "backflow" or reverse flow across the lake outlet

coming from the Seneca River results from the hydrodynamic balance between Seneca River flows and those originating from the lake. Minor tributary discharges were estimated based on AlliedSignal/PTI's field measurements during the period June through November 1992 and extrapolated to cover the entire year (PTI, 1993 and Appendix A). Tributary 5A, East Flume, Bloody Brook and Sawmill Creek were represented in this fashion. While the level of uncertainty concerning flow for these minor tributaries is individually much greater than the gauged flows, the impact of this uncertainty on the overall water balance is minor, probably less than a percent due to the substantially smaller discharges originating from these streams. A summary of the tributary flows for 1992 and their percentage of the annual discharge to the lake is given in Table B-1 of Appendix A, which was slightly modified here to produce Table 2-1.

Precipitation was determined by AlliedSignal/PTI from precipitation records at Hancock Airport, Syracuse and is considered well known.

Groundwater inflow was estimated without the benefit of any site-specific data. As such there is little certainty in the values estimated. In particular, groundwater flows were estimated based on hydraulic gradients and properties near the site but accurate estimates of groundwater flows on the scale of the lake are difficult to achieve without benefit of a measured lake outlet discharge (to be discussed below). Based on the discussion presented in Appendix D of the AlliedSignal/PTI mercury modeling report, the estimate of groundwater discharge at about .5 cfs has at least a factor of two uncertainty associated with it. (The report provides a second estimate of 2.5 cfs and flow to the deepest portion of the lake is completely unconstrained.) Although the flow is relatively small by this estimate, the potential importance of groundwater to the mercury balance for the lake is great. Groundwater represents a potentially important means for mercury migration from the lake sediments to the overlying water column. It is also one of the few if not the only direct source of water to the hypolimnion during summer stratification. This has important ramifications for the water balance and for the Seneca River backflow as discussed below.

The occurrence of the Seneca River backflow was noted and originally estimated by UFI (1992). Seneca River flow, lake discharge, and backflow into the lake from the Seneca River are all effectively regulated by a dam downstream of the confluence of the Seneca River and the Onondaga Lake outlet. Estimation of the backflow was attempted by AlliedSignal/PTI by creating a mass balance for dissolved chloride in the lake. Chloride ions in Onondaga Lake are principally derived from Onondaga Creek and Ninemile Creek discharges. In addition, chloride ion concentration is unaffected by calcite precipitation or organic detritus. Thus it serves as a conservative tracer for the mixing of water within the lake. Using the chloride ion balance, AlliedSignal/PTI estimated the volume of Seneca River backflow required to dilute the calculated lake chloride levels to match those measured in the lake. AlliedSignal/PTI presumed that all of the dilution was accomplished by the Seneca River. However, groundwater can also serve this purpose and may be more important than originally estimated. In fact, there appears to be an inconsistency in the model in the water dynamics for the Seneca River backflow which would suggest a greater groundwater flow, as discussed below

In the model calculation provided by AlliedSignal/PTI, there is no diffusive exchange between the hypolimnion and the epilimnion during the summer months. The model accomplishes some exchange between these two layers via the direct entry of portions of Onondaga Creek and Ninemile Creek to the hypolimnion. However, this mechanism effectively isolates the hypolimnion from the Seneca River backflow for the entire summer simulation. Yet, in the calibration discussion in Chapter 3 of their report, the effect of a Seneca River backflow on the hypolimnion chloride ion concentrations during summer conditions is evident. Specifically, in Figure 14 of the AlliedSignal/PTI report, the model results for the hypolimnion chloride ion concentration yield a closer agreement with the measured chloride concentration when Seneca River backflow is included. This is a clear inconsistency in the model calibration since the model as provided to NYSDEC does not allow the backflow to affect the hypolimnion during this period.

A second issue with the Seneca River backflow is also evident in Figure 4 of the AlliedSignal/PTI report. Specifically, the model calibration yields better agreement with measured

chloride ion concentrations during spring conditions (days 100 to 150) without the Seneca River backflow. Conversely, the model yields better agreement with the measured chloride ion concentration during summer with the Seneca River backflow. This indicates that the scale of the diluting flow (whether Seneca River, groundwater or more extensive vertical mixing) during summer conditions is roughly correct but it is clearly overestimated during spring conditions.

### Hydrological Outputs from the Lake

Water leaves Onondaga Lake via two mechanisms, discharge to the Seneca River and evaporation. Evaporation was estimated by AlliedSignal/PTI but was not explained in the report. Based on model output, it was estimated to be close to the precipitation rate in scale although opposite in effect. This is consistent with other estimates of precipitation and evaporation in the northeastern United States.

Discharge to the Seneca River is not as well known and has not been directly measured, in part due to the regulation of water levels in the lake and Seneca River as part of the Erie Canal system. Thus, the major discharge of water from the lake is not known independently and must be estimated from the discharges to the lake. This is further complicated by the backflow of water from the Seneca River as well as the unknown contribution by groundwater. Lacking independent measures for each of these flows (*i.e.*, total lake discharge, Seneca River backflow and groundwater discharge) prevents closure of the water balance and leaves the three flows only partially constrained. The Seneca River backflow represents only about 7 percent of the annual inflow to the lake and given the uncertainty in its size from season to season, its subsequent inclusion in the outflows leads to perhaps a 7 percent uncertainty in the total lake discharge. Groundwater discharge to the lake also effects the total lake discharge. Although the groundwater discharge was estimated to be more than an order-of-magnitude less than the backflow, the scale of the discharge is only truly constrained by the dilution process and could in fact be equal to the backflow in magnitude.

### Lake Volume

Lake volume varies continuously as the water level in the lake responds to the temporal variation of the various discharges to the lake as well as the water level control efforts for the Erie Canal. Variations in lake water level are recorded by the USGS and were incorporated in the model by AlliedSignal/PTI. This was accomplished via specified changes in the epilimnion volume. The hypolimnion volume was held constant throughout the model simulation. Given that some portion of the tributary discharge is directed to the hypolimnion during various times of the year, it is unlikely that the hypolimnion volume would remain constant over time. However, it is likely that the assumption of constant volume represents a relatively small concern for the model, especially in light of the internal exchange terms which clearly appear to be in error. These are discussed in Section 3 of this report.

### Summary

In summary, the hydrological balance for the lake is fairly well known although some substantive issues are unresolved by the available data. The majority of inputs to the lake are gauged and well known. Output from the lake as well as Seneca River backflow and groundwater discharge are poorly constrained, with the poorest constraints pertaining to groundwater. These flows are important since they provide a means for mercury removal from the lake in the case of the total lake discharge and a means for mercury release from sediments in the case of groundwater. Estimating the mercury input via groundwater, in particular, is problematic as discussed later in this report.

## 2.2 Suspended Solids Balance

AlliedSignal/PTI did not formally present an annual suspended solids balance for the lake although several calculations presented in Appendix E in the AlliedSignal/PTI modeling report assume a solids balance for the lake. Measured water column suspended solids concentrations were essentially "force-fit" in the model calibrations and not estimated by modeled processes. This was

done partially at the direction of NYSDEC since development of a model capable of independently estimating the suspended solids concentrations was deemed not essential to the mercury modeling effort and would make the model even more complex. Nonetheless, estimation of suspended solids loads to the lake as well as within the lake have a direct bearing on several of the important suspended solids-related processes in the lake, specifically resuspension, net sedimentation and remineralization. In turn, these three processes have major implications for the storage and re-release of mercury in the sediments of the lake. Thus, it is essential to obtain reasonable estimates for the annual suspended solids loads. To this end, AlliedSignal/PTI measured tributary suspended solids loads to the lake as well as gross sedimentation at several locations in the lake, both in the epilimnion and hypolimnion. AlliedSignal/PTI also obtained a limited number of sediment cores beneath the hypolimnion which were subsequently dated to establish the depositional history. However, these data sets did not provide data of sufficient precision to support the contentions made by AlliedSignal/PTI concerning annual solids loads to the lake, net sedimentation or remineralization and in fact appear to prove the absence of remineralization in the water column.

### External Suspended Solids Loads to the Lake

Tributary suspended solids loads to the lake were estimated based on an analysis of the relationship between suspended solids and flow for each tributary. The suspended solids data were obtained by AlliedSignal/PTI during their monitoring program in 1992. Unfortunately, AlliedSignal/PTI failed to capture any of the significant high flow events of that year. A subsequent attempt to capture the suspended solids loads at high flows in 1996 also failed. As a result, no data exist to characterize the high flow events typically associated with the spring snowmelt and runoff. Typically, these events transport the vast majority of solids on an annual basis (*e.g.*, Gailani *et al.*, 1991). For example, Bopp, *et al.* (1985) found that for the upper Hudson River, the 18 highest days of flow were responsible for transporting 63 percent of the annual suspended solids load in the year. Because of the nature of sediment deposition and soil erosion, typical suspended solids loads for streams and rivers exhibit a threshold value above which sediment scour and subsequent suspended matter transport significantly increase as flow increases. None of the response curves for flow and

suspended solids developed by AlliedSignal/PTI suggest this kind of behavior, indicating that the sampling did not capture the high flow characteristics. At most, the AlliedSignal/PTI results shown in Figure B-3 to B-6 and B-9 to B-13 of Appendix B of the AlliedSignal/PTI report suggest a slight upward trend with flow for a few tributaries. In all but one instance (*i.e.*, Harbor Brook), the slope of the curve was not statistically different from zero, indicating the absence of a discernable trend with flow.

Failure to properly characterize these conditions leaves the annual suspended solids balance unconstrained. Figure 2-3 shows the daily flow measurements for the four gauged tributaries. Also noted on the diagrams are the days of suspended solids sample collection. In every instance, AlliedSignal/PTI failed to capture the higher flows. The importance of this shortcoming cannot be overemphasized in the context of annual budgets for suspended solids and mercury. Potentially, a very large portion of the annual suspended solids load is delivered during the major flow events and is not correctly represented in the AlliedSignal/PT analysis. In addition to the straightforward uncertainty associated with the suspended solids balance, the calculations concerning gross *vs* net deposition to the lake bottom are rendered useless since no data exist to estimate gross annual tributary suspended solids loads. The importance of the spring suspended solids loads is evident in the few water column data points available for April 1992. As shown in Figure 17 of the AlliedSignal/PTI report, suspended solids concentrations in April represent maximum levels for the period of measurement. While part of the increased suspended solids concentration may be due to resuspension of lake sediments resulting from the spring vertical mixing event, it is certain that external loads are important as well. Note the magnitude and temporal extent of the spring suspended solids peak relative to the fall vertical mixing event around day 290. Thus, failure to characterize the tributary loads to the lake during the period of high flows potentially leaves a large portion of the annual suspended solids budget unconstrained

In their report, AlliedSignal/PTI attempted to deal with this lack of high flow data by simply extrapolating the suspended solids curves shown in Appendix B of their report to the higher flow conditions. However, the lack of data leaves this extrapolation essentially unconstrained. It is unclear

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or during the early spring algal blooms when suspended solids concentrations are typically at their highest

These traps were deployed during the summer stratification period when little vertical mixing is present in the lake. In this manner, the epilimnion traps captured the gross settling input to the hypolimnion. In a similar manner, the hypolimnion traps captured the gross settling input to the sediments. The principle purpose of the traps was to measure the occurence of any mercury input to the hypolimnion via the disintegration of falling particles. This process would be detected by a decrease in the measured gross flux of mercury in the hypolimnion trap relative to the epilimnion trap, implying that mercury had been released during the descent through the hypolimnion. This process was labeled "remineralization" by AlliedSignal/PTI. As part of the preparation of this report, the gross settling results were compared for the two sets of trap data. No evidence was found for the loss of suspended solids within the water column of Onondaga Lake. The evidence for the absence of suspended matter loss between the two traps is compiled in Table 2-2. In most instances, the rate of total suspended solids settling remained the same or increased across the hypolimnion as shown by the column entitled "Relative Change in Sediment Trap Flux Between the Hypolimnion and Epilimnion (H-E/E)" for total dry solids. Only the September 23 - October 21 deployment yielded negative values of any substantive magnitude. The data for organic matter were conclusive but no consistent trend was apparent. Also of note here, the rate of total mercury settling increased across all but one set of deployments. This will be discussed later in the section. Based solely on the absence of substantive trends in either total suspended solids or organic carbon, the premise of a remineralization process which involves the destruction of the falling particles within the water column should be dismissed

AlliedSignal/PTI further proposed that a "remineralization" process occurred at the sediment water interface prior to the incorporation of the falling suspended matter within the lake sediments. This argument was based on the reported occurence in Little Rock Lake in Wisconsin (Hurley, *et al.*, 1991) as well as other lakes (Hurley *et al.*, 1994) wherein mercury was shown to be rapidly released from recently deposited and falling particles under anoxic conditions. These lakes were

characterized as having few dissolved solids (*i.e.*, "soft" water), unlike the nearly brackish conditions found in Onondaga Lake. In particular, these studies showed the process to occur while particles fell through the anoxic portion of the lake, a process whose absence in Onondaga Lake was demonstrated by AlliedSignal/PTI's sediment trap data. Nonetheless, AlliedSignal/PTI incorporated a remineralization term in the model, basing it on differences between the gross sedimentation measurements made during the summer and fall periods of 1992 and 1996 against the annual deposition recorded in two dated sediment cores from the sediments at the bottom of the hypolimnion.

However, AlliedSignal/PTI also collected sediment trap data for this purpose in 1996 by deploying traps for variable lengths of time. As is presented in Appendix B of this report, the long-term traps yielded consistently higher rates of gross particle settling to those obtained from the short-term traps although the net gain may be within measurement uncertainty. This indicated the absence of a particle destruction process for very recently deposited sediments (*i.e.*, less than 16 weeks old). Suspended matter present on the lake bottom for a longer period of time would probably be incorporated in the sediment and thereby become part of a longer-term release process. These results indicate that the inclusion of a remineralization process in the model involving recently deposited sediments that is based on the destruction of the particles themselves is completely unsupported by the available data. Evidence for the absence of an extractive mercury release from recent sediment relative to older sediments is examined in Section 2.3. An extractive release refers to the release of mercury from a particle while leaving the particle otherwise intact

Further support for the dismissal of the remineralization process is obtained from AlliedSignal/PTI derivation of the rate itself which is discussed under the internal mercury loads section. As a prelude to that discussion, it can be noted here that the calculation was based on the assumption that annual gross deposition rate was well known and was equal to the summer-to-fall rate (in g/m$^2$-day) determined from the sediment traps. However, as mentioned previously, water column suspended solids concentrations varied significantly over the period April to November. Based on the measured water column inventory, it is unlikely that the summer-to-fall gross

sedimentation rate would apply throughout the year, particularly in spring. Adding to the uncertainty is the lack of constraint for the annual external suspended solids loads to the lake due to the lack of data. Thus, the annual rate of gross deposition is poorly constrained and renders the calculations based on it largely meaningless.

The last issue concerning internal suspended solids loads is the occurence of settling and resuspension of sediment as a result of wind-driven stirring of the lake. Throughout the portion of the year when the lake is ice-free, wind-driven stirring is able to resuspend sediments in the entire littoral zone (*i.e.*, the portion of the epilimnion underlain by sediments). AlliedSignal/PTI contends that this zone sees little net deposition, in part due to this process since, ultimately, the resuspension of sediment will transport them over the portion of the lake underlain by the hypolimnion where wind-driven stirring is much less frequent and permanent sediment storage is more likely. This process is called focusing of lake sediments.

There is general consensus that this process is occurring in Onondaga Lake. However, the time frame for movement of sediment from the littoral zone sediments to the pelagic zone and hypolimnion is not well known. It is highly likely that suspended matter transported from the tributaries is first deposited in the littoral zone, simply due to the substantial change in water velocity which occurs as a tributary's discharge first enters the lake. Over time, wind-driven stirring will probably serve to resuspend and move much of this sediment to the pelagic zone and hypolimnion. The scale of this sediment movement is unknown but is probably on the scale of months to at least several years based on the depth and level of sediment contamination found in several of the littoral zone cores. In the model simulation, resuspension in the littoral zone is set equal to zero, which clearly contradicts this likely occurrence. This parameterization also contradicts the AlliedSignal/PTI sediment trap data collected in the near-shore environment

Sediment trap samples were collected from two littoral zone stations on a quasi-monthly basis. One trap was situated in the littoral zone near the southeast corner of the lake and one near the outfall of Ninemile Creek. Both sets of data yielded gross deposition rates up to seven times greater

than those found in the center of the lake during the same period (PTI, 1993). These data are summarized in Table 2-2 herein and strongly suggest that temporary sediment storage and resuspension in the littoral zone were occurring. In addition, coring data from the littoral zone shows sediment mercury contamination as deep as 14 cm (*e.g.*, core S73-A), suggesting that sediment storage of mercury in the littoral zone is on-going and can provide a ready reservoir of contaminated sediment for resuspension. Both sediment deposition and resuspension processes would be reflected in the gross settling measurements and represent significant processes for the epilimnion solids balance which are unaccounted for in the AlliedSignal/PTI model.

### Suspended Solids Outputs from the Lake

Removal of suspended solids from the lake is accomplished by two principal processes, specifically, lake discharge to the Seneca River and output to the lake bottom. Discharge to the Seneca River reflects the suspended solids concentration associated with the epilimnion. Estimation of this output is limited by the lack of lake discharge data, by the confounding effect of backflow of the Seneca River, and by the absence of suspended solids concentrations for much of the study period. As can be seen in Figure 15 of Appendix A, epilimnion suspended solids concentrations varied nearly an order-of-magnitude in 992, implying that the output from the lake also varied similarly. Thus for the months without data, the actual magnitude of this output is poorly constrained. Because of the countercurrent flow of water from the Seneca River, the measurement of suspended solids at the lake outlet does not provide an accurate estimate of the concentration of suspended solids being transported with the lake discharge. As an approximation, the suspended matter concentration of the pelagic portion of the epilimnion was used by AlliedSignal/PTI since this zone is relatively well mixed and can be thought of as a mean lake condition. This approximation introduces some uncertainty which cannot easily be estimated due to the lack of a direct discharge measurement. Nonetheless, for the period of measurement, this output is considered relatively well

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AlliedSignal/PTI also attempted to measure a "remineralization" flux at the sediment/water interface. An analysis of this data is presented in Appendix B of this report. The results show the absence of any measurable rate of remineralization, given the variability of the data. Most unfortunate in the AlliedSignal/PTI collection effort was the loss of the longest deployed sediment trap. AlliedSignal/PTI also attempted to estimate a "remineralization" flux based on the difference between the mercury concentration in several sediment cores and the hypolimnion sediment traps. However, the uncertainty in the surface sediment concentrations was quite large relative to the concentrations found in the sediment traps and thus the result was not statistically significant. This is shown in Table E-4 of the AlliedSignal/PTI Mercury Modeling Report. Essentially, only three independent estimates were made of this flux based on this comparison (-100, 200 and 600 $g/m^2$-day). The average remineralization rate of 200 $g/m^2$-day is not statistically different from zero and should be disregarded. The analysis itself is flawed as well since it assumes that the gross deposition rates obtained for the summer to fall conditions can be applied throughout the year. As was previously discussed, the annual input of mercury is not a well-constrained flux. This factor along with the poor constraints on annual suspended solids loads and other factors such as sediment resuspension in both the littoral zone and hypolimnion thereby render the assumption of a well-constrained gross deposition rate of mercury inappropriate. On the basis of both data constraints and statistics, it is clear that a remineralization term applied to very recent deposition is not defensible and does not belong in the model

The lack of a demonstrable remineralization flux coupled with the lack of measured sediment diffusive flux as discussed in the section on external mercury loads implies that the mechanism (or mechanisms) for the transfer of mercury to the hypolimnion from the sediments during summer stratification is completely unknown. It is conceivable that groundwater may provide such a transfer but, at least at this point in the analysis, the actual processes is undefined.

The last internal load component for consideration is the lake inventory itself. Changes in the lake inventory of mercury effectively integrate all of the internal and external loads. Thus, measurements of the lake inventory play an important role in constraining the poorly known loads

to the lake. Like the suspended solids budget, data on the lake mercury inventory is only available from April to November, effectively preventing the construction of an accurate annual budget. Inventory estimates prior to April are considered essentially unconstrained.

### Mercury Outputs from the Lake

Mercury output from the lake occurs via three processes; discharge at the lake outlet, volatilization from the lake surface and storage in the sediments of the lake. Discharge at the lake outlet is a function of the discharge flow and the concentration in the epilimnion. Like suspended solids, this discharge is subject to the same data limitations, with no direct measurement of the lake discharge nor of the concentration in the discharge. Like suspended solids, the mercury discharge concentration was approximated by the epilimnion concentration. Also like the suspended solids, data on the discharge rate was only available for April through November, leaving the rate unconstrained for the other months.

The volatilization rate effects only elemental mercury which, based on AlliedSignal/PTI's measurements, represents a small fraction of the water column mercury inventory. The volatilization process is relatively well known. Given the low concentration of elemental mercury and the well-known process of volatilization, it is likely that this process is sufficiently well constrained for use in the model. However, it is subject to the same issue concerning the lack of constraining data outside of the measurement period.

The last major mercury output is the net storage of mercury in the sediments of the lake. This flux represents the largest output of mercury from the lake. AlliedSignal/PTI attempted to estimate this output from dated sediment cores. While each core does provide an estimate of the local storage rate, the applicability of this rate over large areas of the lake is not well established. AlliedSignal/PTI obtained such data at three locations in the deepest portion of lake. Deposition rates in shallower portions of the hypolimnion as well as in the littoral zone are unknown. Thus, the net deposition rate is poorly constrained as well

## Summary

Information on mercury inputs to the lake is limited by many of the same issues that affect the suspended solids budget. Lack of sufficient data, particularly concerning spring runoff loads, prevents construction of an annual budget. No data were obtained to support the contention of a remineralization process and, in fact, nearly all data designed to determine the remineralization rate appeared to prove its absence. This is not surprising given the many geochemical differences between Onondaga Lake and lakes where remineralization was reported. The actual process of mercury transfer between sediment and hypolimnion is unknown. Lastly, the data supporting interactions between the sediments of the littoral zone and the epilimnion have been ignored. Given the demonstrated presence of mercury in these sediments and their availability for resuspension via wind-driven stirring, the model appears to have excluded a potentially important process.

## 2.4 Methylmercury Balance

Processes related to methylmercury have many of the same limitations associated with suspended solids and total mercury as discussed above. These issues are nearly the same for methylmercury and will not be repeated here The largest additional issue pertaining to methylmercury relates to its production in the water column. AlliedSignal/PTI collected several sample sets designed to estimate the rate of methylmercury production but only one set of samples proved useful, *i.e.*, the set collected in September 1996. All of the other analyses were fraught with inconsistencies (positive and negative fluxes) and should be rejected. This leaves just one set of measurements to estimate the methylation process. As completed by AlliedSignal/PTI, the study yields a net rate of methylation. However, net methylation is undoubtedly the resulting balance of gross rates of methylation and demethylation. It is unclear how the net rate *i.e.*, the balance between the two gross processes will respond under varying conditions without additional measurements under those conditions. Presumably gross methylation will respond differently to environmental changes than gross demethylation. This greatly limits the usefulness of the study results.

A second issue pertaining to the methylation rate is the increased concentration of methylmercury on the suspended solids trapped in the hypolimnion sediment traps relative to the epilimnion sediment trap. AlliedSignal/PTI contends that the increased methylmercury concentrations are the result of methylation during the particles' descent. However, an alternative explanation could be that the enhanced methylmercury concentrations are the result of the special environment which exists within the sediment traps. Specifically, other studies have found that the environment created by the trap itself provides an enhanced opportunity for various bacteria. In this instance those bacteria may be responsible for the methylation seen.

## 2.5 Other Considerations

Other factors pertaining to mercury kinetics and thermodynamics are also impacted by the available data. For example, AlliedSignal/PTI attempted to estimate the mercury partition coefficients for the lake based on lake sample results. The range of values was quite large but not inconsistent with other studies. Values of the log of the partition coefficient for total mercury estimated by AlliedSignal/PTI from field data ranged from 4.73 for partitioning to organic suspended solids to 5.62 for partitioning to total suspended solids (see Table 5 of Appendix A). For mercury, typical values for log of the partition coefficient range from 4 to more than 5 (Thomann and Mueller, 1987 and Mason and Sullivan, 1998). The model sensitivity analysis presented in Section 5 in this report examines the inpact of varying the partition coefficients used in the calibration within their measured range.

Other thermodynamic and kinetic conditions, such as kinetic rate constants and speciation multipliers (pp. 15 - 18 of the report), were specified in the model without benefit of site-specific data. These conditions ultimately add uncertainty to the results but the level of uncertainty is typically not well defined.

## 2.6 Summary of Data Limitations for the Model

In summary, water (and chloride), solids, and mercury balances were performed by AlliedSignal/PTI. The balances presented are not considered acceptable for the following reasons:

Apparent inconsistencies in the treatment of the Seneca River backflow, the chloride balance, and lake stratification;

The annual solids balance is not considered appropriate due to the limited solids data for external loads, lake water column inventory, and internal cycling;

No substantive evidence for "remineralization";

The data supporting interactions between the sediments of the littoral zone and the epilimnion have been ignored; and

The annual mercury balance is not considered appropriate due to the lack of sufficient data for external loads, lake water column inventory, and internal cycling

No well suported mechanism for the release of mercury from the sediments to the hypolimnion

# 3. MODEL CALIBRATION

This section discusses the application of the data to the model calibration. As part of this discussion, the parameters chosen for adjustment in the model calibration process will be discussed along with the ramifications of their adjustment. The inability of the model to reproduce the measured trends in lake inventory as well as the direction of the monthly changes is also examined here. Finally, the discussion covers the representation of internal mixing by the model (*i.e.*, mixing of the epilimnion and hypolimnion) and its ramifications for the speed at which mercury and water are replenished in the lake system. These discussions plus those presented in Sections 4 and 5 form a basis to then examine the validity of the conclusions made by AlliedSignal/PTI.

## 3. Water and Suspended Solids

In the calibration of the model, AlliedSignal/PTI first begins with a chloride ion balance to close the water balance for the lake. The assumption for this closure is that the Seneca River provides a source of low chloride ion water with which to dilute the lake's chloride ion concentration. As discussed in Section 2.1, the water balance constructed by AlliedSignal/PTI in this manner does not do a consistent job of reproducing the measured trend in chloride ion, suggesting that the temporal variation of the Seneca River backflow is not accurately represented. However, as also discussed in Section 2.1, groundwater flow is very poorly constrained and could potentially be much larger than the AlliedSignal/PTI estimate. This flow could provide a similar kind of dilution. Relative to the overall water budget for the lake, the importance of the combined Seneca River backflow and groundwater discharge are small (about seven percent based on Figure 2-2). Although the water balance cannot be closed due to the lack of a direct lake discharge measurement, the general understanding of the lake's hydrology is probably sufficient to establish the water budget for this model

As noted in Section 2.2, the model does not contain an independent suspended solids component. Instead the model is simply forced to replicate the measured suspended solids

conditions. In addition, the model uses a mean particle settling velocity based on the sediment trap data. In this regard the suspended solids "calibration" closely replicates the actual conditions within the lake. For the portion of the simulation covered by both water column suspended solids measurements and gross settling data (*i.e.* June to November), the system is relatively well constrained.

The fact that these two budgets are relatively well constrained during this period provides a relatively good basis for a concurrent mercury model synthesis. Beyond this period, however, the constraints on the mercury model are too poor to potentially yield a defensible model interpretation. Very simply, the basic processes responsible for mercury movement within the lake are not sufficiently well known to subsequently constrain the mercury fluxes. This is an important issue since many of the mercury fluxes have little independent constraint (*e.g.*, net output to the sediment) and must be determined from the model.

## 3.2 Total Mercury

The discussion of the calibration of the mercury model will focus on total mercury since it integrates the various forms of mercury and, in general, issues pertaining to total mercury will apply to the other forms as well. In Figure 21 of the AlliedSignal/PTI report, the agreement between measured and simulated total mercury concentrations for both whole water and dissolved concentrations is plotted as a function of date. The representation shows some disagreement between the model and measured results but suggests that the model output falls within the uncertainty of many of the data points. For the hypolimnion, it indicates that the whole water values produced by the model underestimate the actual water column concentration while the model's dissolved concentrations overestimate the actual conditions. This suggests that at a minimum the sediment-to-water partition coefficient is incorrect since one value overestimates the inventory and one underestimates the inventory. The sediment-to-water partition coefficient was discussed in Section 2 as well as in the sensitivity analysis in Section 5

As part of the examination of the calibration, an attempt was made to reproduce the error bars associated with each data point on Figure 21. It was found that this error bar was based on the standard deviation of the entire set of samples collected in each lake section (*i.e.*, epilimnion and hypolimnion) on the day of sampling. This is not an appropriate representation of the uncertainty associated with each of the data points. In fact, the actual uncertainty is much smaller.

The AlliedSignal/PTI samples were collected as part of vertical profiles or surface to bottom sample collection events. Each of the data points shown in Figure 21 represent only two profiles, one for the north basin and one for the south basin of the lake. Because of the way in which the lake stratifies, samples collected as part of a vertical profile do not typically represent point-to point uncertainty but rather the variation in lake properties as a function of depth. Typically, the vertical profiles yield smoothly varying values which are interpreted in the context of the lake layers (*i.e.*, epilimnion, metalimnion and hypolimnion). In this context, each sample along the profile is then interpreted to represent the lake properties at the depth of collection. In this sense, each sample is representative of a slab of the lake volume similar in shape to a bathymetric contour. That is, if as part of a lake profile samples were collected at depths of 1, 3, 5 and 7 meters , then each sample would be considered representative of all water in the lake over a two meter interval, specifically 0-2, 2-4, 4-6 and 6-8, respectively. True estimates of the lake variability can only be made between lake profiles, *i.e.*, samples collected at the same depth.

The profiles obtained by AlliedSignal/PTI in 1992 are plotted in igure 3-1a, b, and c. The profiles represent the variation in the lake total mercury and dissolved oxygen from month to month. Oxygen is shown here since it can be used as an indicator of the epilimnion and hypolimnion layer thicknesses. Readily evident in the diagrams is the close agreement between each pair of profiles. In nearly every case, the profile-to-profile difference is much smaller than the variation within the profile. This close agreement occurs despite the fact that the profiles were collected nearly one mile apart and indicates how rapidly the lake mixes in the horizontal direction. Estimates for the mean epilimnion and hypolimnion inventories would ideally be made using volume-weighted averages for each lake section. Although it is not explicitly stated, AlliedSignal/PTI appears to have set the

epilimnion/hypolimnion boundary at just below nine meters in the lake, based on the depth of the profundal zone. Lacking a more detailed data set on lake volumes by depth, this analysis could not independently prepare volume-weighted averages for each profile and instead simply averaged samples by section. This yields just two points for each date of collection for each lake section but the difference between the two points is a much truer estimation of the uncertainty in the volume inventories.

In Figure 3-2, the model results for the epilimnion are compared with the measurement data. In the top diagram in the figure, the original AlliedSignal/PTI representation of the measurements is shown. Immediately evident in the diagram is a much poorer level of agreement between the model and data than can be seen in Figure 21 of the report. In all but one instance, the model fails to come close to the exaggerated AlliedSignal/PTI error bars. This is discussed in more detail later in this section. In the second diagram, data points representing the individual profile pairs are shown. The closer pairing of these points further emphasizes the poor fit of the model. In the bottom-most diagram, the lake inventory estimates are plotted on top of each other. In some instances, the center of the data point pairs does not correspond to the center of the AlliedSignal/PTI data points. This may result from the failure to consider the individual lake volumes corresponding to the various samples. Although these estimates of lake inventory may be off on an absolute basis, the data point pairs will be biased in the same direction so that they still provide an estimate of error. In each case, except the April pair, the actual difference in the data point pair was less than one quarter of the $\pm$ one standard deviation error reported by AlliedSignal/PTI

A similar set of diagrams was prepared for the hypolimnion which is shown in Figure 3-3 In this instance, the data points pairs appear shifted to higher values in most cases but the relatively close agreement between profiles again indicates that the error bars badly overestimate the uncertainty of the data. Figure 3.3 also underscores the fact that the model presented in the AlliedSignal/PTI report underpredicts the mercury levels for at least six of the eight monitoring events.

Figure 3-4 compares the profile data point pairs with the model runs for both lake layers. This figure is simply a replicate of the middle diagram in Figures 3-2 and 3-3. Besides the model's failure to represent the summer inventories, the diagrams also show the wide range of conditions in the lake during the spring and the general failure of the model to capture these conditions as well. A likely cause of this failure is the fact that no data are available to capture the large tributary flows occurring at the time. The discrepancy between model and measured inventory provides indirect evidence for the importance of these flows to the April inventory as well as to the annual budget for mercury, further emphasizing the importance of the lack of data to the construction of an annual mass balance for mercury in the lake

The failure of the model to replicate summer water column conditions in the epilimnion raises a second issue with the model. Model outputs of mercury to the sediments and hypolimnion are relatively well known during the summer based on the gross sediment trap data for the hypolimnion and epilimnion. Similarly, output from the lake to the Seneca River is relatively well known since it is essentially proportional to epilimnion concentration and total lake discharge. Input to the lake during the summer months via tributaries is also believed to be well known based on AlliedSignal/PTI's monitoring data. Thus the failure of the model to reproduce the measured trend is probably not due to errors in these terms. Instead, the results suggest that an additional mercury load exists to the epilimnion which has not been well characterized by AlliedSignal/PTI and probably originates within the lake (*i.e.*, the sediments) since the other major inputs and the two major outputs are relatively well constrained by data during this period. The scale of the additional load is not trivial since the water column inventory is off by roughly a factor of two. This implies that a load equivalent to the tributary+Metro inputs may exist, driven by a mercury inventory internal to the lake. Sediment diffusion, groundwater discharge and resuspension of sediments are all likely candidates. Alternatively, it is also possible that the estimates of the known fluxes are in error but the scale of the discrepancy appears to be too great to result solely from errors in these estimates

A similar level of discrepancy exists for the hypolimnion simulation. Again, the known loads are relatively well constrained but the inventory is again off by a factor of two. There is no clear

evidence of remineralization, and that process has been largely dismissed. However, some other process is causing a flux of mercury to the hypolimnion similar in magnitude to the value which AlliedSignal/PTI attributed to remineralization. Such a flux must exist in order to create the water column inventories measured

The failure of the model to replicate the inventory during the summer suggests that the model has a major flaw in its design or calibration. This is further emphasized when examining the month to month changes. Figure 3-5 compares the matched inventory data and model results with the month to month change in inventory for each lake layer. Note that the data points represented in the figure were provided by AlliedSignal/PTI in a computer file entitled LAKE.OBS which was supplied along with the model and are not the averages of the lake samples calculated for this report. In the lower diagrams of Figure 3-5, the month-to-month changes by measurement and model estimate are represented in the bar graphs. For the epilimnion, the scale and direction of the measurement bars are very poorly matched by the model, indicating that the model is clearly out of step with the timing and scale of the processes actually controlling the epilimnion inventory. Conversely, the hypolimnion bar graph indicates that the model tends to replicate the direction of change in the hypolimnion but not the scale. The hypolimnion results suggest that the *ad hoc* flux now represented as remineralization in the model has approximately the correct timing but not the right scale. The epilimnion results are further evidence that the epilimnion fluxes are not properly constructed or, more likely, that a major one has been missed. In both instances, it is clear that the model does not constitute a good representation of the data

## 3.3 Methylmercury

Methylmercury inventories were examined in the same manner as total mercury. Figure 3-6 contains a set of plots similar to those in Figure 3-5. The differences between the model output and measured inventories are less pronounced for both the epilimnion and hypolimnion. However, predicted epilimnion methylmercury levels are still nearly fifty percent too low for the summer period. The large change in the methylmercury inventory in the diagram corresponds to the fall

turnover. Note that the model does not match the direction of change nor the inventory for November at all. Model hypolimnion inventories appear to be 30 to 50 percent too low in most cases, although the model again appears to have captured the direction of change as it did for total mercury in the hypolimnion

Figure 3-7 shows the relationship between the measured lake inventories and the model simulation for both methylmercury and total mercury. For the epilimnion, both the measured and model results maintain a relatively constant ratio, with methylmercury comprising only a very small component of total mercury. Note that the model fails to capture the November inventory trend for both forms of mercury. The hypolimnion trend is better captured and the parallel growth of total and methylmercury is seen in both the measured and model results. It is interesting to note the difference between the peak summer and April inventories. In particular, the April inventory is largely devoid of methylmercury, suggesting that the lake inventory at that time was generated via a different source of mercury relative to the summer inventory

Overall, for both forms of mercury the model falls short of accurately representing the lake inventories, predicting consistently lower levels than actually occur in the lake. The problem is much greater for total mercury than for methylmercury, but neither calibration is acceptable

The inability of the model to match lake inventories, and therefore lake concentrations, for both total mercury and methylmercury has a direct consequence for the biological model component. The bioenergetics model uses the geochemical model output as input to drive the calculation of mercury uptake by the biota. Because the geochemical model output is consistently too low relative to the actual measured concentrations, the driving concentrations for biota uptake are too low as well. Given the relatively large discrepancy between model and measured mercury values for the epilimnion in particular (*e.g.*, May - September measured methylmercury values range from 0.022 to 0.04 ng/L *vs* model values of 0.014 to 0.017), it is clear that the output from the bioenergetics model can not be considered meaningful. As a result, the bioenergetics model was not reviewed in this report

## 3.4 Residence Time and Internal Exchange

As part of the review of the model calibration, the internal workings of the model were examined. As a first step, the residence times of water and mercury in the lake were calculated based on the model output and input files. Residence time is defined here as the time require to replace the entire lake water volume or lake mercury inventory utilizing external lake loads only. If additional internal cycling occurs via gross exchange, between water and sediment for example, this serves to shorten the actual residence time. Thus each estimate generated here represents a maximum residence time for the parameter. Residence time provides a useful insight of the importance of various fluxes to maintaining the lake inventory. If a parameter has a long residence time in the lake, then external fluxes can only slowly change the inventory. Conversely, the inventory of a short residence time parameter is driven by the dynamic balance of the inputs and outputs and thus is very sensitive to errors in these fluxes. The purpose of this exercise then is to evaluate total mercury in this context.

Based on lake flows and the whole lake volume, water residence times are estimated to vary between two and four months as shown in Figure 3-8. The shortest residence time occurs in April as expected when tributary flow rates are at their highest. Mercury residence times were calculated based on the ratio of the volume-weighted measured mercury concentration in the lake to the flow-weighted mean mercury concentration of the incoming flows for each month for the same time period as reported by AlliedSignal/PTI. The ratio of these two concentrations was then multiplied by the water residence time to yield a mercury residence time. Essentially, the flow-weighted average concentration of the incoming water was about 18 ng/L while the volume-weighted mean lake concentration was 4.5 ng/L. Thus, for every volume of water purged from the lake by the tributary flows, approximately 4 masses of mercury were purged. Thus, the residence time of mercury relative to water was about four times shorter. This is also shown in Figure 3-8.

Since no data are available to constrain the early and late parts of the calibration run, this discussion will focus on the summer-to-fall period. As noted above, the model was inaccurate even

during this period so the residence times are not absolute. Nonetheless, the result points out that mercury residence times in the lake are substantially shorter than those for water. Thus, the mercury inventory in the lake, particularly in the summer represents the net yield of loads and losses to the lake over a relatively short period of time, *i.e.*, a few weeks to a month. Due to the rapid replacement of mercury in the water column relative to water there is little "inertia" in the mercury water column level and changes in mercury represent recent changes in the mercury loads and internal cycling. This further illustrates the concern with the underestimation of the mercury inventory by the model since this underestimation is most likely the result of an undetermined flux or an inaccurate flux estimate.

The issue of residence time was further explored based on model output for both the hypolimnion and the epilimnion. These calculations are represented in Figure 3-9. Unlike the whole lake balance, the residence time in each lake layer is subject to additional internal mixing as defined by the vertical dispersion term which serves to move water, solids and mercury between the two layers. The two diagrams in Figure 3-9 show the greatly increased water residence time for the hypolimnion which results from the summer stratification. Within the model, vertical dispersion is set to zero during the summer months, thereby cutting off the hypolimnion completely except for tributary inputs which are directed to the hypolimnion by the model. This construct does enable some vertical displacement of hypolimnion water into the epilimnion but does not permit the reverse. This limitation is strictly a model construct since some level of vertical exchange is believed to occur all year. Consideration of the individual lake layers shows the substantially greater level of variation in residence time for the hypolimnion relative to the epilimnion and the lake as a whole.

The two diagrams in Figure 3-9 also point out the impact of the vertical mixing assumptions made by AlliedSignal/PTI during the rest of the year. The top diagram shows that when the vertical mixing term is considered, water residence times in each lake layer are extremely low outside of summer and yield a minimum residence time in mid-winter. This construct is probably incorrect since some stratification is believed to occur in the lake over the winter although it is not as strongly stratified as in summer. This stratification should serve to increase residence times relative to spring

conditions. Minimum residence time are expected in spring when both tributary flow and vertical mixing are greatest. Vertical mixing reaches a maximum value in spring as the lake becomes isothermal throughout its depth, permitting wind-driven stirring to extend to the lake bottom. When the vertical mixing term is excluded as shown in the lower diagram of Figure 3-9, the residence time variation over the year appears more reasonable.

Figure 3-10 shows the relationship between total tributary flow and the vertical mixing rate as set by the model calibration run. Over the course of a year, the vertical mixing rate is varied from effectively zero to nearly 7,000 cfs ($1.8 \times 10^{10}$ cf/month). In the latter case this exchange dwarfs the tributary inflow and is set to occur during winter months. This would appear incorrect since spring and fall turnover must be the true vertical mixing maxima due to the lack of thermal stratification that occurs then. In addition, the rate of vertical dispersion is nearly ten times the tributary inflow, yielding residence times in the lake layers of less than a week as shown in the top diagram of Figure 3-9.

The vertical mixing term for winter conditions is almost certainly incorrect although the data set lacks any useful data to better constrain vertical mixing in the lake over the winter. Nonetheless, the value chosen for winter conditions is clearly counterintuitive and makes all model results for this period suspect since it will have a significant impact on the internal cycling of mercury in the model.

## 3.5 Summary

Model calibrations for water and solids were fairly successful for the limited period of measurement (summer to fall). The water balance was relatively well constrained by the available tributary discharge data although the Seneca River backflow did not appear to be applied correctly over time. The solids balance was accomplished by a force fit to the data . Model analysis outside this period is relatively unconstrained and largely represents speculation.

The representation of uncertainty in the lake inventory data was done incorrectly. Based on an examination of lake profiles, the actual uncertainty was perhaps one quarter of the range represented in the original AlliedSignal/PTI diagrams. This incorrect presentation of data uncertainty serves to misrepresent the accuracy of the model.

Calibration of the mercury model results was less successful than the other two balances. The total mercury inventory for the epilimnion was underestimated by the model by nearly 50 percent for most of the summer period. Similar underestimation was found for total mercury in the hypolimnion. The size and direction of month-to-month variation in the epilimnion was poorly represented by the model, suggesting that a substantive flux is missing or incorrectly represented by the model. The direction and magnitude of changes in the hypolimnion were better reproduced by the model as compared to the epilimnion result. This suggests that the hypolimnion loads are correctly sequenced but one or more are underestimated in size

The calibration did better for methylmercury as a whole relative to total mercury. Still methylmercury inventories were underestimated by about one-third throughout the period of simulation The direction and scale of the methylmercury changes from month-to-month were consistent with the measured trends in most months.

The model consistently underestimates nearly all forms of mercury even during the relatively well constrained summer-to-fall period. It would appear that much of this shortcoming is the failure of the model processes to better consider sediment-driven fluxes such as resuspension in the littoral zone, direct sediment release or resuspension in the hypolimnion and groundwater advection of porewater into both layers

An examination of the water and mercury residence times for the lake as a whole and for the two main lake layers indicated that mercury is rapidly displaced from the lake by the internal processes. Lake inventories of mercury are purged roughly four times for every volume of water purged. Water residence time reaches a maximum in summer in the hypolimnion as would be

expected due to stratification. Because of the incorrect assignment in the model of maximum vertical mixing rates to winter months, minimum residence times are not achieved during April high flows as would be expected. This error probably renders the winter model simulation results useless. Similarly, vertical mixing is set too low in the summer. However, this error cannot be responsible for the overall underestimates in mercury inventory produced by the model since internal mixing does not introduce additional mercury to the system so as to raise the overall inventory.

# 4. MASS BALANCE

The discussion of the mercury mass balance for the lake is based on the model output produced by the AlliedSignal/PTI model from the calibration input file (CALIB.INP). The mass balance presented in the AlliedSignal/PTI modeling report is given on an annual basis. As discussed extensively throughout this report, it is inappropriate to construct such a balance given the lack of constraints for the early part of the year. For this reason, this discussion will describe the mass balance results only for the period May through November when external loads, internal inventories and internal cycling are relatively well known and constrained by measurements

As a first step in assembling the components of the mass balance, it is useful to examine the water balance to which components contribute the greatest quantity of water to the lake. Figure 4 is a replicate of Figure 2-2 and shows the proportions of the tributary inflows on an annual basis. The top diagram in the figure presents the inflows, the lower figure presents the outflows. Evident in the top diagram is the approximately equal contributions of Onondaga and Ninemile Creeks, roughly in proportion to their drainage areas. Metro is the next largest contributor of water. Outflow from the lake is clearly dominated by flow out to the Seneca River as would be expected. The flow balance for May through November is very similar to the annual balance and is shown in Figure 4-2. The inflows and outflows are again dominated by the same major contributors as the annual budget as expected

When the mercury mass balance is examined in the same manner, the relationships among the tributaries change markedly The upper diagram in igure 4-3 represents the loads from tributaries alone. The portion assigned to Ninemile Creek jumps up drastically relative to flow to nearly 50 percent of the total tributary loads This is expected given the presence of the AlliedSignal facilities in its watershed. The next biggest contributor is the Metro plant at just under a third of the load. When the tributary component is compared with the rest of the inputs to the lake as compiled by AlliedSignal/PTI in the lower diagram in Figure 4-3, it is still clearly the largest one. However, it is important to keep in mind here that the model run on which this pie chart is based does not

reproduce the lake inventory. The analyses presented in Sections 2 and 3 suggest that a relatively large flux of mercury is unaccounted for. Based on the fact that the model-based mercury inventories in the lake typically underestimate the lake inventory by 40 to 50 percent, it would appear that a load of the scale of 50 to 100 percent of the combined tributary load is missing. For this reason it is likely that the overall importance of the tributaries to the lake mercury inventory is overstated by this diagram. Given the relatively tight constraints on the tributary loads during this period, it is likely that the sediments are the source of this additional load. However, the mechanism or mechanisms for this transfer to the water column are not well known but probably include resuspension, based on the sediment trap data obtained by AlliedSignal/PTI for the littoral zone

In their discussion of the total mercury mass balance for the lake, AlliedSignal/PTI assert that atmospheric deposition is the major source of mercury to the lake and its tributaries. This assertion conflicts with many of the current measurements on the importance of atmospheric deposition in similar settings (*e.g.*, Mason and Brooks, 1997; Mason *et al.* 1997). An upper bound on the atmospheric component of the mercury loads to the lake can be obtained from the data collected by AlliedSignal/PTI. An examination of the yields of mercury per unit area of watershed reveals that upper Ninemile Creek and Ley Creek have the lowest yield of mercury per unit area, approximately 3.5 g/ $km^2$-yr or 3.5 $\mu g/m^2$-yr. Assuming an annual atmospheric deposition rate for the region of around 20 $\mu g/m^2$-year, this runoff rate would represent a yield of just under 20 percent of atmospheric deposition. This value falls between the yield rate obtained by Mason and Brooks (1997) and Mason *et al.* (1997) for urban and rural runoff rates. The yield rate of 3.5 $\mu g/m^2$-year can then be compared with the other tributaries to estimate their local anthropogenic input. This is shown in Table 4- The results show that at least 79 percent of the Ninemile Creek load is a local anthropogenic input based on the period May through November. Similarly, 24 percent of Onondaga Creek and 55 percent of Harbor Brook's mercury load appears to be locally derived.

The Metro plant's load requires some additional computation to obtain an upper bound in its local component. Because its drainage area largely consists of paved areas, it is likely that most of the atmospheric deposition is washed into its collection system by rainfall. Thus its input load is

closer to the 20 $\mu g/m^2$-year value suggested for direct atmospheric deposition. Given its annual load to the lake of 3.3 kg/year, the atmospheric component would represent about 16 percent, indicating that 84 percent of its load was derived by local anthropogenic inputs. This is an upper bound on the atmospheric component since it assumes that all of the atmospheric input is subsequently released to the lake. Given that Ninemile Creek and Metro are the two largest contributors of mercury to the lake, it is clear that the majority of the mercury load to the lake is locally derived and not the result of atmospheric deposition, indirect or otherwise.

Mass balance results were also compiled for methylmercury as shown in Figure 4-4. The diagrams in the figure correspond to those of Figure 4-3 with the upper diagram showing only tributary loads and the lower diagram summing all external loads. Again the tributary component is the largest component of the entire external load summation. However, this time, the Metro plant is the largest single tributary. In examining the total load diagram, a substantive sediment flux is seen. It is inappropriate to interpret very much from the methylmercury balance, however, knowing that the total mercury balance is incomplete. It is unclear how the lower diagram would change if total mercury were more accurately represented.

AlliedSignal/PTI attempted to measure net methylation in the water column on several occasions and did manage to obtain one set of values for this flux. Based on this value, internal methylmercury production was estimated as part of the modeling effort. The results for their calibration run are summarized in Figure 4-5. The top diagram is a bar chart showing the month-to-month fluxes for methylmercury for the whole lake. Evident in the diagram are two predominant fluxes, net water column methylation (labelled "methylation") and particle settling (labelled "settling"). These results suggest that water column methylmercury levels are principally controlled by the balance between these two fluxes. In the last month of simulation, the model shows a large uptake of methylmercury by fish but at the same time fails to mimic the measured trend so this flux may not be valid.

In the lower diagram, the measured methylmercury inventory in the hypolimnion is plotted with the model run. This result shows that the model is consistently underestimating methylmercury as was discussed in Section 3. If the methylation rate measured by AlliedSignal/PTI is accurate, then the results suggest that another methylmercury load is present, perhaps related to the missing total mercury flux or simply due to an underestimate of the sediment flux already represented in Figure 4-4

## Summary

A mass balance for the lake was constructed solely for the period May through November since data are insufficient to construct a mass balance for the whole year. Mass balance results for the AlliedSignal/PTI model run show the importance of the known major mercury contributors to the lake, Ninemile Creek and Metro. Ninemile Creek is the major contributor of total mercury while Metro is the largest external source for methylmercury. Atmospheric deposition was shown not to represent the major source of mercury to the lake based on yields from background tributaries. The calculation points out the continued importance of local mercury release to the lake. Internal generation of methylmercury appears to be the single largest source of methylmercury to the lake but the estimate is based on a single measurement. Methylmercury output from the lake appears to occur chiefly by settling to the sediments at the lake bottom. Since AlliedSignal/PTI measured net methylation and not gross rates of methylation and demethylation, it is unclear how methylmercury levels will respond to changes in lake conditions

# 5. MODEL SENSITIVITIES

As stated by AlliedSignal/PTI (1997), the objective of a model sensitivity analysis is to evaluate the effects of individual input parameters on model results. An attempt was made by AlliedSignal/PTI to vary many of the internal parameters and, in some cases, loadings to match the model to the observed data (*i.e.*, model calibration). The model sensitivity analysis performed by AlliedSignal/PTI included internal parameters such as mercury partition coefficients, water column methylation rates, and remineralization rates, as well as a loading term, specifically sediment flux. AlliedSignal/PTI performed the sensitivity analysis by modifying these four parameters by ±10% and ±20%, compared to the values used in the model calibration. AlliedSignal/PTI concluded that the model results for total mercury water column concentrations were slightly to moderately sensitive to changes to partition coefficients, insensitive to both sediment flux and net methylation rate, and slightly sensitive to remineralization rate (PTI, 1997a, Table 13). For methylmercury water column concentrations, the model results were moderately to very sensitive to partition coefficients, insensitive to sediment flux, slightly to moderately sensitive to net methylation, and slightly sensitive to remineralization. However, the sensitivity analysis performed by AlliedSignal/PTI is insufficient since the model parameters are frequently not known to an accuracy greater than 50 percent and the sensitivity analysis does not consider a wide enough range in the parameter values.

To evaluate the effects of a larger range in parameter values supported by the data and/or literature, a limited sensitivity analysis was performed by TAMS. Table 5-1 summarizes the changes to the calibration input file for each model sensitivity run. The parameters and loads modified herein include the same parameters modified by AlliedSignal/PTI (partitioning, sediment flux incorporating possible remineralization, and methylation). In addition, groundwater and atmospheric loadings, specified as external mass inputs to the model, were modified in this sensitivity study. The values specified in the calibrated model for each parameter or loading are summarized in Table 5-1 as well as the modified values used in the model sensitivity runs. Comments are provided in the table indicating the basis for each modification.

The results of the different model sensitivity runs are presented by a series of graphs (time vs. concentration) and mass balance tables, for both total mercury and methylmercury in the water column. These graphs and tables were produced directly from the OLMM post-processor without any modification. Figures 5-1 and 5-2 generally reproduce the model calibration as documented by PTI (1997a), as no modifications were made to the calibration input file. Also, the mass balance tables for the calibrated model are included herein as Tables 5-2 and 5-3 for total mercury and methylmercury, respectively. The monthly and annual (1992) masses (g/day) of the different sources (*e.g.*, tributary and Metro surface water inflows, atmospheric deposition, groundwater inflows, and sediment flux) and sinks (*e.g.*, outflow, volatilization, and settling) are included in the tables. The annual masses (kg/year) of the different sources and sinks for both total mercury and methylmercury, as presented in Table 11 of the OLMM Report (PTI, 1997a), are reproduced in Tables 5-2 and 5-3 herein. A discussion of the model calibration inadequacies is provided in Section 3 of this report. The model sensitivity results are compared to the calibration results as described below.

As indicated in Table 5- , the first model sensitivity run consisted of a modification of the groundwater source terms. The weekly loadings of ionic mercury and methylmercury to the littoral zone (model segment 2) which are included in the calibration input file were increased by a factor of ten. The mercury concentration in groundwater specified by AlliedSignal/PTI was for remote areas or at waste bed areas "unaffected by mercury contamination." An ambient background concentration of total mercury of 4 ng/L was used to calculate the loading. This value is mainly based on mercury concentrations in surface water in Bloody Brook and Sawmill Creek during periods of low flow, suggestive of a groundwater discharge period (PTI, 1997, Appendix D). It should be noted that both of these creeks are on the northern side of the lake, whereas mercury concentrations in other creeks around the lake exhibited higher concentrations also during periods of low flows. Thus, to conservatively account for potentially more contaminated inflow, the groundwater loading inputs were increased by a factor of ten (*i.e.*, 4 ng/L to 40 ng/L at the same flow). No other modifications to the calibration input file were made. The results for this model run for total mercury and methyl mercury are shown in Figures 5-3 and 5-4, respectively. The mass inputs and model-calculated sinks for total mercury and methylmercury are included as Tables 5-4

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on AlliedSignal/PTI's calibration and -7.6 g/day for run 2). Also, with the resultant increase in methylmercury concentrations, the amount "processed by fish" approximately doubles. Thus, the model output is very sensitive to the range of the partition coefficients that can be expected to occur in the lake.

Model sensitivity runs 3 and 4 consisted of modifications of the average annual methylation rate specified by AlliedSignal/PTI in the calibration file. The value used in the calibration input (0.035/day) was increased by a factor of ten (model run 3) and also decreased by a factor of ten (model run 4) based on the range of the 1996 measured values as specified by AlliedSignal/PTI (AlliedSignal/PTI, 1997, Table 2). The predictions for total mercury and methylmercury for model run 3 (methylation rate increase) are shown in Figures 5-7 and 5-8, respectively. As compared to the calibration, the peak total mercury concentrations show a moderate increase whereas methylmercury concentrations show a significant increase. The mass balance tables for model run 3 are included as Tables 5-8 and 5-9. As indicated in Table 5-9 for methylmercury, the "kinetics" annual average mass increased by a factor of about three (6.2 g/day) when compared to the calibration results (1.8 g/day, Table 5-3). Also, the amount processed by fish increased. A decrease in the methylation rate by a factor of ten (model run 4) had the opposite effect, as shown in Figures 5-9 and 5-10 and Tables 5-10 and 5-1 Thus, the model can be considered very sensitive to modifications of the average methylation rate.

Model sensitivity run 5 consisted of changes in the sediment flux terms specified by AlliedSignal/PTI in the calibration file. Weekly sediment loadings (kg/day) to the water column are specified for both ionic mercury and methylmercury as input to both the littoral zone segment of the epilimnion (model segment 2) and the hypolimnion (model segment 3). A summary of the range of values used in the calibration as well as the sensitivity run is included in Table 5-1. Sediment flux values were increased by roughly two orders-of-magnitude (*i.e.*, a factor of 100) to incorporate the magnitude of the load which AlliedSignal/PTI ascribed to "remineralization" into the sediment flux term. As shown in Figure 26 of the OLMM Report (PTI, 1997a), the remineralization term which was specified for total mercury (3.8 kg/year) is nearly two orders-of-magnitude greater than the

sediment flux term (0.069 kg/year). The model results for total mercury and methylmercury when the sediment flux term is set equal to the flux which AlliedSignal/PTI specified as "remineralization" are shown in Figures 5-11 and 5-12. This results in a doubling of the rate of re-release of mercury to the water column from the sediments and settling particles. Model predictions for both total mercury and methylmercury show a significant increase in water column concentrations, especially for the hypolimnion, when compared to the calibration results. The mass balance tables for this run are included as Tables 5-12 and 5-13 herein. As indicated in Table 5-12 for this run and Table 5-2 for the calibration, the annual sediment flux for total mercury increased from 0.19 g/day to 19 g/day, consistent with the changes in the input file. The sediment flux (source term) in this model run (19 g/day) is approximately one-half of the model-predicted settling flux (sink term, 37 g/day), whereas the sediment flux in the calibration (0.19 g/day) is less than 1% of the model-predicted settling flux (23 g/day). Thus, the model is very sensitive to the sediment fluxes specified by the modeler. Given the absence of data for remineralization, this sensitivity points out the need for an accurate estimate of the scale and mechanism of the sediment release.

Atmospheric loadings directly to the lake surface were modified in model sensitivity run 6 as indicated in Table 5-1. For ionic mercury, wet and dry deposition is specified as a loading to the epilimnion, which includes both the littoral zone (model segment 2) and the pelagic zone (model segment 1). For methylmercury, wet deposition is specified to both segments. All values were decreased by 50 percent as indicated in Table 5- . Results for this simulation are shown in Figures 5-13 and 5-14 and Tables 5-14 and 5-15. Only very slight decreases in water column concentrations are noted when compared to the calibration results. As indicated in Tables 5-2 and 5-14, the annual atmospheric mass inputs for total mercury for the calibration run and this sensitivity run are approximately 1.2 g/day and 0.6 g/day, both representing only a minor fraction of the total inflow load from tributaries and Metro estimated by AlliedSignal/PTI (28 g/day). Thus, the model is not very sensitive to a 50 percent reduction in direct atmospheric loading to the lake.

# 6. SUMMARY AND CONCLUSIONS

The mercury model developed by AlliedSignal/PTI contains a large number of parameters and processes which must be estimated in order to make the model yield useful information. Overall, the model's development and usefulness were severely limited by the lack of annual loads for the lake as well as the lack of data on lake conditions covering a 12-month period. In addition, no data on lake conditions were obtained outside the year of study (1992), thereby also limiting the certainty with which the observations seen in 1992 can be applied to other periods (*i.e.*, no model verification was performed). Internal cycling of mercury as well as sediment-related loads were poorly constrained due to lack of appropriate data or unsuccessful laboratory studies of the sediment processes. AlliedSignal/PT attempted to fit the model to the available data but were largely unsucessful in replicating measured lake conditions for total mercury. The model results were somewhat better for methylmercury although the discrepancies between model and measured conditions were still not acceptable. Review of AlliedSignal/PTI's use of the data revealed a questionable application to estimate measurement uncertainty as well as the apparent failure to review evidence which indicates the absence of a "remineralization" flux. Mass balance calculations prepared by AlliedSignal/PTI based on the model were shown to be of questionable value due to the failure of the model to accurately represent the measured lake inventories. The results suggested the presence of a substantial mercury flux to the epilimnion which was currently unaccounted for in the model mechanisms.

The model is limited in its usefulness primarily by the lack of data to define annual TSS and mercury loads and to define the internal cycling of mercury. For this reason, the model cannot be relied upon to accurately define the impacts of changes in external loads to the lake's mercury cycle. In particular, the rate of internal mercury release from the sediments is defined only on the basis of the change in hypolimnion inventory. Thus, it is difficult at best to accurately predict the response of the lake system as a whole to changes in the external loads (e.g., Ninemile Creek remediation). Mercury residence time in the sediments is not well known. In total, one of the major objectives for

the construction of this model, *i.e.*, the ability to predict future conditions under various hypothetical conditions, has not been met.

The following is a short, bulleted list of the major conclusions of this report:

Deficiencies in the suspended solids data present a major impediment to the construction of an annual suspended solids balance. These deficiencies include the lack of suspended solids data for external loads during high flow conditions, absence of lake inventory data prior to April or after November and lack of internal cycling data such as gross settling before June or after November.

Sediment trap data collected by AlliedSignal/PTI provide no evidence for the destruction of falling particles in the water column or at the sediment/water interface.

Only a limited data set is available to characterize the net sediment deposition rate. In addition, recent changes in the rate of sediment deposition are not accounted for in the net sedimentation rate estimates used in the model.

Processes affecting the suspended solids and sediments in the littoral zones of the lake, such as resuspension, are not accounted for in the model, despite evidence for their existence.

The available data on tributary flow and lake inventory are insufficient to permit an accurate estimation of the mercury budget for the lake during spring runoff events.

No evidence of a remineralization process was found in sediment trap data comparing epilimnion and hypolimnion gross settling, in sediment trap data collected

near the sediment/water interface over variable deployment periods nor in a comparison of sediment and suspended matter mercury concentrations.

The representation of the measured lake inventories in the various model calibration plots (i.e., AlliedSignal/PTI's figure 21) is incorrect. Except for the month of April, the actual uncertainty is perhaps one quarter of the error bar range represented in the diagrams. This incorrect presentation of data uncertainty serves to misrepresent the accuracy of the model.

The failure of the model calibration to accurately reproduce water column total mercury inventories and the direction of the month-to-month variations for the epilimnion strongly suggests that one or more additonal substantive loads exist which are not reflected in the model processes. The short residence time for mercury in the lake relative to water indicates that this missing load or loads is an important part of maintaining the water column inventory of mercury.

The model also fails to reproduce water column inventories in the hypolimnion by nearly a factor of two although the month-to-month changes in the measured and model inventories suggest that the timing of the hypolimnion loads is relatively accurate, as compared to the epilimnion results.

Internal mixing betwen the epilimnion and hypolimnion is inaccurately represented in the model, with maximum vertical mixing occuring in winter when the lake should be partially stratified. Peak vertical mixing should occur during spring and fall turnover when the lake is isothermal.

Mass balance results for the lake are limited in their usefulness due to the model's inability to accurately represent lake inventories even for the May to November period.

Mass loading estimates for many fluxes such as groundwater transport of mercury and sediment diffusion are based on little data or ambigous (at best) laboratory studies, leaving these flux estimates poorly constrained as a basis for constructing a mass balance.

Mass balance considerations for atmospheric deposition to the lake watershed indicate that atmospheric deposition is not the most important mercury load to this system and that local inputs constitute the major external source of mercury to the lake.

Model sensitivity analysis was redone using a wider range of reasonable values for some of the internal parameters and loadings. The analysis indicated that water column concentrations of mercury were moderately to very sensitive to changes in partition coefficients, methylation rates and sediment flux, the latter flux comparable to the original rate of "remineralization" reported in PTI (1997a).

The mercury model does not effectively simulate the concentrations of types of mercury in the water column of Onondaga Lake using the 1992 field investigation database. The errors range from 33 percent to more than 50 percent.

The primary external source of total mercury to the lake is not atmospheric deposition to or runoff from the drainage basin, but discharge from Ninemile Creek and Metro which reflect local anthropogenic input.

The contention that net methylmercury production in the hypolimnion provides approximately two-thirds of the methylmercury input to the lake cannot be substantiated due to the inability of the model to balance the major mercury inputs and outputs to the lake.

The flux of the mercury species to the hypolimnion is primarily from the sediments of the hypolimnetic zone although the mode of transfer is unclear. No evidence for water column or near-surface remineralization could be obtained from samples designed to measure just such a flux.

# REFERENCES


Ambrose, R. B., T. A. Wool, and J. L. Martin.1993. *The Water Quality Analysis Simulation Program, WASP5 Part B: The WASP5 Input Dataset. Version 5.0.* Environmental Research Laboratory, and AScI Corporation, Athens, GA. USEPA. May 31, 1993.

Ambrose, R. B., T. A. Wool, and J. L. Martin.1993. *The Water Quality Analysis Simulation Program, WASP5 Part A: Model Documentation* Prepared by the Environmental Research Laboratory, and AscI Corporation, Athens, GA. USEPA. May 31, 1993

Bopp, R.F., H. J. Simpson, B.L. Deck, 1985. Final Report to NYSDEC: Release Of Polychlorinated Biphenyls From Contaminated Hudson River Sediments. Prepared by Columbia University. June 30, 1985.

Effler, S. W., and Carol M. Brooks. 1998. Dry Weight Deposition in Polluted Onondaga Lake, New York, USA. *Water, Air, and Soil Pollution.* In Press.

Gailani, J., C. K. Ziegler, and W. Lick. 1991. Transport of Suspended Solids in the Lower Fox River. *J. Great lakes Res.* 17(4):479-494.

Hewett, S. W. and B.J. Johnson. 1991. Fish Bioenergetics Model 2: An Upgrade of a Generalized Bioenergetics Model of Fish Growth for Microcomputers. University of Wisconsin Sea Grant Institute. Madison, NJ.

Hurley, J. P. *et al.* 1994. Cycling of Mercury Across the Sediments - Water Interface in Seepage Lakes. *Environmental Chemistry of Lakes and Reservoirs.* ACS. 425-449.

Hurley, J. P., C. J. Watras, N. S. Bloom. 1991. Mercury Cycling in a Northern Wisconsin Seepage Lake: The Role of Particulate Matter in Vertical Transport. *Water, Air, and Soil Pollution.* 56:543- 551.

Larson, T. 1997. Letter to Alfred J. Labuz, Allied Signal, Inc. Solvay, NY. Re: Onondaga Lake RI/FS (734030) - Draft Mercury Modeling Report, June, 1997. December 12, 1997.

Martin, J. L.1992. *Draft: Mercury Transport and Kinetics Model Beta Test Version 1.0, Model Theory and User's Guide.* AscI Corp. for USEPA. July 22, 1922.

Mason, R. 1998. Personal Communication to Kevin C. Murphy, Devorsetz, Stinziano, Gilberti, Heintz, and Smith, PC. Re: Onondaga Lake RI/FS Mercury Modeling Report, June, 1997. February 27, 1998.

Mason, R. P. and K. A. Sullivan. 1998. Mercury and Methylmercury Transport Through an Urban Watershed. *Water Resources*. 32:321-330.

Mason, R. P., N. M. Lawton, and K. A. Sullivan. 1997. Atmospheric Deposition to the Chesapeake Bay Watershed - Regional and Local Sources. *Atmospheric Environment*. 31:3531-3540.

PTI Environmental Services. 1998. *Technical Memorandum: Response to NYSDEC 1/28/98 Comments on the Onondaga Lake Remedial Investigation Mercury Modeling Report*. Prepared for Allied Signal, Inc. Solvay, NY. February, 1998.

PTI Environmental Services. 1997a. *Onondaga Lake RI/FS Mercury Modeling Report*. Prepared for Allied Signal, Inc. Solvay, NY. June, 1997.

PTI Environmental Services. 1997b. *Onondaga Lake RI/FS Supplemental Mercury Methylation and Remineralization Studies Data Report*. Prepared for Allied Signal, Inc. Solvay, NY. June, 1997.

PTI Environmental Services. 1993. *Mercury and Calcite Mass Balance Investigation Data Report, Vol. 1. Onondaga Lake RI/FS*. Prepared for Allied Signal, Inc. September, 1993.

Thomann, R. V. and J. A. Mueller. 1987. *Principles of Surface Water Quality Modeling and Control*. Harper Collins Publishers, New York, NY.

Upstate Freshwater Institute. 1992. Hydrologic Budget Considerations and Mass Balance Modeling of Onondaga Lake. Prepared for Onondaga Lake Management Conference. Syracuse, NY. Upstate Freshwater Institute, Syracuse, NY.

USGS. 1998. Web Site: Water.USGS.Gov.

# APPENDIX A

## Onondaga Lake RI/FS, Mercury Modeling Report
## PTI Environmental Services
## June 1997

Prepared for AlliedSignal, Inc.
Solvay, NewYork

Previously submitted by
AlliedSignal, Inc.

# APPENDIX B

## Analysis of Multiple-Period Sediment Trap Deployments to Assess the Extent/Rate of (re-)Mineralization

## Analysis of Multiple-Period Sediment Trap Deployments to Assess the Extent/Rate of (re-) Mineralization

The process of (re-)mineralization, as described/defined by AlliedSignal/PTI, should manifest itself in the results of the sediment trap measurements (see Table 15, p.33, June 1997 supplemental report, PTI, 1997) in the following way. The sum of multiple two-week collections of Hg (total and methyl) should be systematically higher than longer *in situ* collections (*e.g.*, four to six and eight weeks) that cover the same interval. In other words, the longer deployments allow for greater losses of recently deposited Hg via the hypothesized loss process of remineralization (see Wodka *et al.* 1985, Limnol. Oceanog., 30:833-843). For example, over the interval, July 2 to August 12, three two-week trap collections and a single continuous (~six week) collections were made (Table 15 of supplemental 1997 PTI report). If a significant remineralization process exists, the summation of the three deployments should substantially exceed the deposition measured for the single continuous deployment. In fact, the opposite was observed for both total and methyl Hg (Table 1); the depositions(s) measured for the single continuous six-week deployment was in fact greater than the sum of the three two-week deployments.

Additional comparisons are made for solids, total, and methyl Hg in Table 1. Deposition of the two mercury fractions was calculated for each deployment as the product of dry-weight specific concentrations ($ng/g^{-1}$ dry weight) times the reported mass of solids (g) collected. Overall the results are highly variable, and do not support the operation of the hypothesized process. In some cases, as described above, deposition from the long-term collections exceeds the summation of shorter-term collections (inconsistent with the (re-)mineralization process). In other cases, results are consistent with the operation of a loss process. Overall, the primary outcome of the study yields no substantive trend and suggests that the ability to measure this flux, if it exists, is limited due to the variations in the mercury deposition measurements. This further suggests that the remineralization flux, if it exists, must be smaller than the inherent variability in the measurements

## Table 1

**Comparison of Hg Deposition Determinations for Two-Week and Longer-Term Sediment Trap Deployments (PTI Supplemental 1996 Study)**

| Deployment interval | Solids Deposition (g) | | Hg Deposition (ng) | | | |
|---|---|---|---|---|---|---|
| | | | Total | | Methyl | |
| | 2-week | Long-term | 2-week | Long-term | 2-week | Long-term |
| 1. *June 5 - July 2 | 1.252 | 1.649 | 2580 | 3495 | 175 | 198 |
| 2. *July 2 - August 12 | 4.864 | 5.155 | 4457 | 4823 | 201 | 240 |
| 3. August 12 - October 7 | 2.689 | 3.043 | 4231 | 3685 | 118 | 74 |

* Results contrary to a remineralization process for mercury.

# TABLES

**Table 2-1**
**Tributary Flow Summary for 1992**

| Tributary | Percent Contribution to Total Annual Flow |
|---|---|
| Onondaga Creek | 31 |
| Ninemile Creek | 30 |
| Ley Creek | 7.8 |
| Harbor Brook | 1.9 |
| Tributary 5A | 0.9 |
| East Flume | 0.5 |
| METRO | 18 |
| Groundwater | 0.3 |
| Seneca River- Backflow | 6.8 |
| Precipitation | 2.4 |

Source: PTI (1997) and USGS Water Records TAMS

Table 2-2

Summary of 1992 Sediment Trap Data for Onondaga Lake

| | | | | | | | | | | | Relative Change in Sediment Trap Flux Between the Hypolimnion and Epilimnion (H-E)/E | | | | Ratio of Littoral to Pelagic Zone Sediment Trap (%) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample ID | Basin | | Date Deployed | Date Retrieved | Total Dry Solids (g/m2-d) | Total Organic Carbon (g/m2-d) | Total Mercury (ug/kg) | Total Mercury Mass (g/m2-d) | Methyl Mercury (ug/kg) | Methyl Mercury Mass (g/m2-d) | Total Dry Solids | Total Organic Carbon | Total Mercury | Methyl Mercury | Total Dry Solids | Total Organic Carbon | Total Mercury | Methyl Mercury |
| W1-E | | | 5/30/92 | | 9.0 | 0.3 | 292 | 2.6E-06 | 3 | 2.7E-08 | -1% | 35% | 86% | 824% | 496% | 496% | 1316% | 2810% |
| W1-H | | | 5/30/92 | | 8.9 | 0.4 | 548 | 4.9E-06 | 28 | 2.5E-07 | | | | | | | | |
| W15 | | | 5/30/92 | | 44.5 | 1.3 | 775 | 3.4E-05 | 17 | 7.6E-07 | | | | | | | | |
| W16 | | | 5/30/92 | | 27.4 | 0.7 | 940 | 2.6E-05 | 10 | 2.7E-07 | | | | | | | | |
| W1-E | | Pelagic | 6/26/92 | | 7.4 | 0.4 | 1,197 | 8.9E-06 | 20 | 1.5E-07 | 36% | -3% | 100% | 480% | 693% | 411% | 1538% | 1662% |
| W1-H | | Hypolimnion | 6/26/92 | | 10.2 | 0.4 | 1,752 | 1.8E-05 | 85 | 8.6E-07 | | | | | | | | |
| W2-E | | Pelagic | 7/2/92 | | 10.3 | 0.6 | 1,183 | 1.2E-05 | 27 | 2.8E-07 | 5% | -24% | 18% | 172% | 522% | 248% | 871% | 676% |
| W2-H | | Hypolimnion | 7/2/92 | | 10.8 | 0.5 | 1,328 | 1.4E-05 | 70 | 7.6E-07 | | | | | | | | |
| W15 | | Littoral | 6/26/92 | | 53.2 | 1.9 | 2,659 | 1.4E-04 | 48 | 2.6E-06 | | | | | | | | |
| W16 | | Littoral | 6/25/92 | | 42.0 | 1.2 | 1,976 | 8.3E-05 | 35 | 1.5E-06 | | | | | | | | |
| W1-E | South | Pelagic | 7/28/92 | 8/26/92 | 11.6 | 0.5 | 815 | 9.5E-06 | 73 | 8.5E-07 | 21% | 18% | 41% | 1% | 420% | 323% | 1250% | 253% |
| W1-H | South | Hypolimnion | 7/28/92 | 8/26/92 | 14.1 | 0.5 | 952 | 1.3E-05 | 61 | 8.6E-07 | | | | | | | | |
| W2-H | North | Hypolimnion | 7/28/92 | 8/27/92 | 12.1 | 0.5 | 797 | 9.6E-06 | 53 | 6.4E-07 | | | | | | | | |
| W15 | South | Littoral | 7/27/92 | 8/26/92 | 47.2 | 1.4 | 2,426 | 1.1E-04 | 44 | 2.1E-06 | | | | | | | | |
| W16 | North | Littoral | 7/27/92 | 8/26/92 | 68.4 | 2.0 | 1,740 | 1.2E-04 | 58 | 4.0E-06 | | | | | | | | |
| W1-E | South | Pelagic | 8/27/92 | 9/23/92 | 7.3 | 0.2 | 1,750 | 1.3E-05 | 39 | 2.9E-07 | 26% | 11% | 61% | 149% | 478% | 408% | 984% | 662% |
| W1-H | South | Hypolimnion | 8/27/92 | 9/23/92 | 9.3 | 0.3 | 2,230 | 2.1E-05 | 77 | 7.1E-07 | | | | | | | | |
| W2-E | North | Pelagic | 7/28/92 | 9/23/92 | 6.3 | 0.2 | 1,310 | 8.2E-06 | 46 | 2.9E-07 | 63% | 113% | 18% | 104% | 841% | 874% | 1166% | 985% |
| W2-HSum | North | Hypolimnion | 7/28/92 | 9/23/92 | 11.2 | 0.4 | 942 | 1.1E-05 | 58 | 6.5E-07 | | | | | | | | |
| W2-H | North | Hypolimnion | 8/27/92 | 9/23/92 | 8.2 | 0.2 | 1,180 | 9.6E-06 | 65 | 5.3E-07 | | | | | | | | |
| W15 | South | Littoral | 8/26/92 | 9/23/92 | 33.9 | 1.0 | 3,600 | 1.2E-04 | 54 | 1.8E-06 | | | | | | | | |
| W16 | North | Littoral | 8/26/92 | 9/23/92 | 33.9 | 0.9 | 1,980 | 6.7E-05 | 45 | 1.5E-06 | | | | | | | | |
| W16Sum | North | Littoral | 8/26/92 | 9/23/92 | 51.7 | 1.5 | 1,816 | 9.4E-05 | 54 | 2.8E-06 | | | | | | | | |
| W1-E | South | Pelagic | 9/23/92 | 10/21/92 | 7.2 | 0.5 | 1,560 | 1.1E-05 | 56 | 4.0E-07 | -10% | -37% | 12% | 10% | 315% | 335% | 907% | 523% |
| W1-HCalc | South | Hypolimnion | 9/23/92 | 10/21/92 | 6.5 | 0.3 | 1,950 | 1.3E-05 | 69 | 4.5E-07 | | | | | | | | |
| W1-H | South | Hypolimnion | 10/12/92 | 10/21/92 | 6.5 | 0.3 | 1,950 | 1.3E-05 | 69 | 4.5E-07 | | | | | | | | |
| W2-E | North | Pelagic | 9/23/92 | 10/21/92 | 10.2 | 0.6 | 2,120 | 2.2E-05 | 92 | 9.4E-07 | -48% | -36% | -65% | -63% | 139% | 180% | 129% | 80% |
| W2-H | North | Hypolimnion | 9/23/92 | 10/21/92 | 5.3 | 0.4 | 1,430 | 7.6E-06 | 66 | 3.5E-07 | | | | | | | | |
| W | South | Littoral | 9/23/92 | 10/21/92 | 22.7 | 1.5 | 4,490 | 1.0E-04 | 93 | 2.1E-06 | | | | | | | | |
| W16 | North | Littoral | 9/23/92 | 10/21/92 | 14.2 | 1.0 | 1,960 | 2.8E-05 | 53 | 7.5E-07 | | | | | | | | |
| W1-E | South | Pelagic | 10/21/92 | 11/24/92 | 4.9 | 0.4 | 1,760 | 8.5E-06 | 143 | 6.9E-07 | | | | | | | | |
| W2-E | North | Pelagic | 10/21/92 | 11/24/92 | 4.9 | 0.3 | 1,370 | 6.7E-06 | 167 | 8.2E-07 | 2% | -58% | -2% | -3% | 101% | 88% | 129% | 91% |
| W2-H | North | Hypolimnion | 10/21/92 | 11/24/92 | 5.0 | 0.1 | 1,310 | 6.6E-06 | 158 | 8.0E-07 | | | | | | | | |
| W16 | South | Littoral | 10/21/92 | 11/24/92 | 5.0 | 0.3 | 1,750 | 8.7E-06 | 151 | 7.5E-07 | | | | | | | | |

Notes:

1. Data from PTI (1993).
2. Sediment Trap area is 0.0314 $m^2$.
3. W2-HCalc is an extrapolation of the measured values to achieve comparable deployment durations.
4. W16Sum and W1-HSum represent combined samples to achieve comparable deployment durations.

Table 4-1

Calculation of Atmospheric and Local Mercury Contributions to Onondaga Lake via the Tributaries

| Tributary | Drainage Area (km^2) | Measured Annual Load (kg/year) | Mercury Yield (g/km^2-yr) | Atmospheric Component[1] (kg/year) | Local Input (kg/year) | Fraction Locally Derived (%) |
|---|---|---|---|---|---|---|
| Ley Creek | 77.4 | 0.24 | 3.1 | 0.27 | 0 | 0 |
| Upper Ninemile Cr. | 238 | 0.87 | 3.6 | 0.83 | 0 | 0 |
| Harbor | 29.3 | 0.23 | 7.8 | 0.10 | 0.13 | 55% |
| Onondaga Creek | 285 | 1.32 | 4.6 | 1.00 | 0.32 | 24% |
| Ninemile Cr. (total) | 298 | 4.95 | 16.6 | 1.04 | 3.91 | 79% |
| Metro | 26 | 3.30 | 126.9 | 0.52 [2] | 2.78 | 84% |

Notes:

TAMS

1. Assumes an atmospherically-derived runoff rate of 3.5 g/km^2-yr.
2. Assumes an atmospherically-derived runoff rate of 20 g/km^2-yr.

## Table 5-1

## Model Sensitivity Analysis

| Model Run | Parameter | Calibration | | Model Sensitivity Modification | | Comments |
|---|---|---|---|---|---|---|
| 1 | Groundwater | Loadings in model ($1.56 \times 10^{-5}$ kg/d for $Hg^{+2}$ and $8.2 \times 10^{-7}$ kg/d for $CH_3Hg$) based on Total Hg = 4 ng/L, $CH_3Hg$ = 0.2 ng/L, and, Flow = $1.4 \times 10^{9}$ L/yr. | | Loadings increased by a factor of 10 ($1.56 \times 10^{-4}$ kg/d for $Hg^{+2}$ and $8.2 \times 10^{-6}$ kg/d for $CH_3Hg$) based on Total Hg = 40 ng/L, $CH_3Hg$ = 2 ng/L, and, Flow = $1.4 \times 10^{9}$ L/yr. | | Calibration - Total Hg and $CH_3Hg$ are based on PTI, p.36. Flow is based on PTI, Table D-3.<br><br>Model Sensitivity Modification - Total Hg and $CH_3Hg$ loadings are based on slightly more contaminated groundwater concentrations. |
| 2 | Partition Coefficients | Inorganic Solids:<br>$Hg^{+2}$: Log K = 5.12<br>$CH_3Hg$: Log K = 4.65 | Organic Solids:<br>$Hg^{+2}$: Log K = 4.78<br>$CH_3Hg$: Log K =4.88 | Inorganic Solids:<br>$Hg^{+2}$: Log K = 4.0<br>$CH_3Hg$: Log K = 4.0 | Organic Solids:<br>$Hg^{+2}$: Log K = 4.45<br>$CH_3Hg$: Log K = 4.36 | Calibration - PTI, Table 5.<br><br>Model Sensitivity Modification -<br>Inorganic Solids: Assume typical minimum for inorganics ($K=10^4$ L/kg, Thomann and Mueller, 1987); no data for inorganic solids in PTI, Table 5.<br>Organic Solids: Based on minimum values estimated from field data in PTI, Table 5. |
| 3 | Methylation | 0.035/day | | Increased annual average by a factor of 10 (0.35/day) | | Model Sensitivity Modification - Modified value is near high end of range of 1996 measured values in PTI ,Table 2. |
| 4 | Methylation | 0.035/day | | Decreased annual average by a factor of 10 (0.0035/day) | | Model Sensitivity Modification - Near low end of range of 1996 measured values in PTI, Table 2. |
| 5 | Sediment Flux | Approximate range of weekly loadings (kg/d) for both epilimnion and hypolimnion:<br>$Hg^{+2}$: $1.0 \times 10^{-5}$ to $0.2 \times 10^{-3}$<br>$CH_3Hg$: $0.5 \times 10^{-6}$ to $0.3 \times 10^{-3}$ | | Approximate range of weekly loadings (kg/d) for both epilimnion and hypolimnion:<br>$Hg^{+2}$: $1.0 \times 10^{-3}$ to $0.2 \times 10^{-1}$<br>$CH_3Hg$: $0.5 \times 10^{-4}$ to $0.3 \times 10^{-1}$ | | Increased sediment fluxes by approximately two orders of magnitude to incorporate remineralization used by PTI into sediment flux term. |
| 6 | Atmospheric Flux | Weekly loadings, based on 37 $\mu g/m^2$-yr (Total Hg) | | All values reduced by 50% based on < 20 $\mu g/m^2$-yr | | Calibration - PTI, p. 39.<br><br>Model Sensitivity Modification - flux obtained from Mason et al., 1997, "Atmospheric Deposition to the Chesapeake Bay Watershed-Regional and Local Sources". |

Source: Calibration values from OLMM "CALIB.INP" File and/or PTI, 1997.

# Table 5-2

## PTI's Model Calibration - Total Mercury Mass Balance

### MERC4 Simulation - Onondaga Lake
### Mass Balance : Total Mercury

| | Jan 92 | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | ANNUAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Inflow | 2.18e+001 | 2.34e+001 | 3.44e+001 | 4.96e+001 | 2.62e+001 | 2.22e+001 | 2.74e+001 | 3.02e+001 | 2.27e+001 | 2.31e+001 | 2.51e+001 | 2.61e+001 | 2.77e+001 |
| Atmospheric Depositic | 9.65e-001 | 7.87e-001 | 1.11e+000 | 1.44e+000 | 1.16e+000 | 1.18e+000 | 2.16e+000 | 1.02e+000 | 1.73e+000 | 1.06e+000 | 1.21e+000 | 7.76e-001 | 1.22e+000 |
| Groundwater Inflow | 1.64e-002 | 1.65e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 |
| Outflow | -5.83e+000 | -5.95e+000 | -7.20e+000 | -8.03e+000 | -3.78e+000 | -5.83e+000 | -5.26e+000 | -6.88e+000 | -4.67e+000 | -5.09e+000 | -5.14e+000 | -6.07e+000 | -5.81e+000 |
| Volatilization | -6.92e-002 | -7.00e-002 | -7.05e-002 | -5.81e-002 | -5.42e-002 | -8.39e-002 | -1.16e-001 | -1.25e-001 | -1.20e-001 | -9.35e-002 | -8.17e-002 | -7.31e-002 | -8.47e-002 |
| Kinetics | -4.19e-009 | -4.66e-010 | 4.07e-009 | 3.67e-009 | -3.73e-009 | 4.00e-004 | 5.00e-004 | 3.00e-004 | -5.00e-004 | -5.00e-004 | 6.98e-009 | -1.05e-009 | 1.72e-005 |
| Settling | -1.80e+001 | -1.80e+001 | -2.86e+001 | -5.20e+001 | -2.09e+001 | -1.00e+001 | -1.55e+001 | -2.91e+001 | -1.53e+001 | -2.96e+001 | -1.73e+001 | -1.64e+001 | -2.26e+001 |
| Resuspension | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sediment Exchange | 4.16e-002 | 4.18e-002 | 4.42e-002 | 4.84e-002 | 1.33e-001 | 3.44e-001 | 3.79e-001 | 4.03e-001 | 4.28e-001 | 2.79e-001 | 6.59e-002 | 4.76e-002 | 1.89e-001 |
| Processed by Fish | -7.84e-002 | -5.82e-002 | -6.53e-002 | 3.39e-002 | 1.11e-001 | -1.81e-001 | -1.23e-001 | -3.24e-001 | -8.58e-001 | -3.91e+000 | -6.95e-001 | -2.00e-001 | -5.37e-001 |
| SUM | -1.13e+000 | 1.42e-001 | -3.03e-001 | -8.91e+000 | 2.93e+000 | 7.60e+000 | 8.93e+000 | -4.86e+000 | 3.92e+000 | -1.42e+001 | 3.25e+000 | 4.20e+000 | 1.15e-001 |

Note:
1. All values in grams/day; + value is a source (input), - value is a sink (loss)
Source:
1. OLMM "CALIB.INP" File

## Table 5-3

## PTI's Model Calibration - Methyl Mercury Mass Balance

### MERC4 Simulation - Onondaga Lake
### Mass Balance : Methyl Mercury

| | Jan 92 | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | ANNUAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Inflow | 6.22e-001 | 6.52e-001 | 8.73e-001 | 1.18e+000 | 7.07e-001 | 6.37e-001 | 7.38e-001 | 7.94e-001 | 6.31e-001 | 6.39e-001 | 6.74e-001 | 6.99e-001 | 7.38e-001 |
| Atmospheric Depositic | 1.27e-002 | 1.01e-002 | 1.21e-002 | 1.75e-002 | 1.64e-002 | 1.44e-002 | 3.05e-002 | 1.14e-002 | 2.41e-002 | 1.42e-002 | 1.65e-002 | 9.35e-003 | 1.58e-002 |
| Groundwater Inflow | 8.20e-004 | 8.23e-004 | 8.20e-004 | 8.20e-004 | 8.17e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 |
| Outflow | -2.44e-001 | -2.54e-001 | -3.22e-001 | -3.92e-001 | -2.23e-001 | -2.55e-001 | -2.89e-001 | -4.11e-001 | -3.22e-001 | -8.97e-001 | -3.73e-001 | -2.67e-001 | -3.55e-001 |
| Volatilization | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Kinetics | 0 | 0 | 0 | 0 | 2.60e-001 | 2.96e+000 | 4.59e+000 | 5.59e+000 | 5.51e+000 | 2.24e+000 | 0 | 0 | 1.77e+000 |
| Settling | -2.94e-001 | -3.12e-001 | -5.39e-001 | -1.08e+000 | -4.99e-001 | -1.02e+000 | -2.37e+000 | -5.37e+000 | -3.86e+000 | -4.37e+000 | -5.47e-001 | -2.90e-001 | -1.72e+000 |
| Resuspension | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sediment Exchange | 1.83e-003 | 1.83e-003 | 1.93e-003 | 2.12e-003 | 5.47e-002 | 2.10e-001 | 2.32e-001 | 2.47e-001 | 2.62e-001 | 1.48e-001 | 2.89e-003 | 2.09e-003 | 9.78e-002 |
| Processed by Fish | -7.84e-002 | -9.82e-002 | -6.53e-002 | 3.39e-002 | 1.11e-001 | -1.81e-001 | -1.23e-001 | -3.24e-001 | -8.58e-001 | -3.91e+000 | -6.95e-001 | -2.00e-001 | -5.37e-001 |
| SUM | 2.13e-002 | 6.56e-004 | -3.87e-002 | -2.37e-001 | 4.28e-001 | 2.37e+000 | 2.82e+000 | 5.37e-001 | 1.39e+000 | -6.14e+000 | -9.21e-001 | -4.60e-002 | 8.48e-003 |

Note:
1. All values in grams/day; + value is a source (input)  value is a sink (loss)
Source:
1. OLMM "CALIB.INP" File

Table 5-4

## Model Run 1 - Total Mercury Mass Balance

### MERC4 Simulation - Onondaga Lake
### Mass Balance : Total Mercury

| | Jan 92 | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | ANNUAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Inflow | 2.18e+001 | 2.34e+001 | 3.44e+001 | 4.96e+001 | 2.62e+001 | 2.22e+001 | 2.74e+001 | 3.02e+001 | 2.27e+001 | 2.31e+001 | 2.51e+001 | 2.61e+001 | 2.77e+001 |
| Atmospheric Deposit | 9.65e-001 | 7.87e-001 | 1.11e+000 | 1.44e+000 | 1.16e+000 | 1.18e+000 | 2.16e+000 | 1.02e+000 | 1.73e+000 | 1.06e+000 | 1.21e+000 | 7.76e-001 | 1.22e+000 |
| Groundwater Inflow | 1.64e-001 | 1.65e-001 | 1.64e-001 | 1.64e-001 | 1.64e-001 | 1.64e-001 | 1.64e-001 | 1.64e-001 | 1.64e-001 | 1.64e-001 | 1.64e-001 | 1.64e-001 | 1.64e-001 |
| Outflow | -5.85e+000 | -5.99e+000 | -7.25e+000 | -8.08e+000 | -3.80e+000 | -5.87e+000 | -5.29e+000 | -6.92e+000 | -4.70e+000 | -5.13e+000 | -5.17e+000 | -6.11e+000 | -5.84e+000 |
| Volatilization | -6.92e-002 | -7.01e-002 | -7.07e-002 | -5.83e-002 | -5.44e-002 | -8.44e-002 | -1.16e-001 | -1.25e-001 | -1.21e-001 | -9.41e-002 | -8.22e-002 | -7.35e-002 | -8.51e-002 |
| Kinetics | 4.66e-010 | -4.19e-009 | -1.86e-009 | -2.33e-010 | 4.10e-008 | -5.00e-004 | 3.00e-004 | 7.00e-004 | 5.00e-004 | 1.00e-004 | 5.36e-009 | -3.26e-009 | 9.34e-005 |
| Settling | -1.80e+001 | -1.81e+001 | -2.87e+001 | -5.21e+001 | -2.10e+001 | -1.01e+001 | -1.56e+001 | -2.93e+001 | -1.54e+001 | -2.98e+001 | -1.74e+001 | -1.65e+001 | -2.27e+001 |
| Resuspension | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sediment Exchange | 4.16e-002 | 4.18e-002 | 4.42e-002 | 4.84e-002 | 1.33e-001 | 3.44e-001 | 3.79e-001 | 4.03e-001 | 4.28e-001 | 2.79e-001 | 6.59e-002 | 4.76e-002 | 1.89e-001 |
| Processed by Fish | -7.93e-002 | -1.00e-001 | -6.74e-002 | 3.25e-002 | 1.07e-001 | -1.85e-001 | -1.27e-001 | -3.30e-001 | -8.66e-001 | -3.94e+000 | -7.00e-001 | -2.02e-001 | -5.43e-001 |
| SUM | -1.03e+000 | 1.61e-001 | -3.17e-001 | -8.95e+000 | 2.96e+000 | 7.68e+000 | 8.95e+000 | -4.89e+000 | 3.95e+000 | -1.43e+001 | 3.28e+000 | 4.21e+000 | 1.24e-001 |

Note:
1. All values in grams/day; + value is a source (input), - value is a sink (loss)
Source:
1. OLMM "TAMS01.INP" File

Table 5-5

Model Run 1 - Methyl Mercury Mass Balance

## MERC4 Simulation - Onondaga Lake
## Mass Balance : Methyl Mercury

| | Jan 92 | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | ANNUAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Inflow | 6.22e-001 | 6.52e-001 | 8.73e-001 | 1.18e+000 | 7.07e-001 | 6.37e-001 | 7.38e-001 | 7.94e-001 | 6.31e-001 | 6.39e-001 | 6.74e-001 | 6.99e-001 | 7.38e-001 |
| Atmospheric Depositi | 1.27e-002 | 1.01e-002 | 1.21e-002 | 1.75e-002 | 1.64e-002 | 1.44e-002 | 3.05e-002 | 1.14e-002 | 2.41e-002 | 1.42e-002 | 1.65e-002 | 9.35e-003 | 1.58e-002 |
| Groundwater Inflow | 8.20e-003 | 8.23e-003 | 8.20e-003 | 8.20e-003 | 8.17e-003 | 8.20e-003 | 8.20e-003 | 8.20e-003 | 8.20e-003 | 8.20e-003 | 8.20e-003 | 8.20e-003 | 8.20e-003 |
| Outflow | -2.45e-001 | -2.56e-001 | -3.24e-001 | -3.95e-001 | -2.25e-001 | -2.57e-001 | -2.90e-001 | -4.13e-001 | -3.23e-001 | -9.02e-001 | -3.76e-001 | -2.69e-001 | -3.57e-001 |
| Volatilization | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Kinetics | 0 | 0 | 0 | 0 | 2.62e-001 | 2.98e+000 | 4.62e+000 | 5.61e+000 | 5.54e+000 | 2.25e+000 | 0 | 0 | 1.78e+000 |
| Settling | -2.95e-001 | -3.14e-001 | -5.43e-001 | -1.09e+000 | -5.01e-001 | -1.02e+000 | -2.38e+000 | -5.40e+000 | -3.88e+000 | -4.39e+000 | -5.51e-001 | -2.92e-001 | -1.73e+000 |
| Resuspension | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sediment Exchange | 1.83e-003 | 1.83e-003 | 1.93e-003 | 2.12e-003 | 5.47e-002 | 2.10e-001 | 2.32e-001 | 2.47e-001 | 2.62e-001 | 1.48e-001 | 2.89e-003 | 2.09e-003 | 9.78e-002 |
| Processed by Fish | -7.93e-002 | -1.00e-001 | -6.74e-002 | 3.25e-002 | 1.07e-001 | -1.85e-001 | -1.27e-001 | -3.30e-001 | -8.66e-001 | -3.94e+000 | -7.00e-001 | -2.02e-001 | -5.43e-001 |
| SUM | 2.60e-002 | 2.26e-003 | -3.97e-002 | -2.39e-001 | 4.29e-001 | 2.38e+000 | 2.83e+000 | 5.35e-001 | 1.40e+000 | -6.17e+000 | -9.25e-001 | -4.55e-002 | 8.93e-003 |

Note:
1. All values in grams/day; + value is a source (input), - value is a sink (loss)
Source:
1. OLMM "TAMS01.INP" File

Table 5-6

Model Run 2 - Total Mercury Mass Balance

MERC4 Simulation - Onondaga Lake
Mass Balance : Total Mercury

| | Jan 92 | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | ANNUAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Inflow | 2.18e+001 | 2.34e+001 | 3.44e+001 | 4.96e+001 | 2.62e+001 | 2.22e+001 | 2.74e+001 | 3.02e+001 | 2.27e+001 | 2.31e+001 | 2.51e+001 | 2.61e+001 | 2.77e+001 |
| Atmospheric Depositi | 9.65e-001 | 7.87e-001 | 1.11e+000 | 1.44e+000 | 1.16e+000 | 1.18e+000 | 2.16e+000 | 1.02e+000 | 1.73e+000 | 1.06e+000 | 1.21e+000 | 7.76e-001 | 1.22e+000 |
| Groundwater Inflow | 1.64e-002 | 1.65e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 |
| Outflow | -7.93e+000 | -1.10e+001 | -1.79e+001 | -2.82e+001 | -1.69e+001 | -1.60e+001 | -1.65e+001 | -2.10e+001 | -1.51e+001 | -1.69e+001 | -1.78e+001 | -1.81e+001 | -1.70e+001 |
| Volatilization | -7.53e-002 | -9.50e-002 | -1.26e-001 | -1.50e-001 | -2.31e-001 | -3.39e-001 | -4.97e-001 | -5.70e-001 | -5.83e-001 | -4.19e-001 | -3.51e-001 | -2.88e-001 | -3.12e-001 |
| Kinetics | -1.19e-008 | 1.00e-008 | -1.77e-008 | -1.68e-008 | 1.33e-007 | 5.44e-007 | -4.40e-007 | 5.07e-007 | 2.00e-003 | -5.59e-008 | -1.86e-009 | 4.19e-009 | 1.64e-004 |
| Settling | -2.43e+000 | -3.59e+000 | -9.11e+000 | -2.39e+001 | -1.03e+001 | -2.52e+000 | -3.44e+000 | -6.82e+000 | -4.36e+000 | -1.27e+001 | -6.33e+000 | -4.89e+000 | -7.55e+000 |
| Resuspension | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sediment Exchange | 4.16e-002 | 4.18e-002 | 4.42e-002 | 4.84e-002 | 1.33e-001 | 3.44e-001 | 3.79e-001 | 4.03e-001 | 4.28e-001 | 2.79e-001 | 6.59e-002 | 4.76e-002 | 1.89e-001 |
| Processed by Fish | 8.33e-002 | 4.45e-002 | 3.71e-002 | 5.56e-002 | 1.92e-001 | -5.82e-003 | -1.23e-001 | -6.30e-001 | -1.28e+000 | -7.13e+000 | -2.65e+000 | -7.26e-001 | -1.02e+000 |
| SUM | 1.25e+001 | 9.67e+000 | 8.46e+000 | -1.07e+000 | 3.15e-001 | 4.88e+000 | 9.33e+000 | 2.60e+000 | 3.55e+000 | -1.27e+001 | -7.51e-001 | 2.96e+000 | 3.28e+000 |

Note:
1. All values in grams/day; + value is a source (input), - value is a sink (loss)
Source:
1. OLMM "TAMS02.INP" File

## Table 5-7

## Model Run 2 - Methyl Mercury Mass Balance

### MERC4 Simulation - Onondaga Lake
### Mass Balance : Methyl Mercury

| | Jan 92 | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | ANNUAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Inflow | 6.22e-001 | 6.52e-001 | 8.73e-001 | 1.18e+000 | 7.07e-001 | 6.37e-001 | 7.38e-001 | 7.94e-001 | 6.31e-001 | 6.39e-001 | 6.74e-001 | 6.99e-001 | 7.38e-001 |
| Atmospheric Deposit | 1.27e-002 | 1.01e-002 | 1.21e-002 | 1.75e-002 | 1.64e-002 | 1.44e-002 | 3.05e-002 | 1.14e-002 | 2.41e-002 | 1.42e-002 | 1.65e-002 | 9.35e-003 | 1.58e-002 |
| Groundwater Inflow | 8.20e-004 | 8.23e-004 | 8.20e-004 | 8.20e-004 | 8.17e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 |
| Outflow | -2.94e-001 | -3.76e-001 | -5.67e-001 | -8.12e-001 | -4.99e-001 | -5.89e-001 | -7.78e-001 | -1.25e+000 | -1.11e+000 | -4.31e+000 | -3.19e+000 | -1.95e+000 | -1.32e+000 |
| Volatilization | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Kinetics | 0 | 0 | 0 | 0 | 1.30e+000 | 7.60e+000 | 7.56e+000 | 8.94e+000 | 9.02e+000 | 4.28e+000 | 0 | 0 | 3.24e+000 |
| Settling | -8.44e-002 | -1.15e-001 | -2.53e-001 | -5.92e-001 | -2.87e-001 | -7.57e-001 | -1.62e+000 | -3.69e+000 | -2.75e+000 | -4.70e+000 | -1.15e+000 | -5.28e-001 | -1.39e+000 |
| Resuspension | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sediment Exchange | 1.83e-003 | 1.83e-003 | 1.93e-003 | 2.12e-003 | 5.47e-002 | 2.10e-001 | 2.32e-001 | 2.47e-001 | 2.62e-001 | 1.48e-001 | 2.89e-003 | 2.09e-003 | 9.78e-002 |
| Processed by Fish | 8.33e-002 | 4.45e-002 | 3.71e-002 | 5.56e-002 | 1.92e-001 | -5.82e-003 | -1.23e-001 | -6.30e-001 | -1.28e+000 | -7.13e+000 | -2.65e+000 | -7.26e-001 | -1.02e+000 |
| SUM | 3.45e-001 | 2.18e-001 | 1.04e-001 | -1.46e-001 | 1.49e+000 | 7.12e+000 | 6.03e+000 | 4.43e+000 | 4.79e+000 | -1.10e+001 | -6.31e+000 | -2.50e+000 | 3.68e-001 |

Note:
1. All values in grams/day; + value is a source (input), - value is a sink (loss)

Source:
1. OLMM "TAMS02.INP" File

## Table 5-8

## Model Run 3 Total Mercury Mass Balance

### MERC4 Simulation - Onondaga Lake
### Mass Balance : Total Mercury

| | Jan 92 | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | ANNUAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Inflow | 2.18e+001 | 2.34e+001 | 3.44e+001 | 4.96e+001 | 2.62e+001 | 2.22e+001 | 2.74e+001 | 3.02e+001 | 2.27e+001 | 2.31e+001 | 2.51e+001 | 2.61e+001 | 2.77e+001 |
| Atmospheric Deposit | 9.65e-001 | 7.87e-001 | 1.11e+000 | 1.44e+000 | 1.16e+000 | 1.18e+000 | 2.16e+000 | 1.02e+000 | 1.73e+000 | 1.06e+000 | 1.21e+000 | 7.76e-001 | 1.22e+000 |
| Groundwater Inflow | 1.64e-002 | 1.65e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 |
| Outflow | -5.83e+000 | -5.95e+000 | -7.20e+000 | -8.03e+000 | -3.78e+000 | -5.81e+000 | -5.28e+000 | -8.95e+000 | -4.74e+000 | -5.46e+000 | -5.18e+000 | -6.10e+000 | -5.86e+000 |
| Volatilization | -6.92e-002 | -7.00e-002 | -7.05e-002 | -5.81e-002 | -5.42e-002 | -8.32e-002 | -1.14e-001 | -1.22e-001 | -1.17e-001 | -8.46e-002 | -7.05e-002 | -6.59e-002 | -8.17e-002 |
| Kinetics | -4.19e-009 | -4.66e-010 | 4.07e-009 | 3.67e-009 | 3.00e-004 | 4.00e-003 | 3.50e-003 | 4.40e-003 | -1.90e-003 | -3.00e-004 | -5.36e-009 | -3.14e-009 | 8.44e-004 |
| Settling | -1.80e+001 | -1.80e+001 | -2.86e+001 | -5.20e+001 | -2.07e+001 | -7.61e+000 | -1.29e+001 | -2.63e+001 | -1.42e+001 | -2.70e+001 | -1.67e+001 | -1.63e+001 | -2.16e+001 |
| Resuspension | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sediment Exchange | 4.16e-002 | 4.18e-002 | 4.42e-002 | 4.84e-002 | 1.33e-001 | 3.44e-001 | 3.79e-001 | 4.03e-001 | 4.28e-001 | 2.79e-001 | 6.59e-002 | 4.76e-002 | 1.89e-001 |
| Processed by Fish | -7.84e-002 | -9.82e-002 | -6.53e-002 | 3.39e-002 | 9.81e-002 | -4.53e-001 | -5.67e-001 | -1.21e+000 | -2.24e+000 | -1.14e+001 | -1.72e+000 | -2.58e-001 | -1.52e+000 |
| SUM | -1.13e+000 | 1.42e-001 | -3.03e-001 | -8.91e+000 | 3.05e+000 | 9.77e+000 | 1.11e+001 | -3.03e+000 | 3.52e+000 | -1.95e+001 | 2.75e+000 | 4.20e+000 | 1.22e-001 |

Note:
1. All values in grams/day; + value is a source (input), - value is a sink (loss)
Source:
1. OLMM "TAMS03.INP" File

## Table 5-9

## Model Run 3 - Methyl Mercury Mass Balance

### MERC4 Simulation - Onondaga Lake
### Mass Balance : Methyl Mercury

| | Jan 92 | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | ANNUAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Inflow | 6.22e-001 | 6.52e-001 | 8.73e-001 | 1.18e+000 | 7.07e-001 | 6.37e-001 | 7.38e-001 | 7.94e-001 | 6.31e-001 | 6.39e-001 | 6.74e-001 | 6.99e-001 | 7.38e-001 |
| Atmospheric Deposit | 1.27e-002 | 1.01e-002 | 1.21e-002 | 1.75e-002 | 1.64e-002 | 1.44e-002 | 3.05e-002 | 1.14e-002 | 2.41e-002 | 1.42e-002 | 1.85e-002 | 9.35e-003 | 1.58e-002 |
| Groundwater Inflow | 8.20e-004 | 8.23e-004 | 8.20e-004 | 8.20e-004 | 8.17e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 |
| Outflow | -2.44e-001 | -2.54e-001 | -3.22e-001 | -3.92e-001 | -2.26e-001 | -3.22e-001 | -4.06e-001 | -6.77e-001 | -5.72e-001 | -2.36e+000 | -7.87e-001 | -4.04e-001 | -5.84e-001 |
| Volatilization | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Kinetics | 0 | 0 | 0 | 0 | 2.10e+000 | 1.23e+001 | 1.61e+001 | 2.02e+001 | 1.41e+001 | 8.88e+000 | 0 | 0 | 6.18e+000 |
| Settling | -2.94e-001 | -3.12e-001 | -5.39e-001 | -1.08e+000 | -6.20e-001 | -3.90e+000 | -8.17e+000 | -1.77e+001 | -1.12e+001 | -1.26e+001 | -1.18e+000 | -4.44e-001 | -4.87e+000 |
| Resuspension | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sediment Exchange | 1.83e-003 | 1.83e-003 | 1.93e-003 | 2.12e-003 | 5.47e-002 | 2.10e-001 | 2.32e-001 | 2.47e-001 | 2.62e-001 | 1.48e-001 | 2.89e-003 | 2.09e-003 | 9.78e-002 |
| Processed by Fish | -7.84e-002 | -9.82e-002 | -8.83e-002 | 3.39e-002 | 9.51e-002 | -4.53e-001 | -5.67e-001 | -1.21e+000 | -2.24e+000 | -1.14e+001 | -1.72e+000 | -2.58e-001 | -1.52e+000 |
| SUM | 2.13e-002 | 6.56e-004 | -3.87e-002 | -2.37e-001 | 2.12e+000 | 8.44e+000 | 7.98e+000 | 1.69e+000 | 1.07e+000 | -1.67e+001 | -2.99e+000 | -3.98e-001 | 6.57e-002 |

Note:
1. All values in grams/day; + value is a source (input), - value is a sink (loss)
Source:
1. OLMM "TAMS03.INP" File

Table 5-10

## Model Run 4 - Total Mercury Mass Balance

### MERC4 Simulation - Onondaga Lake
### Mass Balance : Total Mercury

| | Jan 92 | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | ANNUAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Inflow | 2.18e+001 | 2.34e+001 | 3.44e+001 | 4.96e+001 | 2.62e+001 | 2.22e+001 | 2.74e+001 | 3.02e+001 | 2.27e+001 | 2.31e+001 | 2.51e+001 | 2.61e+001 | 2.77e+001 |
| Atmospheric Deposiit | 9.65e-001 | 7.87e-001 | 1.11e+000 | 1.44e+000 | 1.16e+000 | 1.18e+000 | 2.16e+000 | 1.02e+000 | 1.73e+000 | 1.06e+000 | 1.21e+000 | 7.76e-001 | 1.22e+000 |
| Groundwater Inflow | 1.64e-002 | 1.65e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 |
| Outflow | -5.83e+000 | -5.95e+000 | -7.20e+000 | -8.03e+000 | -3.78e+000 | -5.83e+000 | -5.25e+000 | -6.86e+000 | -4.64e+000 | -4.96e+000 | -5.12e+000 | -6.06e+000 | -5.79e+000 |
| Volatilization | -6.92e-002 | -7.00e-002 | -7.05e-002 | -5.81e-002 | -5.42e-002 | -8.40e-002 | -1.16e-001 | -1.26e-001 | -1.22e-001 | -9.72e-002 | -8.61e-002 | -7.59e-002 | -8.58e-002 |
| Kinetics | -4.19e-009 | -4.66e-010 | 4.07e-009 | 3.67e-009 | -9.99e-006 | -1.77e-008 | -1.00e-004 | -2.65e-008 | -2.00e-004 | 1.00e-004 | -9.31e-009 | -3.26e-009 | -1.73e-005 |
| Settling | -1.80e+001 | -1.80e+001 | -2.86e+001 | -5.20e+001 | -2.09e+001 | -1.06e+001 | -1.64e+001 | -3.02e+001 | -1.61e+001 | -3.07e+001 | -1.75e+001 | -1.65e+001 | -2.30e+001 |
| Resuspension | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sediment Exchange | 4.16e-002 | 4.18e-002 | 4.42e-002 | 4.84e-002 | 1.33e-001 | 3.44e-001 | 3.79e-001 | 4.03e-001 | 4.28e-001 | 2.79e-001 | 8.59e-002 | 4.76e-002 | 1.89e-001 |
| Processed by Fish | -7.84e-002 | -9.82e-002 | -6.63e-002 | 3.39e-002 | 1.12e-001 | -1.34e-001 | 1.07e-002 | -3.12e-002 | -2.92e-001 | -9.30e-001 | -3.11e-001 | -1.77e-001 | -1.64e-001 |
| SUM | -1.13e+000 | 1.42e-001 | -3.03e-001 | -8.91e+000 | 2.91e+000 | 7.05e+000 | 8.16e+000 | -5.58e+000 | 3.74e+000 | -1.22e+001 | 3.43e+000 | 4.19e+000 | 1.11e-001 |

Note:
1. All values in grams/day; + value is a source (input), - value is a sink (loss)
Source:
1. OLMM "TAMS04.INP" File

## Table 5-11

## Model Run 4 - Methyl Mercury Mass Balance

### MERC4 Simulation - Onondaga Lake
### Mass Balance : Methyl Mercury

| | Jan 92 | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | ANNUAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Inflow | 6.22e-001 | 6.52e-001 | 8.73e-001 | 1.18e+000 | 7.07e-001 | 6.37e-001 | 7.38e-001 | 7.94e-001 | 6.31e-001 | 6.39e-001 | 6.74e-001 | 6.99e-001 | 7.38e-001 |
| Atmospheric Deposit | 1.27e-002 | 1.01e-002 | 1.21e-002 | 1.75e-002 | 1.64e-002 | 1.44e-002 | 3.05e-002 | 1.14e-002 | 2.41e-002 | 1.42e-002 | 1.65e-002 | 9.35e-003 | 1.58e-002 |
| Groundwater Inflow | 8.20e-004 | 8.23e-004 | 8.20e-004 | 8.20e-004 | 8.17e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 |
| Outflow | -2.44e-001 | -2.54e-001 | -3.22e-001 | -3.92e-001 | -2.23e-001 | -2.45e-001 | -2.54e-001 | -3.26e-001 | -2.22e-001 | -3.17e-001 | -2.17e-001 | -2.15e-001 | -2.69e-001 |
| Volatilization | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Kinetics | 0 | 0 | 0 | 0 | 2.66e-002 | 3.36e-001 | 5.54e-001 | 6.79e-001 | 7.30e-001 | 2.81e-001 | 0 | 0 | 2.18e-001 |
| Settling | -2.94e-001 | -3.12e-001 | -5.39e-001 | -1.08e+000 | -4.85e-001 | -3.26e-001 | -6.32e-001 | -1.34e+000 | -9.13e-001 | -1.23e+000 | -3.07e-001 | -2.32e-001 | -6.44e-001 |
| Resuspension | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sediment Exchange | 1.83e-003 | 1.83e-003 | 1.93e-003 | 2.12e-003 | 5.47e-002 | 2.10e-001 | 2.32e-001 | 2.47e-001 | 2.62e-001 | 1.48e-001 | 2.89e-003 | 2.09e-003 | 9.78e-002 |
| Processed by Fish | -7.84e-002 | -9.82e-002 | -6.53e-002 | 3.39e-002 | 1.12e-001 | -1.34e-001 | 1.07e-002 | -3.12e-002 | -2.92e-001 | -9.30e-001 | -3.11e-001 | -1.77e-001 | -1.64e-001 |
| SUM | 2.13e-002 | 6.56e-004 | -3.87e-002 | -2.37e-001 | 2.11e-001 | 4.94e-001 | 6.80e-001 | 3.15e-002 | 2.21e-001 | -1.39e+000 | -1.41e-001 | 8.59e-002 | -6.52e-003 |

Note:
1. All values in grams/day; + value is a source (input), - value is a sink (loss)
Source:
1. OLMM "TAMS04.INP" File

## Table 5-12

## Model Run 5 - Total Mercury Mass Balance

### MERC4 Simulation - Onondaga Lake
### Mass Balance : Total Mercury

| | Jan 92 | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | ANNUAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Inflow | 2.18e+001 | 2.34e+001 | 3.44e+001 | 4.96e+001 | 2.62e+001 | 2.22e+001 | 2.74e+001 | 3.02e+001 | 2.27e+001 | 2.31e+001 | 2.51e+001 | 2.61e+001 | 2.77e+001 |
| Atmospheric Deposit | 9.65e-001 | 7.87e-001 | 1.11e+000 | 1.44e+000 | 1.16e+000 | 1.18e+000 | 2.16e+000 | 1.02e+000 | 1.73e+000 | 1.06e+000 | 1.21e+000 | 7.76e-001 | 1.22e+000 |
| Groundwater Inflow | 1.64e-002 | 1.65e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 |
| Outflow | -6.20e+000 | -6.77e+000 | -8.14e+000 | -8.78e+000 | -4.28e+000 | -6.72e+000 | -6.07e+000 | -8.10e+000 | -5.90e+000 | -1.06e+001 | -7.78e+000 | -7.76e+000 | -7.26e+000 |
| Volatilization | -6.99e-002 | -7.32e-002 | -7.60e-002 | -6.33e-002 | -5.96e-002 | -9.39e-002 | -1.29e-001 | -1.38e-001 | -1.34e-001 | -1.11e-001 | -1.05e-001 | -9.36e-002 | -9.57e-002 |
| Kinetics | -6.05e-009 | 3.61e-009 | -6.05e-009 | 4.66e-010 | 1.14e-008 | -1.00e-004 | 3.00e-004 | -2.99e-004 | -3.40e-003 | 6.00e-004 | -2.79e-009 | -6.75e-009 | -2.37e-004 |
| Settling | -1.94e+001 | -2.08e+001 | -3.27e+001 | -5.71e+001 | -2.59e+001 | -2.41e+001 | -3.90e+001 | -6.78e+001 | -4.24e+001 | -6.57e+001 | -2.46e+001 | -2.06e+001 | -3.68e+001 |
| Resuspension | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sediment Exchange | 4.17e+000 | 4.19e+000 | 4.42e+000 | 4.84e+000 | 1.33e+001 | 3.44e+001 | 3.79e+001 | 4.04e+001 | 4.29e+001 | 2.79e+001 | 6.60e+000 | 4.77e+000 | 1.89e+001 |
| Processed by Fish | -9.77e-002 | -1.42e-001 | -1.11e-001 | 6.79e-003 | -9.17e-002 | -1.08e+000 | -1.24e+000 | -2.28e+000 | -4.37e+000 | -2.37e+001 | -3.63e+000 | -4.45e-001 | -3.13e+000 |
| SUM | 1.26e+000 | 6.81e-001 | -1.03e+000 | -1.00e+001 | 1.03e+001 | 2.58e+001 | 2.10e+001 | -6.78e+000 | 1.45e+001 | -4.79e+001 | -3.12e+000 | 2.82e+000 | 5.55e-001 |

Note:
1. All values in grams/day; + value is a source (input), - value is a sink (loss)
Source:
1. OLMM "TAMS05.INP" File

Table 5-13

Model Run 5 Methyl Mercury Mass Balance

MERC4 Simulation - Onondaga Lake
Mass Balance : Methyl Mercury

| | Jan 92 | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | ANNUAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Inflow | 6.22e-001 | 6.52e-001 | 8.73e-001 | 1.18e+000 | 7.07e-001 | 6.37e-001 | 7.38e-001 | 7.94e-001 | 6.31e-001 | 6.39e-001 | 6.74e-001 | 6.99e-001 | 7.38e-001 |
| Atmospheric Depositi | 1.27e-002 | 1.01e-002 | 1.21e-002 | 1.75e-002 | 1.64e-002 | 1.44e-002 | 3.05e-002 | 1.14e-002 | 2.41e-002 | 1.42e-002 | 1.65e-002 | 9.35e-003 | 1.58e-002 |
| Groundwater Inflow | 8.20e-004 | 8.23e-004 | 8.20e-004 | 8.20e-004 | 8.17e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 |
| Outflow | -2.62e-001 | -2.94e-001 | -3.74e-001 | -4.44e-001 | -2.82e-001 | -4.91e-001 | -5.98e-001 | -1.03e+000 | -9.66e-001 | -4.75e+000 | -1.54e+000 | -6.84e-001 | -9.83e-001 |
| Volatilization | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Kinetics | 0 | 0 | 0 | 0 | 3.95e-001 | 5.24e+000 | 7.83e+000 | 8.69e+000 | 9.85e+000 | 3.71e+000 | 0 | 0 | 2.99e+000 |
| Settling | -3.21e-001 | -3.71e-001 | -6.54e-001 | -1.26e+000 | -1.22e+000 | -8.32e+000 | -1.65e+001 | -3.11e+001 | -2.20e+001 | -2.58e+001 | -2.35e+000 | -7.66e-001 | -9.29e+000 |
| Resuspension | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sediment Exchange | 1.83e-001 | 1.83e-001 | 1.94e-001 | 2.12e-001 | 5.47e+000 | 2.11e+001 | 2.32e+001 | 2.47e+001 | 2.63e+001 | 1.48e+001 | 2.89e-001 | 2.09e-001 | 9.78e+000 |
| Processed by Fish | -9.77e-002 | -1.42e-001 | -1.11e-001 | 6.79e-003 | -9.17e-002 | -1.08e+000 | -1.24e+000 | -2.28e+000 | -4.37e+000 | -2.37e+001 | -3.63e+000 | -4.45e-001 | -3.13e+000 |
| SUM | 1.38e-001 | 3.94e-002 | -5.95e-002 | -2.88e-001 | 5.00e+000 | 1.71e+001 | 1.34e+001 | -1.63e-001 | 9.46e+000 | -3.51e+001 | -6.53e+000 | -9.79e-001 | 1.22e-001 |

Note:
1. All values in grams/day; + value is a source (input), - value is a sink (loss)
Source:
1. OLMM "TAMS05.INP" File

## Table 5-14

## Model Run 6 - Total Mercury Mass Balance

### MERC4 Simulation - Onondaga Lake
### Mass Balance : Total Mercury

| | Jan 92 | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | ANNUAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Inflow | 2.18e+001 | 2.34e+001 | 3.44e+001 | 4.96e+001 | 2.62e+001 | 2.22e+001 | 2.74e+001 | 3.02e+001 | 2.27e+001 | 2.31e+001 | 2.51e+001 | 2.61e+001 | 2.77e+001 |
| Atmospheric Deposit | 4.83e-001 | 3.94e-001 | 5.56e-001 | 7.22e-001 | 5.80e-001 | 5.89e-001 | 1.08e+000 | 5.12e-001 | 8.64e-001 | 5.31e-001 | 6.07e-001 | 3.88e-001 | 6.10e-001 |
| Groundwater Inflow | 1.64e-002 | 1.65e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 | 1.64e-002 |
| Outflow | -5.77e+000 | -5.86e+000 | -7.06e+000 | -7.85e+000 | -3.68e+000 | -5.67e+000 | -5.08e+000 | -5.73e+000 | -4.52e+000 | -4.95e+000 | -4.98e+000 | -5.94e+000 | -5.67e+000 |
| Volatilization | -8.91e-002 | -6.96e-002 | -6.98e-002 | -5.73e-002 | -5.33e-002 | -8.18e-002 | -1.12e-001 | -1.21e-001 | -1.17e-001 | -9.08e-002 | -7.93e-002 | -7.11e-002 | -8.28e-002 |
| Kinetics | -6.64e-009 | -6.98e-010 | 3.84e-009 | -1.57e-009 | -1.00e-004 | -1.00e-004 | 3.91e-007 | 7.00e-004 | -3.00e-004 | 5.00e-004 | -1.86e-009 | 4.31e-009 | 6.05e-005 |
| Settling | -1.79e+001 | -1.78e+001 | -2.82e+001 | -5.13e+001 | -2.05e+001 | -9.79e+000 | -1.51e+001 | -2.84e+001 | -1.49e+001 | -2.89e+001 | -1.68e+001 | -1.61e+001 | -2.22e+001 |
| Resuspension | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sediment Exchange | 4.16e-002 | 4.18e-002 | 4.42e-002 | 4.84e-002 | 1.33e-001 | 3.44e-001 | 3.79e-001 | 4.03e-001 | 4.28e-001 | 2.79e-001 | 8.59e-002 | 4.76e-002 | 1.89e-001 |
| Processed by Fish | -7.75e-002 | -9.68e-002 | -8.36e-002 | 3.55e-002 | 1.14e-001 | -1.74e-001 | -1.11e-001 | -3.12e-001 | -8.35e-001 | -3.82e+000 | -8.80e-001 | -1.97e-001 | -8.23e-001 |
| SUM | -1.42e+000 | 1.11e-001 | -3.20e-001 | -8.80e+000 | 2.82e+000 | 7.42e+000 | 8.51e+000 | -4.46e+000 | 3.58e+000 | -1.38e+001 | 3.24e+000 | 4.22e+000 | 7.81e-002 |

Note:
1. All values in grams/day; + value is a source (input), - value is a sink (loss)
Source:
1. OLMM "TAMS06.INP" File

## Table 5-15

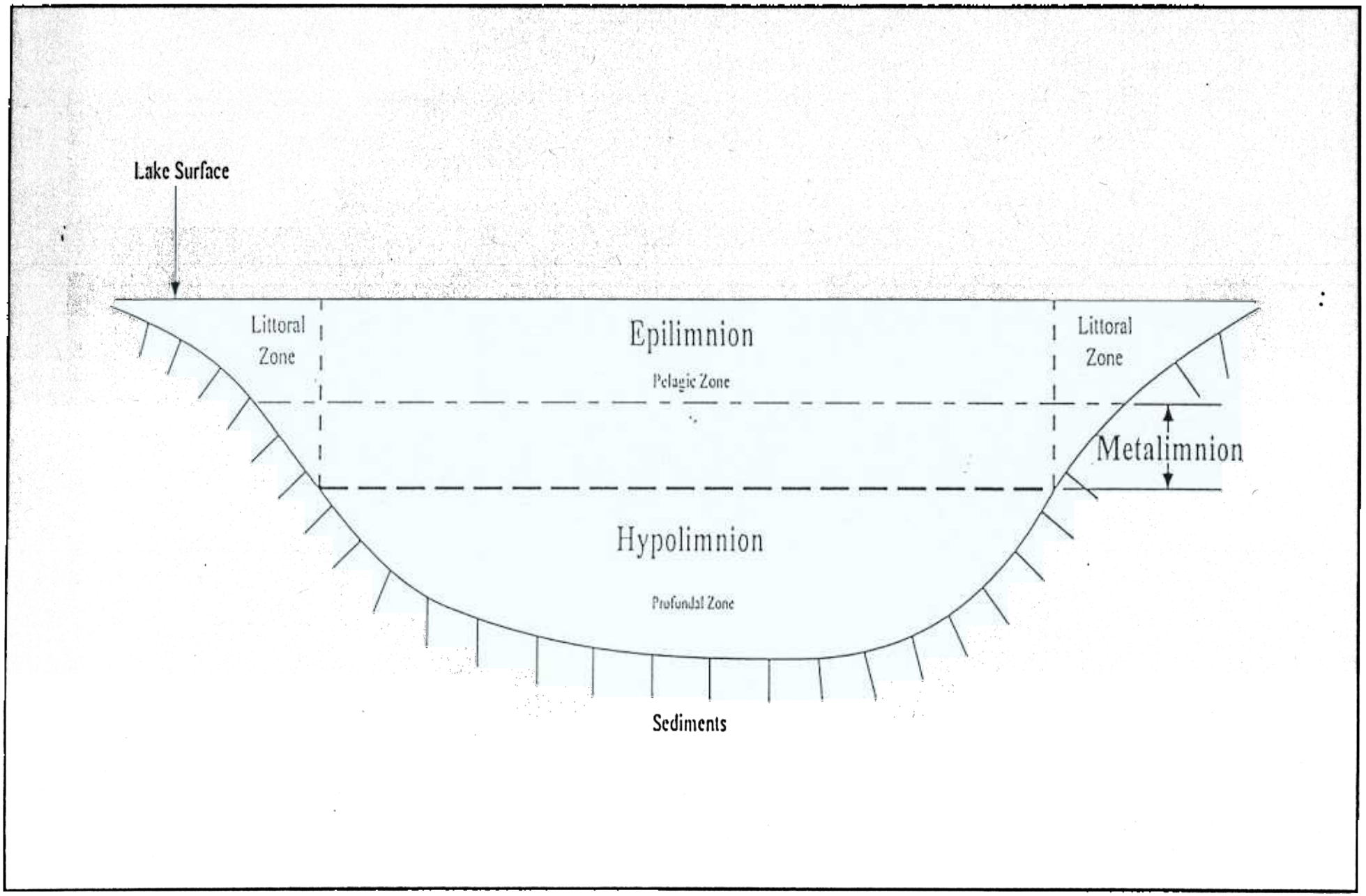
## Model Run 6 - Methyl Mercury Mass Balance

### MERC4 Simulation - Onondaga Lake
### Mass Balance : Methyl Mercury

| | Jan 92 | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec | ANNUAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Inflow | 6.22e-001 | 6.52e-001 | 8.73e-001 | 1.18e+000 | 7.07e-001 | 6.37e-001 | 7.38e-001 | 7.94e-001 | 6.31e-001 | 6.39e-001 | 6.74e-001 | 6.99e-001 | 7.38e-001 |
| Atmospheric Deposit | 6.37e-003 | 5.06e-003 | 6.07e-003 | 6.76e-003 | 8.23e-003 | 7.22e-003 | 1.52e-002 | 5.73e-003 | 1.21e-002 | 7.12e-003 | 8.24e-003 | 4.68e-003 | 7.91e-003 |
| Groundwater Inflow | 8.20e-004 | 8.23e-004 | 8.20e-004 | 8.20e-004 | 8.17e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 | 8.20e-004 |
| Outflow | -2.43e-001 | -2.52e-001 | -3.20e-001 | -3.89e-001 | -2.22e-001 | -2.54e-001 | -2.86e-001 | -4.07e-001 | -3.17e-001 | -8.79e-001 | -3.67e-001 | -2.64e-001 | -3.51e-001 |
| Volatilization | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Kinetics | 0 | 0 | 0 | 0 | 2.54e-001 | 2.89e+000 | 4.45e+000 | 5.44e+000 | 5.39e+000 | 2.18e+000 | 0 | 0 | 1.73e+000 |
| Settling | -2.93e-001 | -3.11e-001 | -5.37e-001 | -1.08e+000 | -4.96e-001 | -9.97e-001 | -2.31e+000 | -5.23e+000 | -3.78e+000 | -4.27e+000 | -5.38e-001 | -2.87e-001 | -1.69e+000 |
| Resuspension | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sediment Exchange | 1.83e-003 | 1.83e-003 | 1.93e-003 | 2.12e-003 | 5.47e-002 | 2.10e-001 | 2.32e-001 | 2.47e-001 | 2.62e-001 | 1.48e-001 | 2.89e-003 | 2.09e-003 | 9.78e-002 |
| Processed by Fish | -7.75e-002 | -9.68e-002 | -6.36e-002 | 3.55e-002 | 1.14e-001 | -1.74e-001 | -1.11e-001 | -3.12e-001 | -8.35e-001 | -3.82e+000 | -6.80e-001 | -1.97e-001 | -5.23e-001 |
| SUM | 1.73e-002 | 3.17e-005 | -3.86e-002 | -2.36e-001 | 4.22e-001 | 2.32e+000 | 2.72e+000 | 5.44e-001 | 1.36e+000 | -6.00e+000 | -8.99e-001 | -4.22e-002 | 7.40e-003 |

Note:
1. All values in grams/day; + value is a source (input), - value is a sink (loss)
Source:
1. OLMM "TAMS06.INP" File

# FIGURES

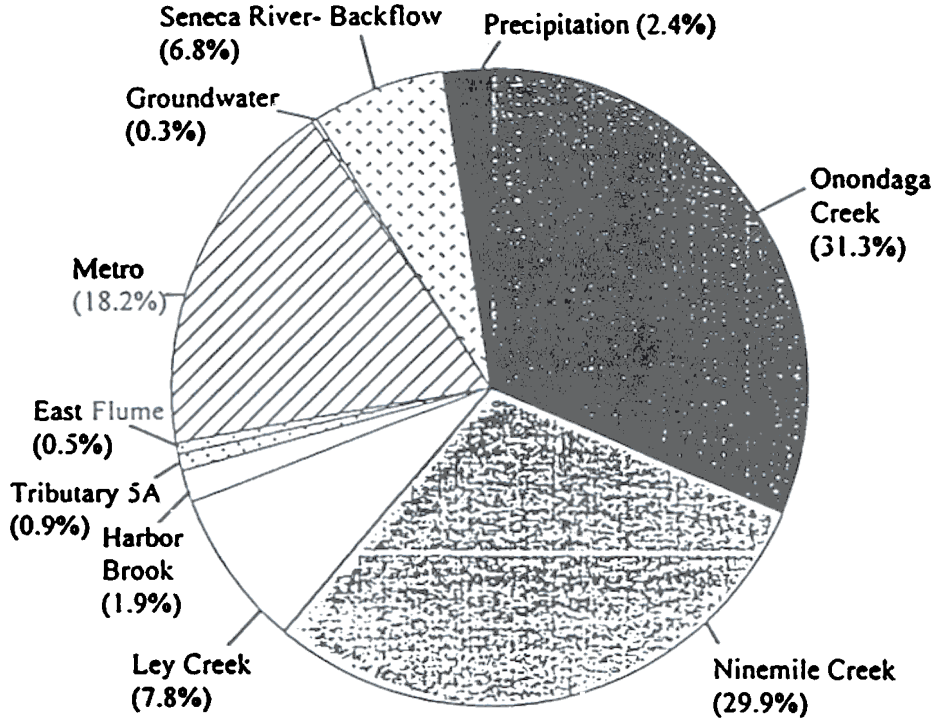



AMS

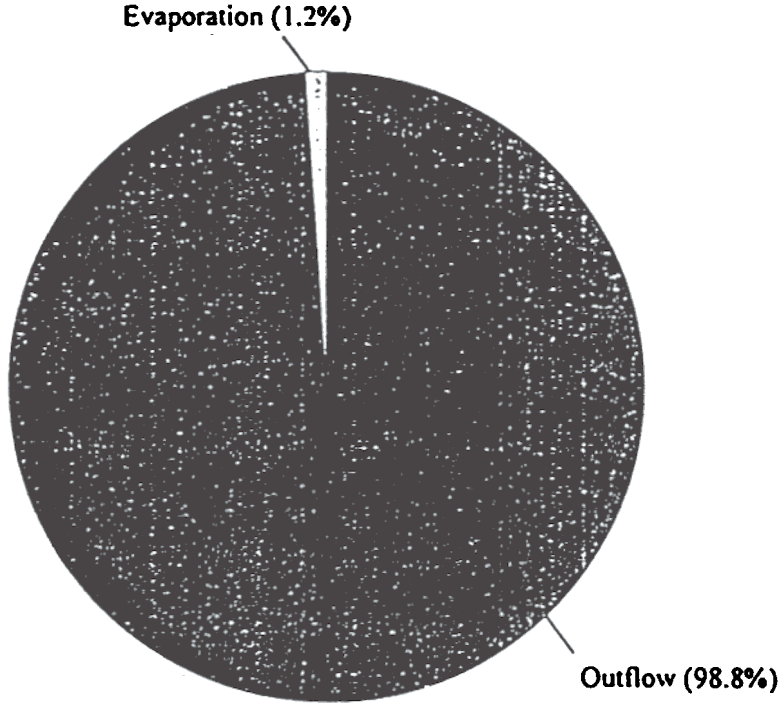
F 1

M j L m g C mp f O d L

## 1992 Inflows



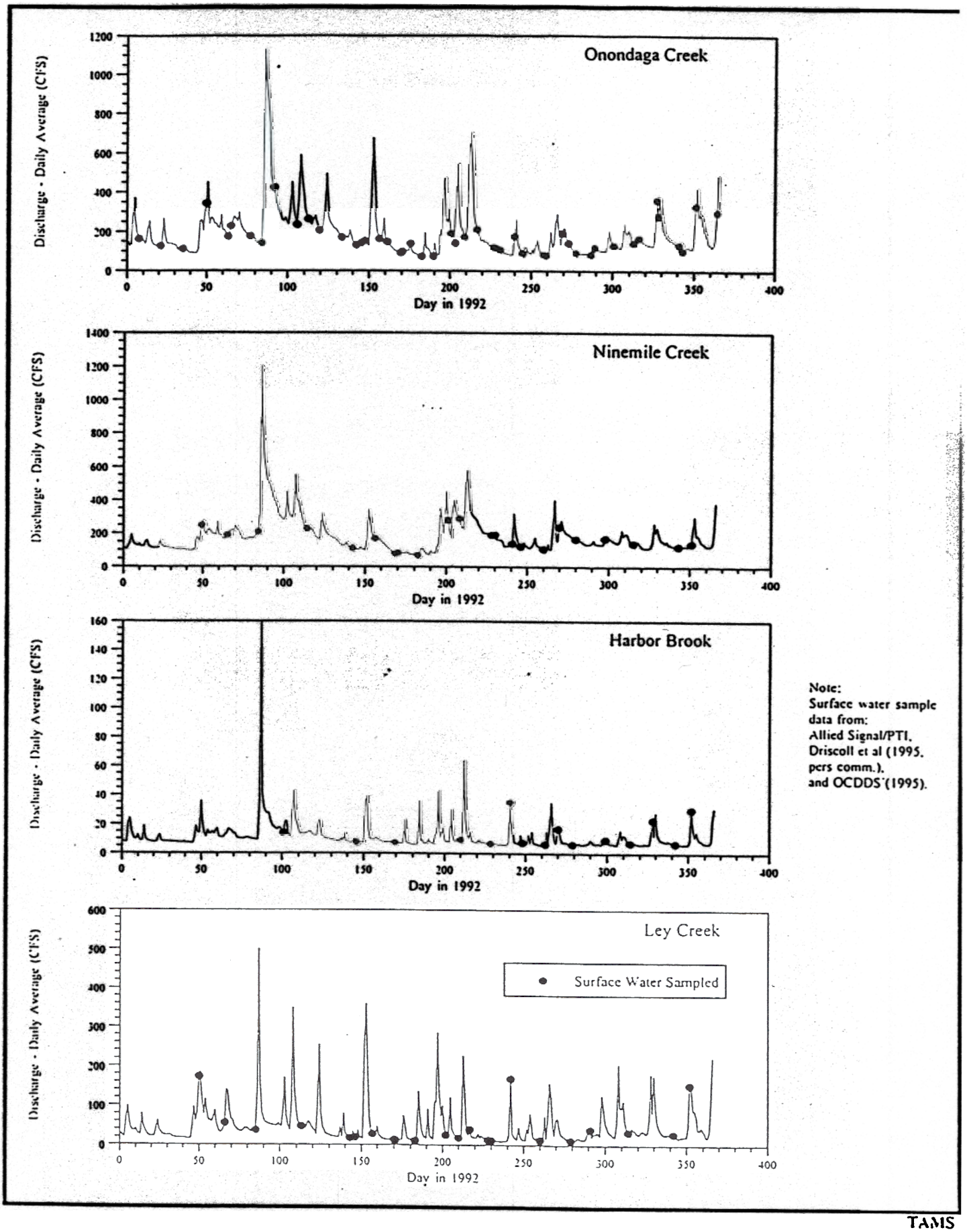

## 1992 Outflows




Source: PTI. 1997: OLMM: "CALIB.OUT" File

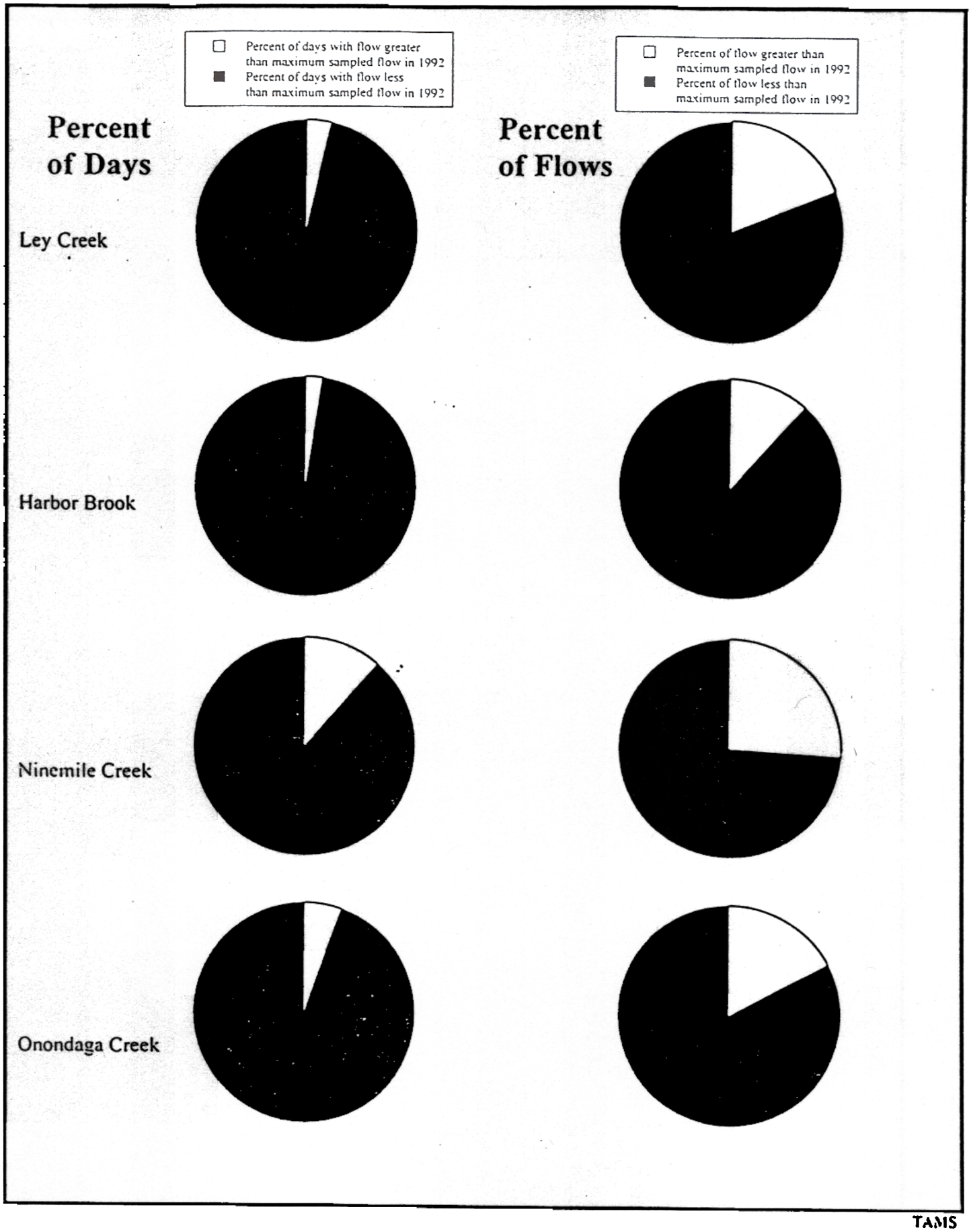
TAMS

Figure 2-2
OLMM 1992 Inflow and Outflow Volumes



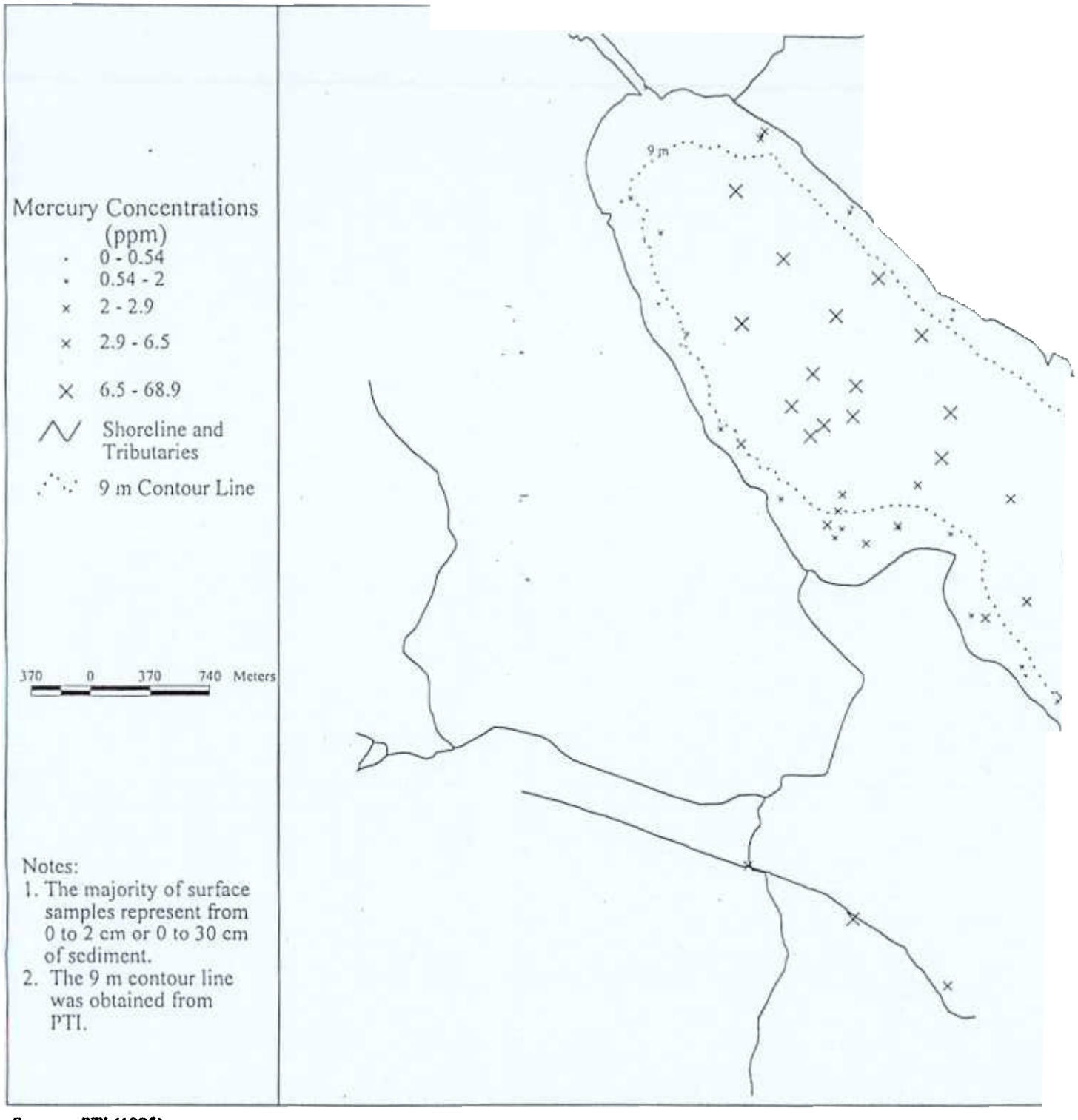

TAMS

Figure 2-3
Tributary Flow to Onondaga Lake Showing Dates of Suspended Solids and Mercury Sampling in 1992



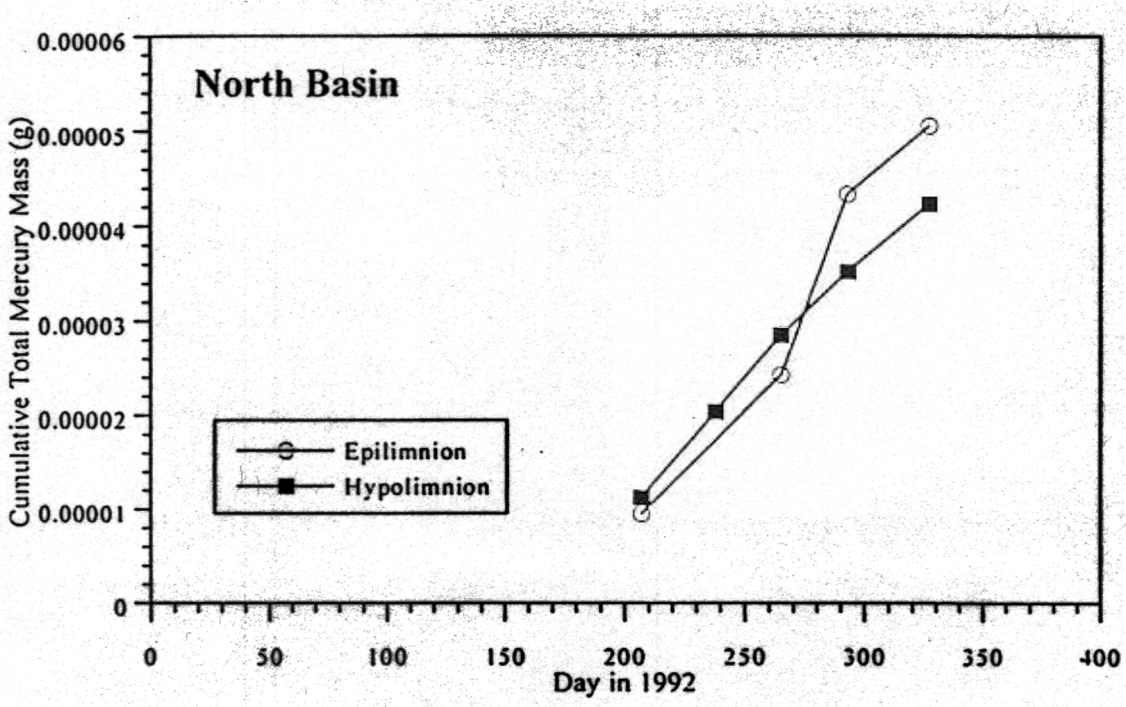

TAMS

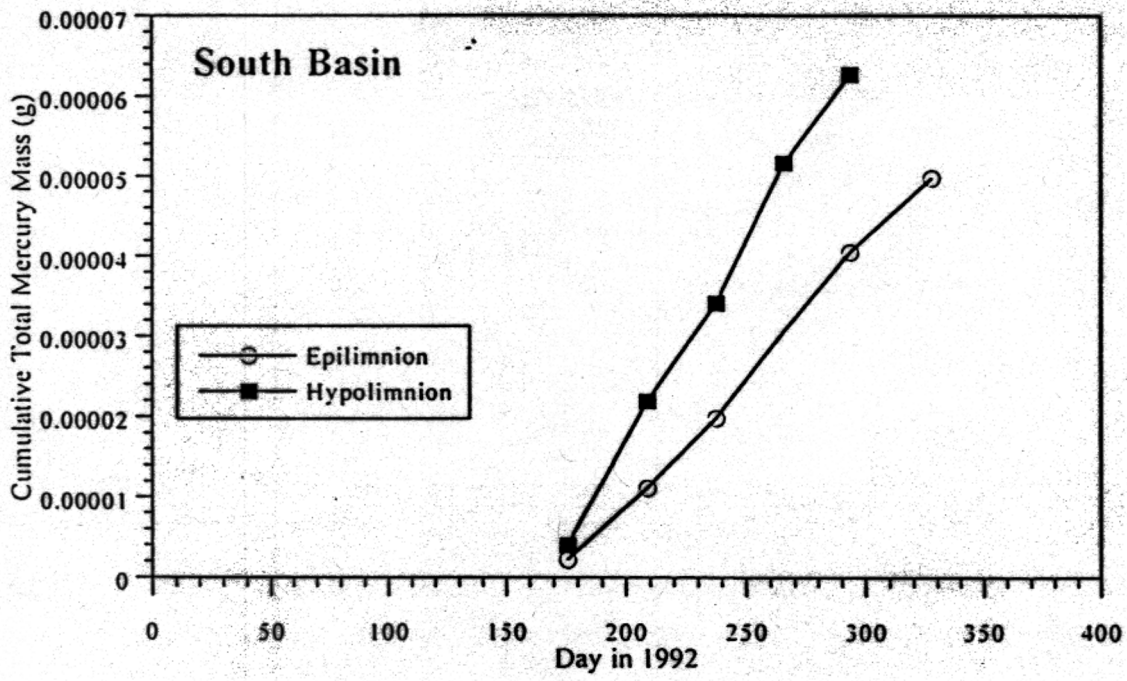
**Figure 2-4**
**Tributary Flow to Onondaga Lake**




Sources: PTI (1995)

Figure 2-5

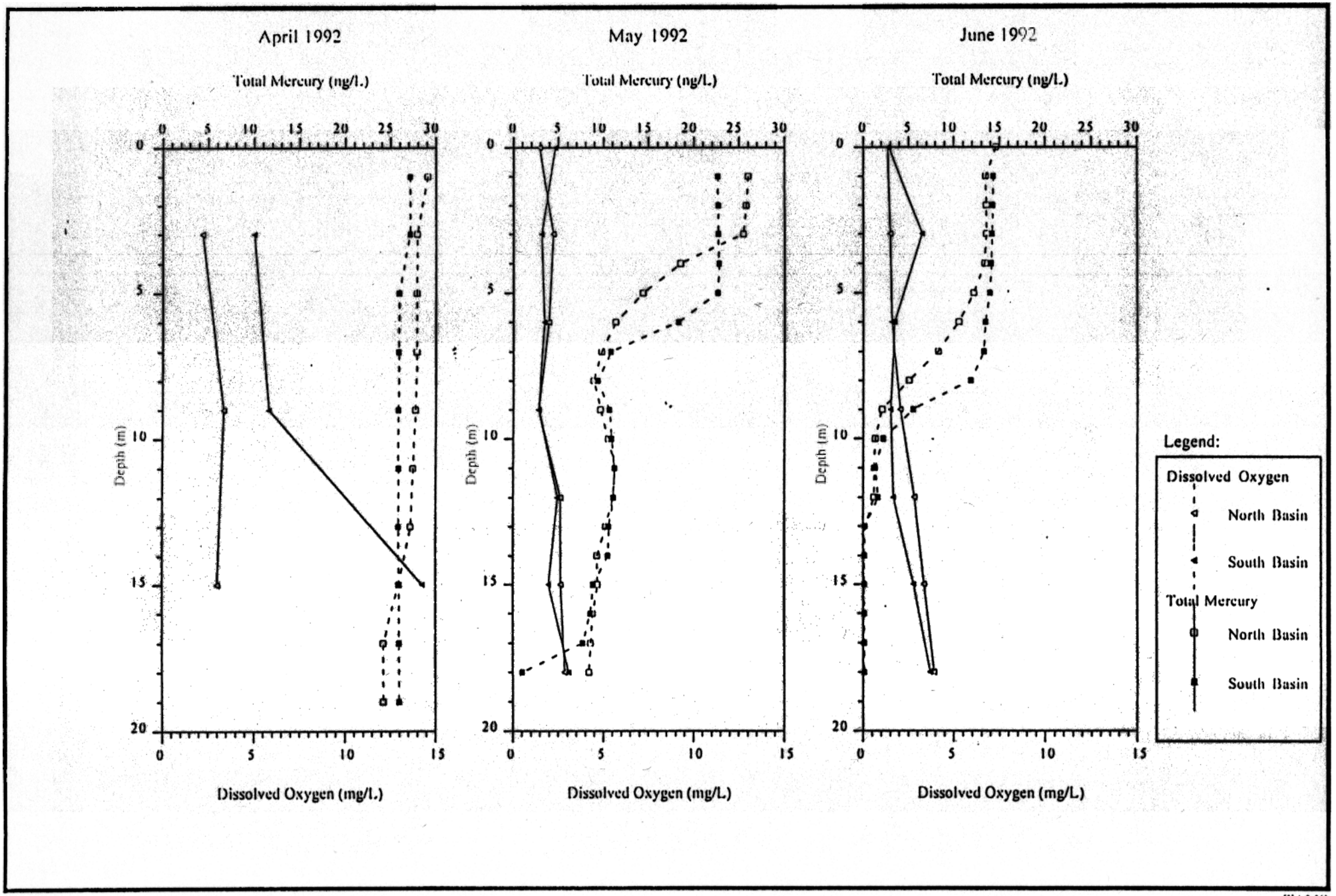



Source: PTI, 1993

TAMS

**Figure 2-6**
**Cumulation Mercury Load in Sediment Traps for 1992**

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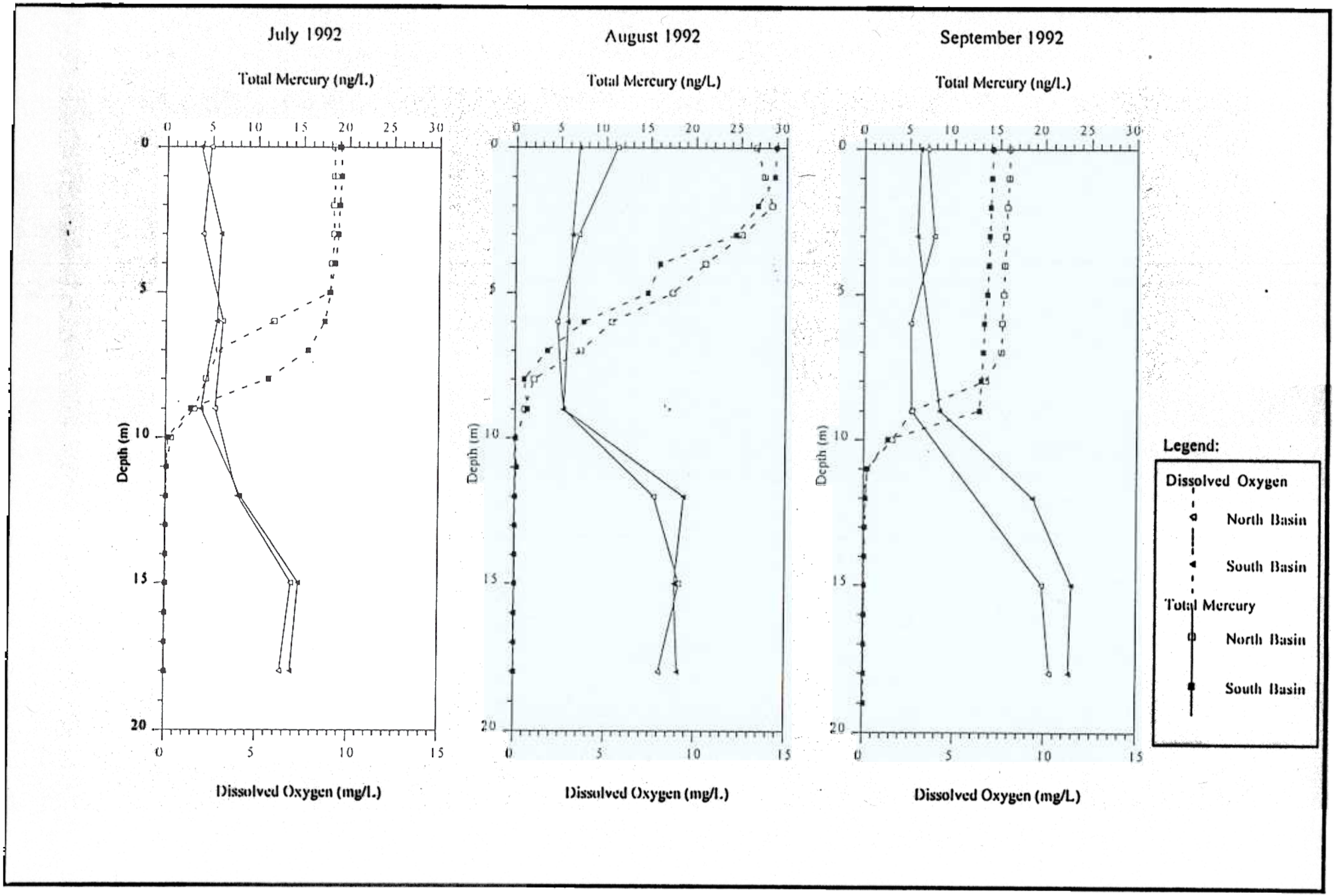


TAMS

Figure 3-1B
Water Column Total Mercury and Dissolved Oxygen Profiles in Onondaga Lake

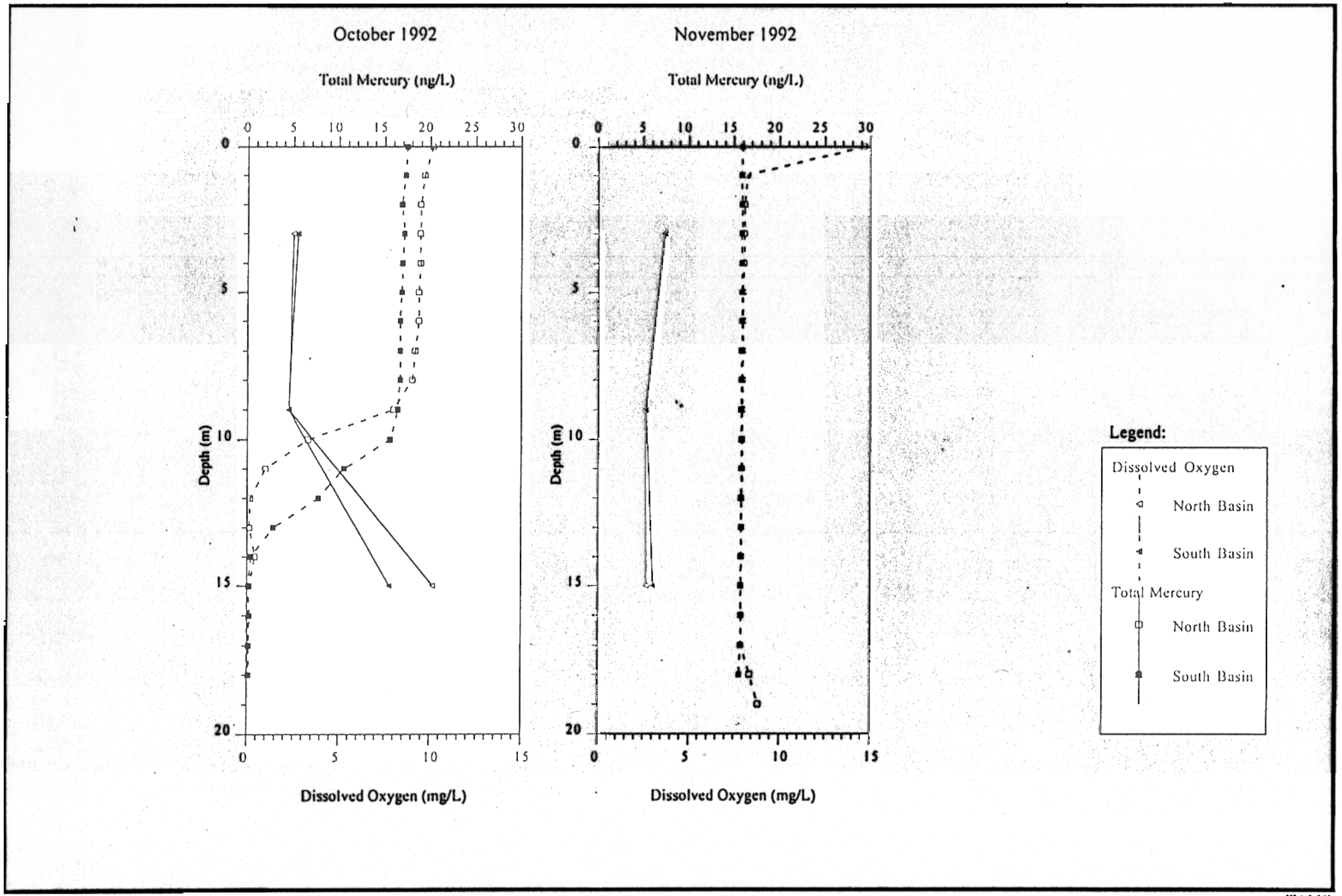


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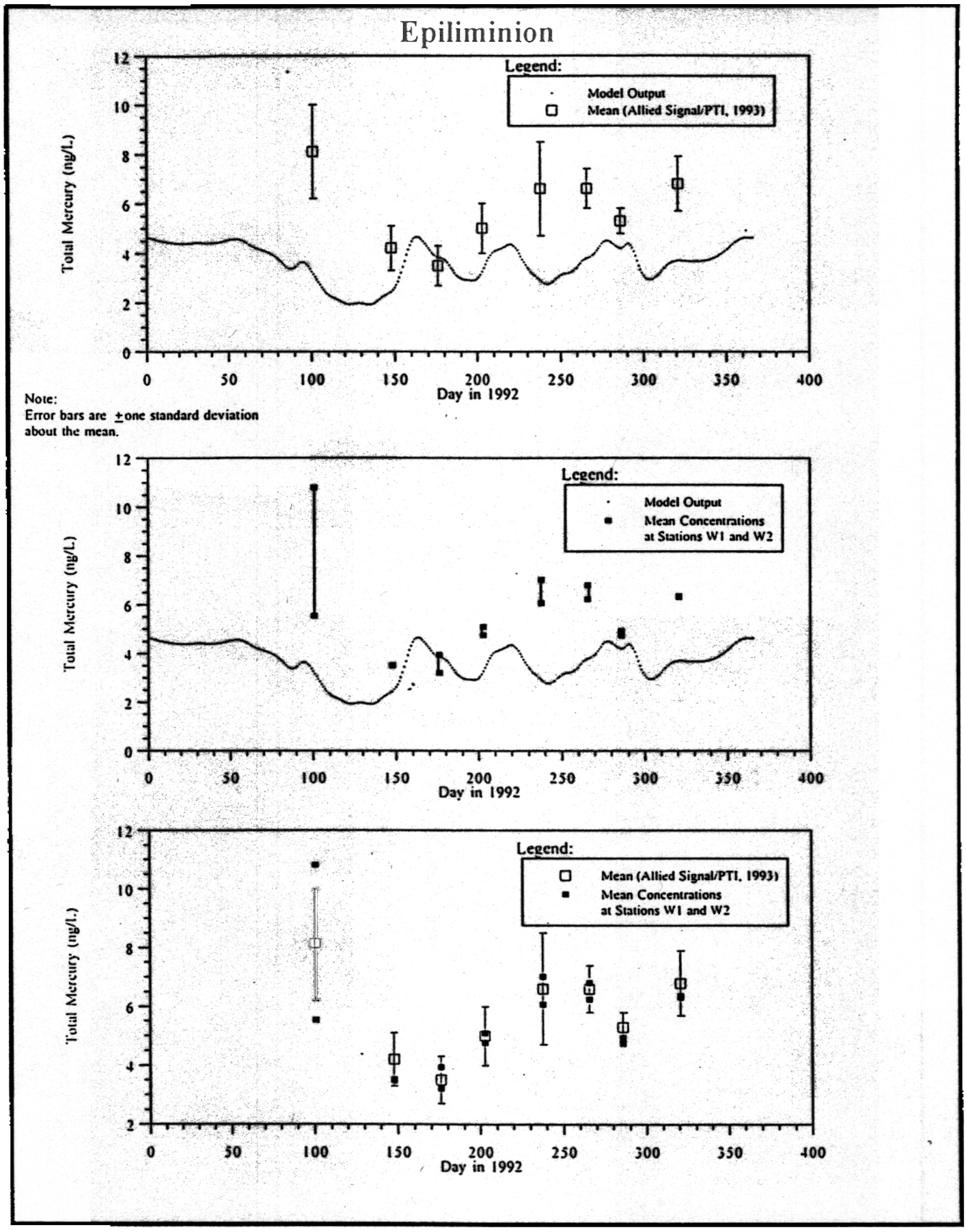
**Figure 3-1C**
**Water Column Total Mercury and Dissolved Oxygen Profiles in Onondaga Lake**




TAMS

**Figure 3-2**
**Comparison of the Model Output to Concentration Measurements in the Epilimnion**

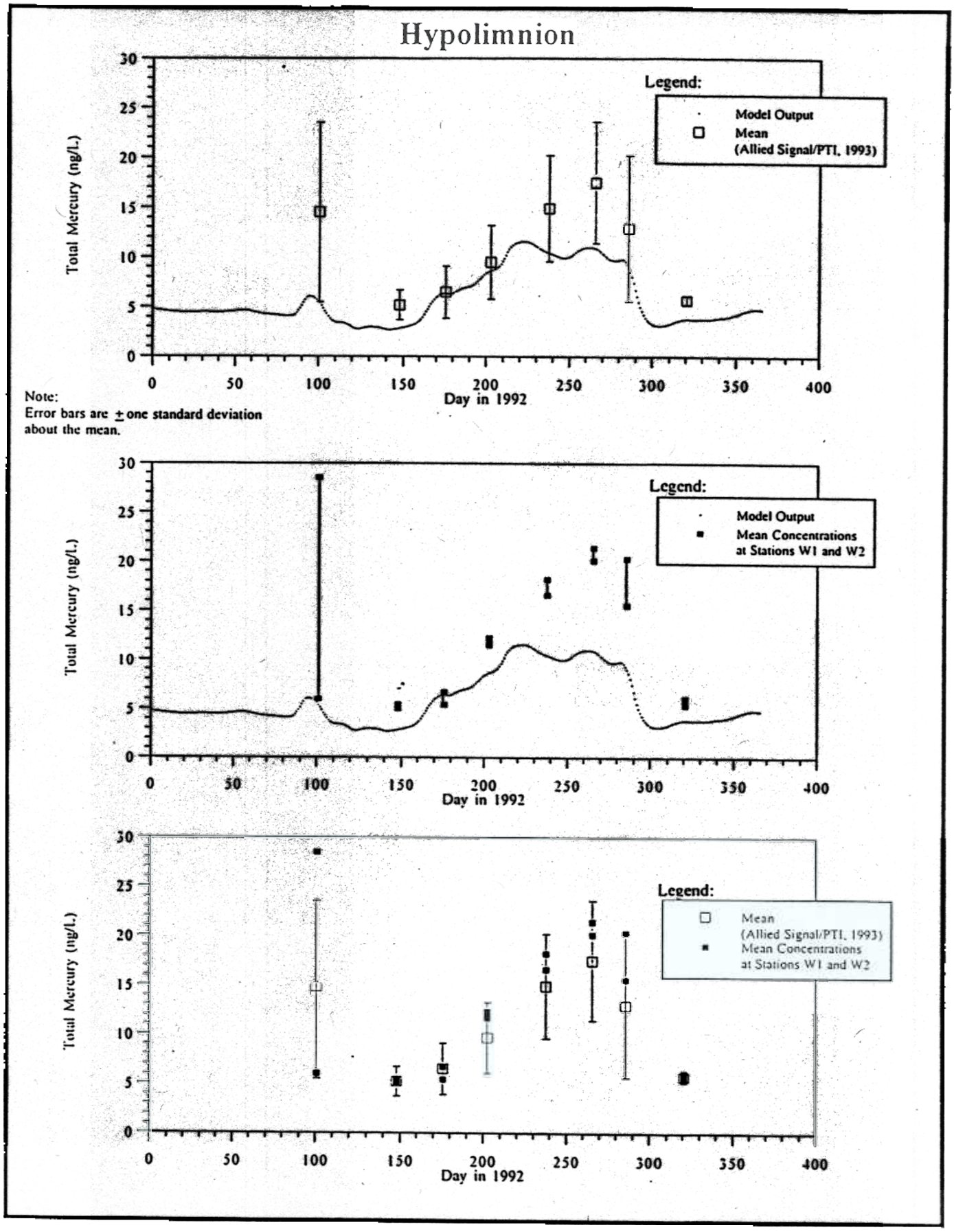



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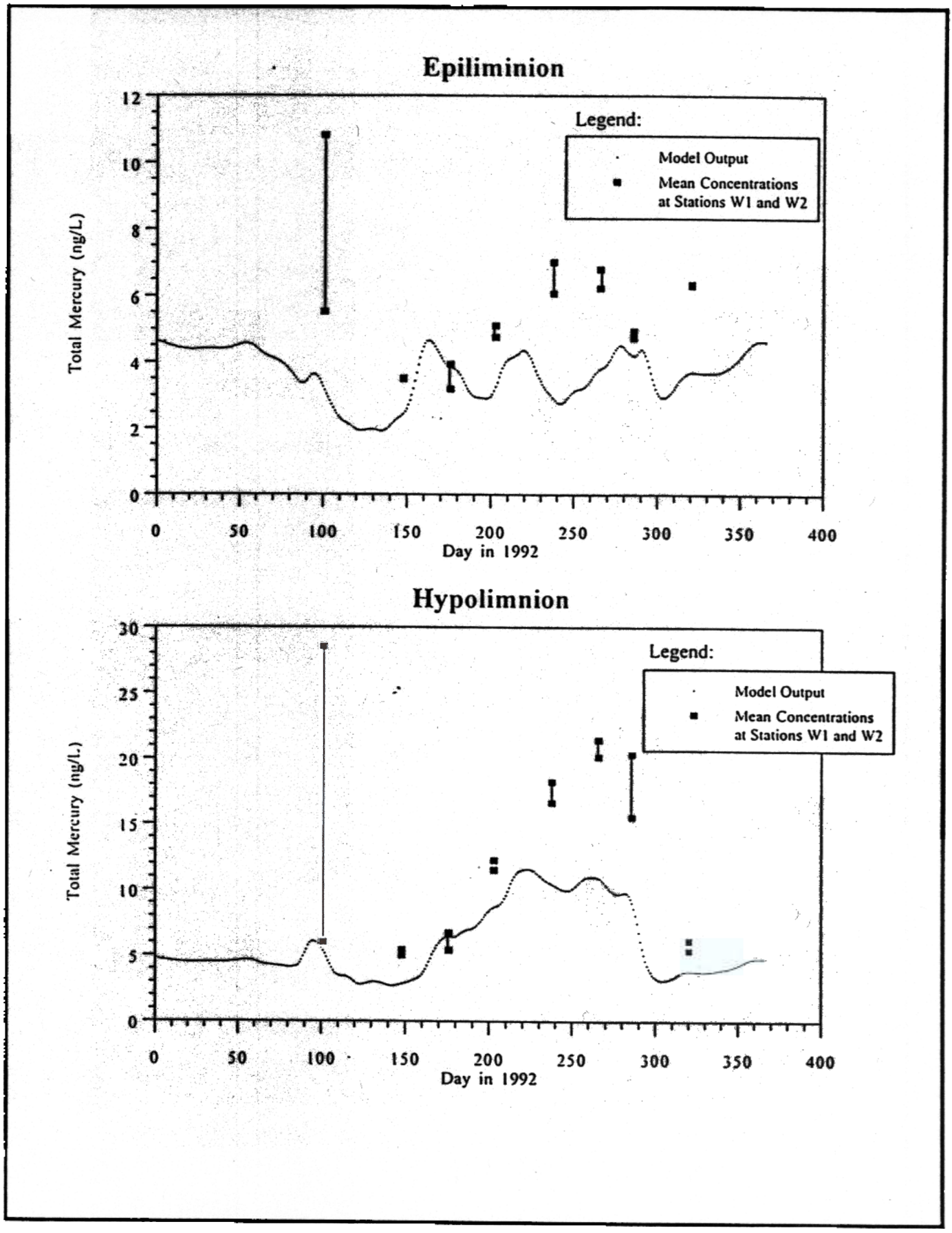
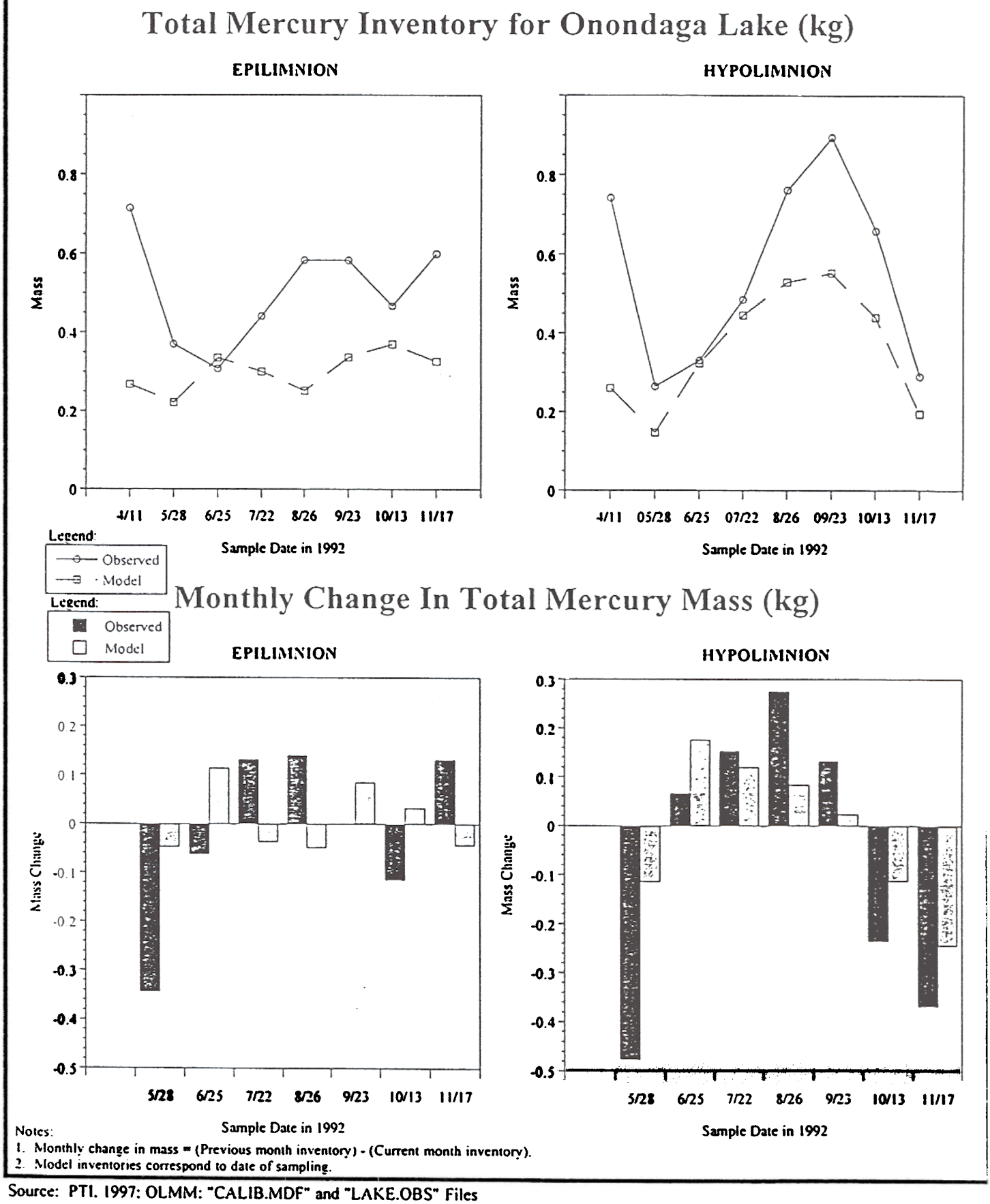
**Figure 3-3**
**Comparison of the Model Output to Concentration Measurements in the Hypolimnion**




TAMS

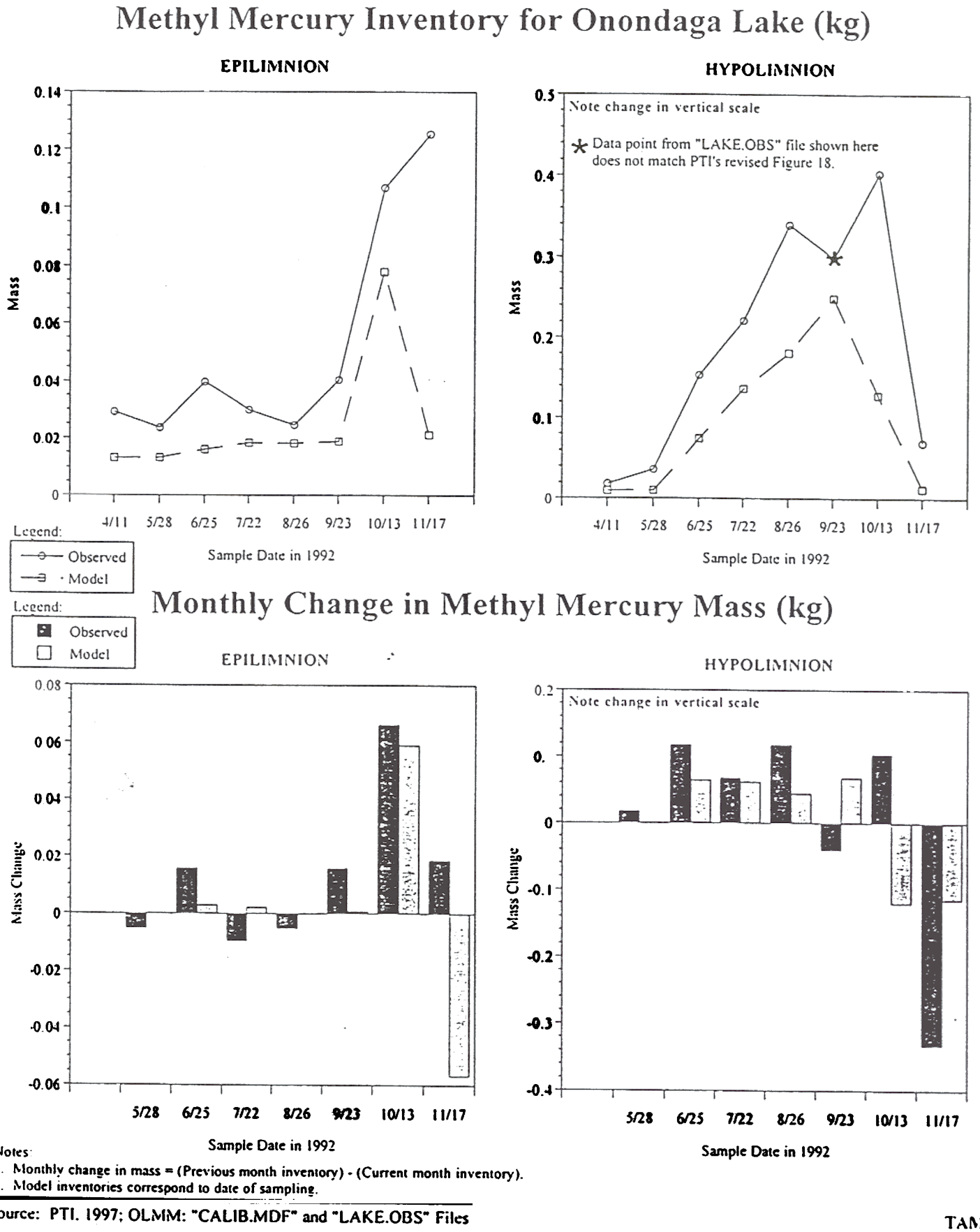
**Figure 3-4**
**Comparison of the Model Output to Concentration Measurements in the Epilimnion and Hypolimnion**




Notes:
1. Monthly change in mass = (Previous month inventory) - (Current month inventory).
2. Model inventories correspond to date of sampling.

Source: PTI. 1997: OLMM: "CALIB.MDF" and "LAKE.OBS" Files

**Figure 3-5**
**Total Mercury: OLMM Model and PTI Data**




Notes:
1. Monthly change in mass = (Previous month inventory) - (Current month inventory).
2. Model inventories correspond to date of sampling.

Source: PTI. 1997; OLMM: "CALIB.MDF" and "LAKE.OBS" Files

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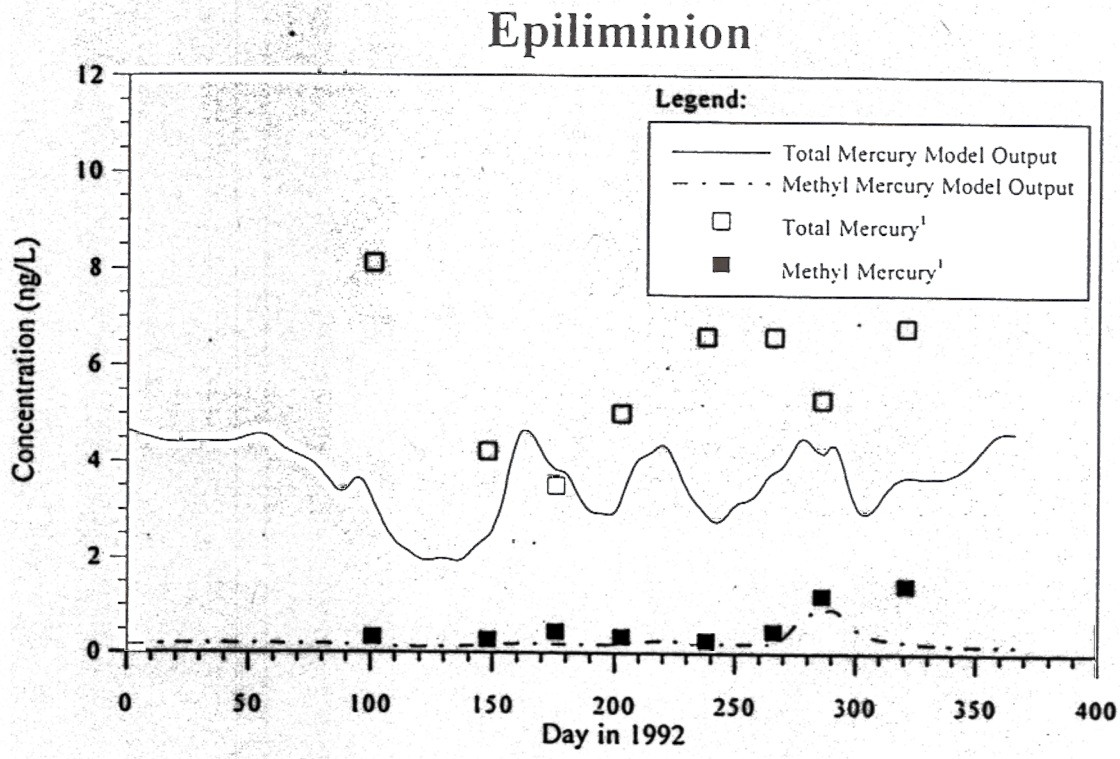
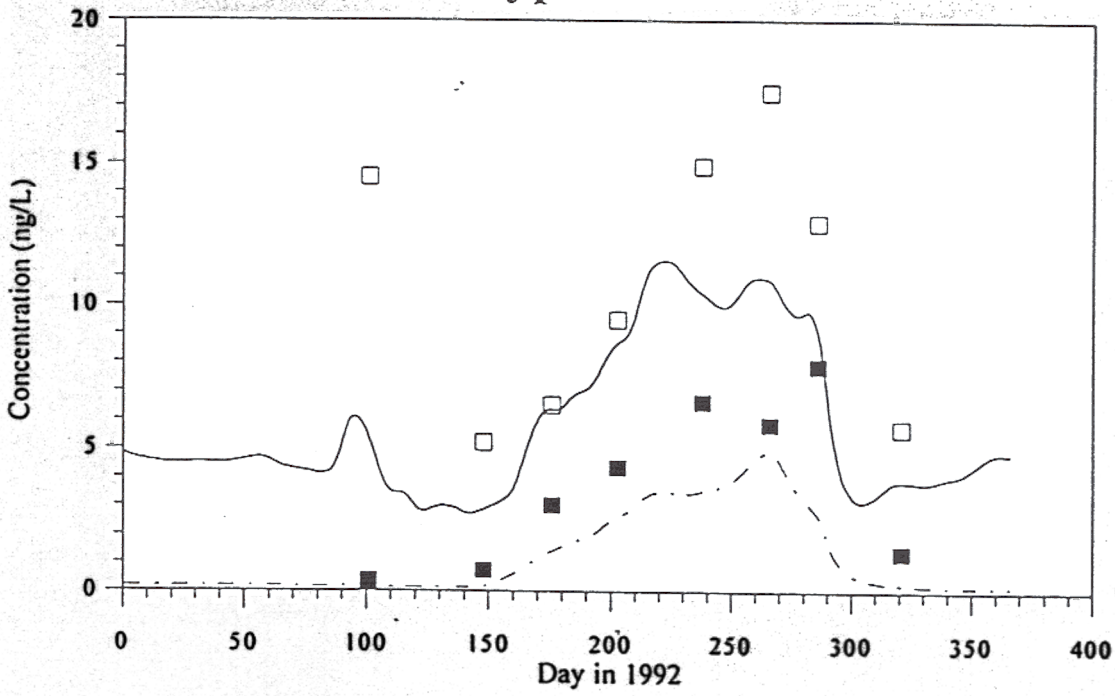
**Figure 3-6**
**Methyl Mercury: OLMM Model and PTI Data**




Note:
1. Data points are from PTI (1997).

Source: PTI. 1997: OLMM:"CALIB.MDF" and "LAKE.OBS" Files

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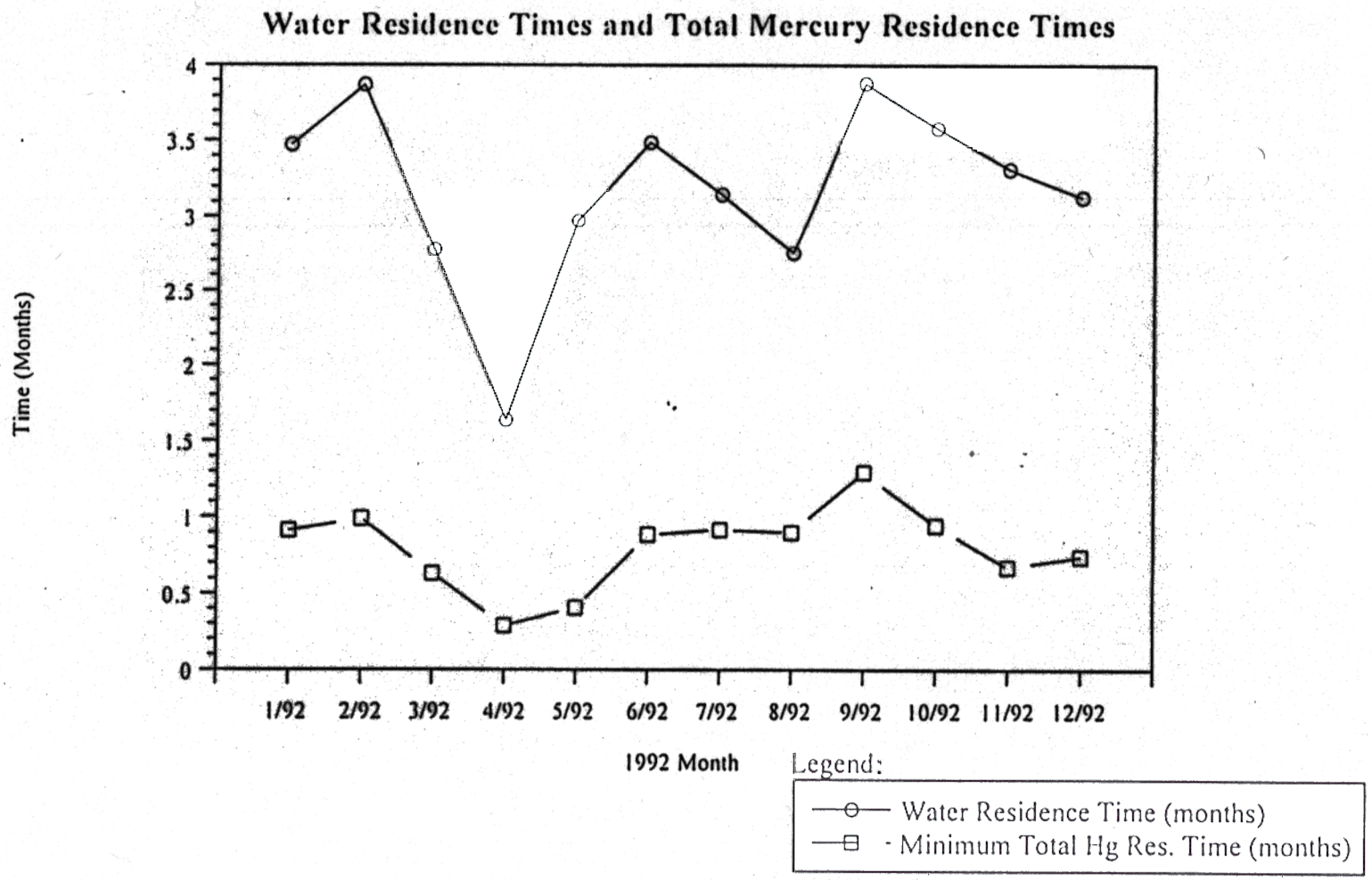
**Figure 3-7**
**Comparison Methyl Mercury and Total Mercury Concentrations in the Epilimnion and Hypolimnion**

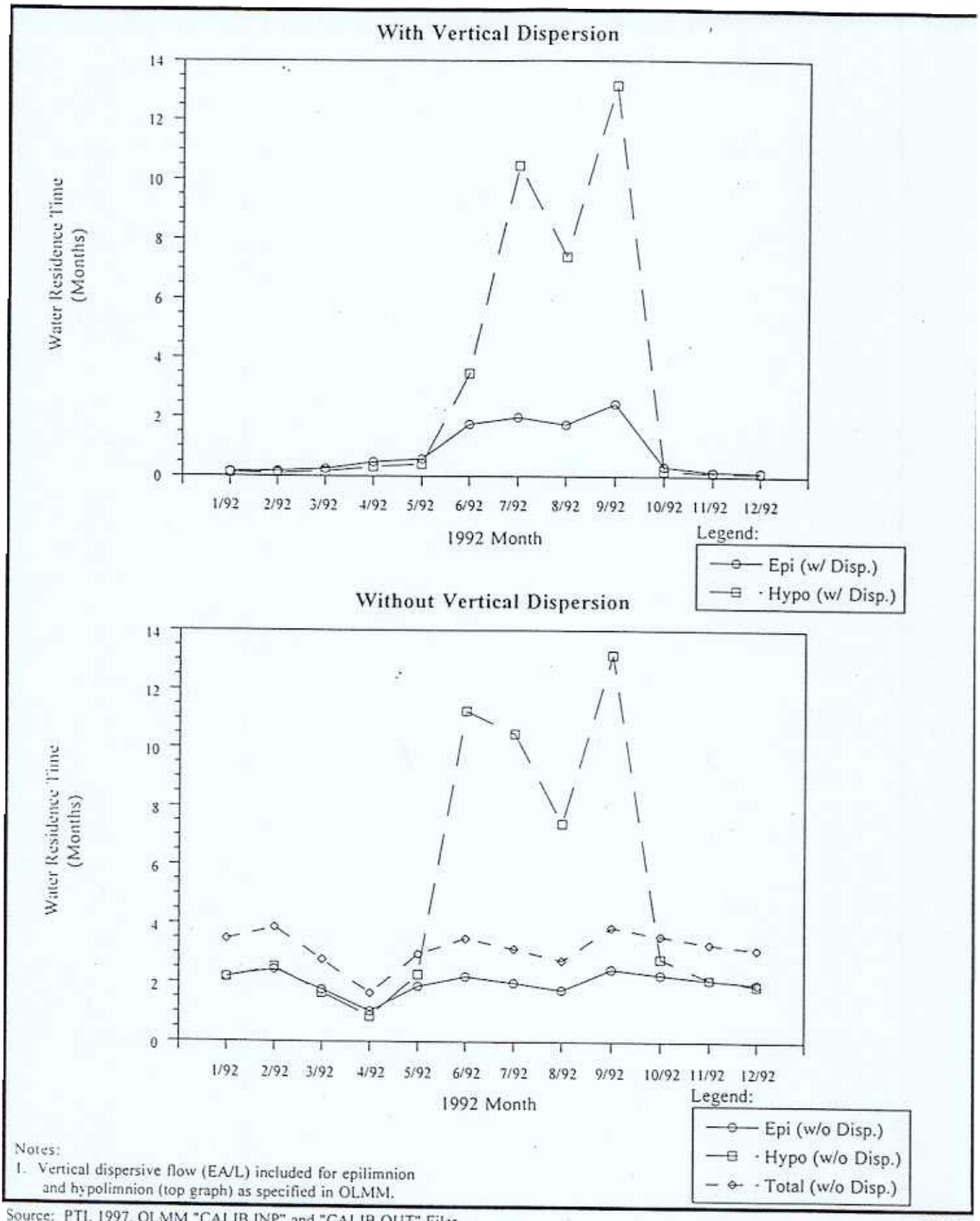



Notes:
1. Monthly flushing times represented by total lake volume divided by sum of inflows (tributaries, METRO, groundwater and precipitation).
2. Monthly total mercury residence times represented by a ratio of average lake concentration to average inflow concentration multiplied by water flushing time.

Source: PTI, 1997; OLMM "CALIB" Output Files

TAMS

**Figure 3-8**
**Calculated Lake Water Residence Times and Mercury Residence Times Based on the OLMM**

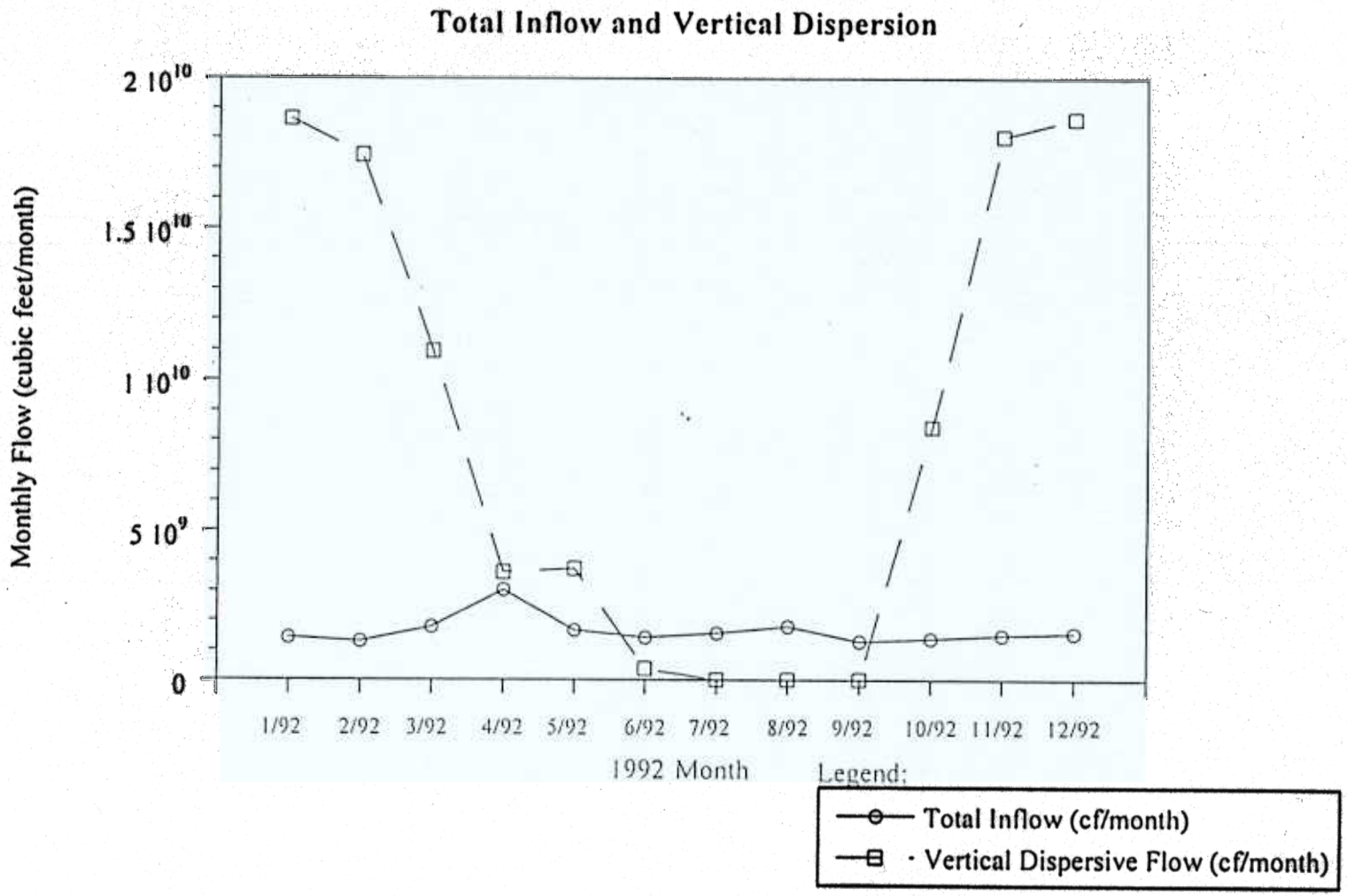



Notes:
1. Vertical dispersive flow (EA/L) included for epilimnion and hypolimnion (top graph) as specified in OLMM.

Source: PTI. 1997. OLMM "CALIB.INP" and "CALIB.OUT" Files

TAMS

**Figure 3-9**
**Calculated Lake Water Residence Times Based on the OLMM**




Notes:
1. Total inflow includes tributaries, METRO, groundwater and precipitation inputs, as specified in the OLMM.
2. Vertical dispersive flows (EA/L) as specified in OLMM input.

Source: PTI, 1997; OLMM "CALIB.INP" File

TAMS

**Figure 3-10**
**OLMM Total Inflow and Vertical Dispersion**

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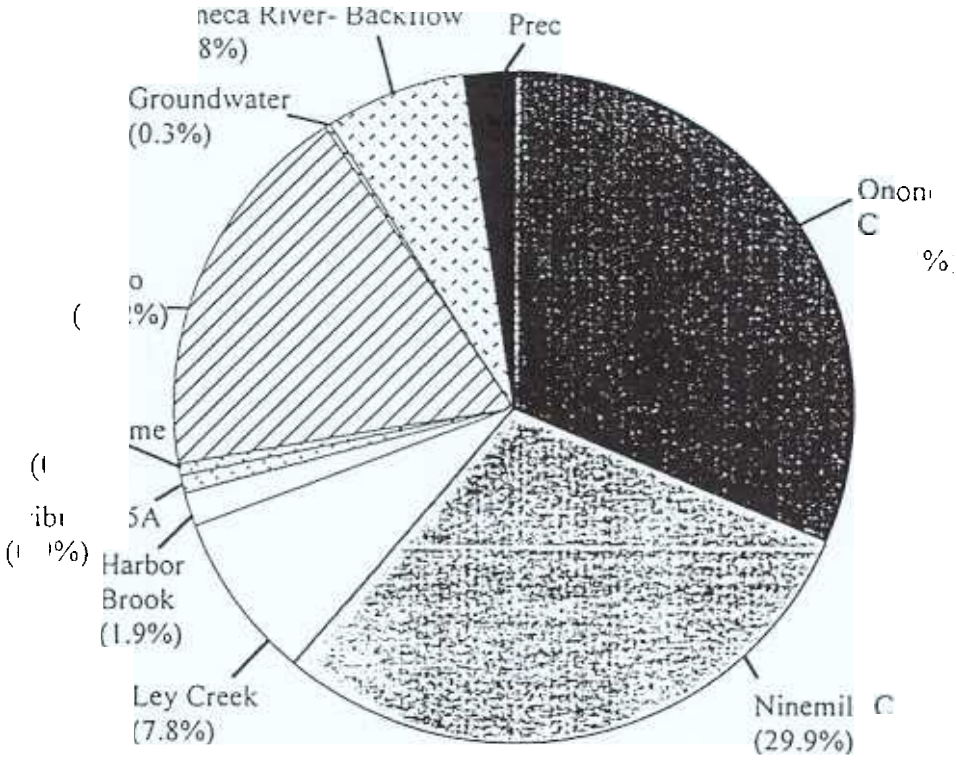
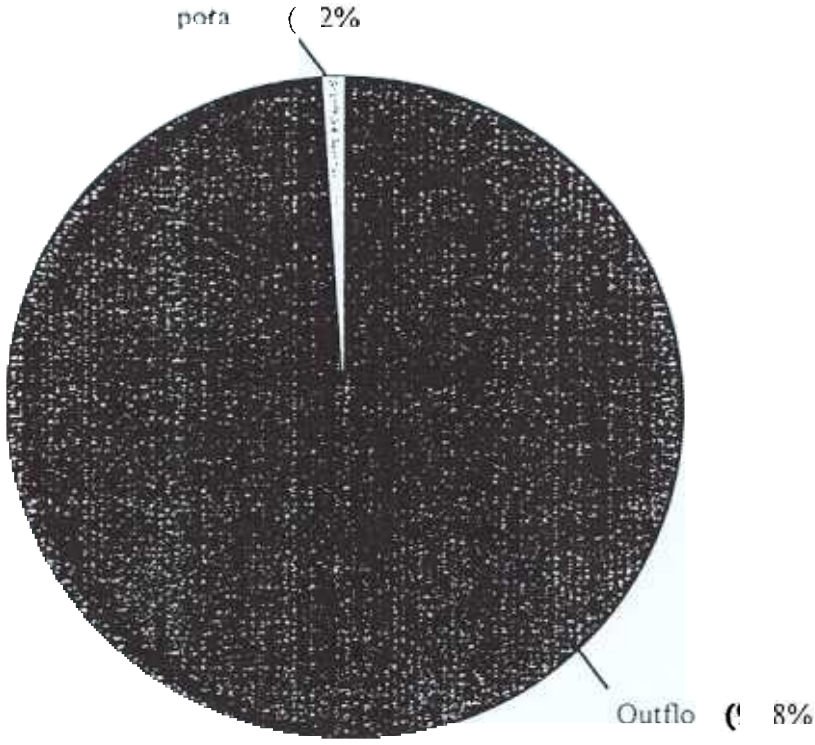



## 1 9 O flo

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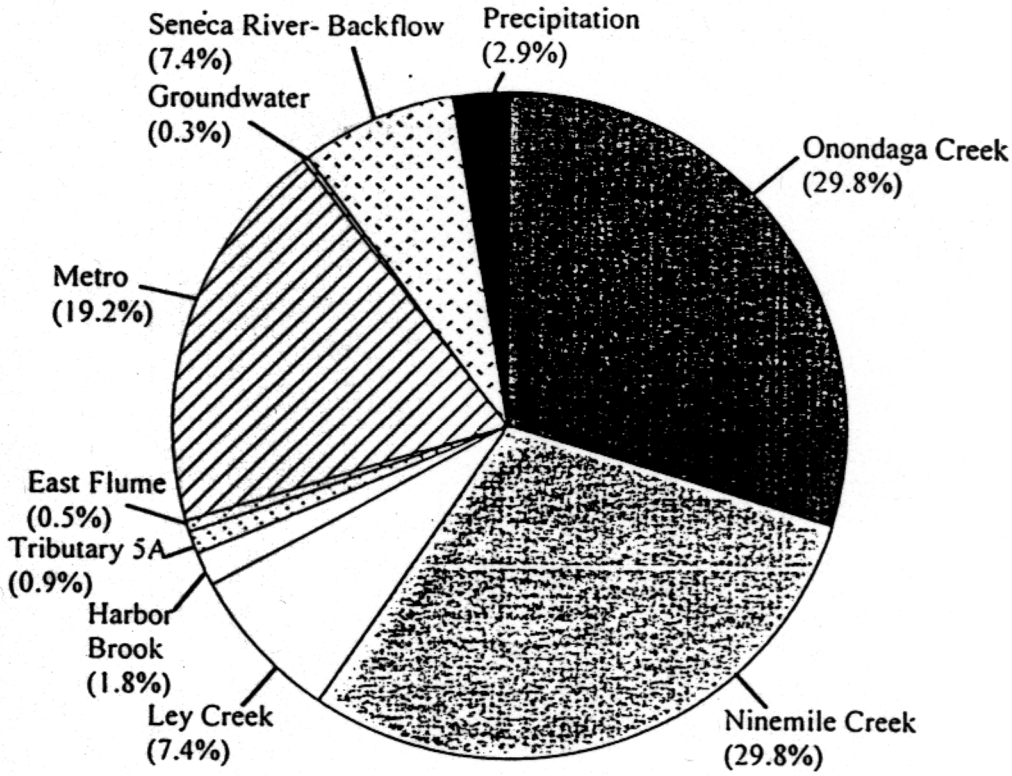
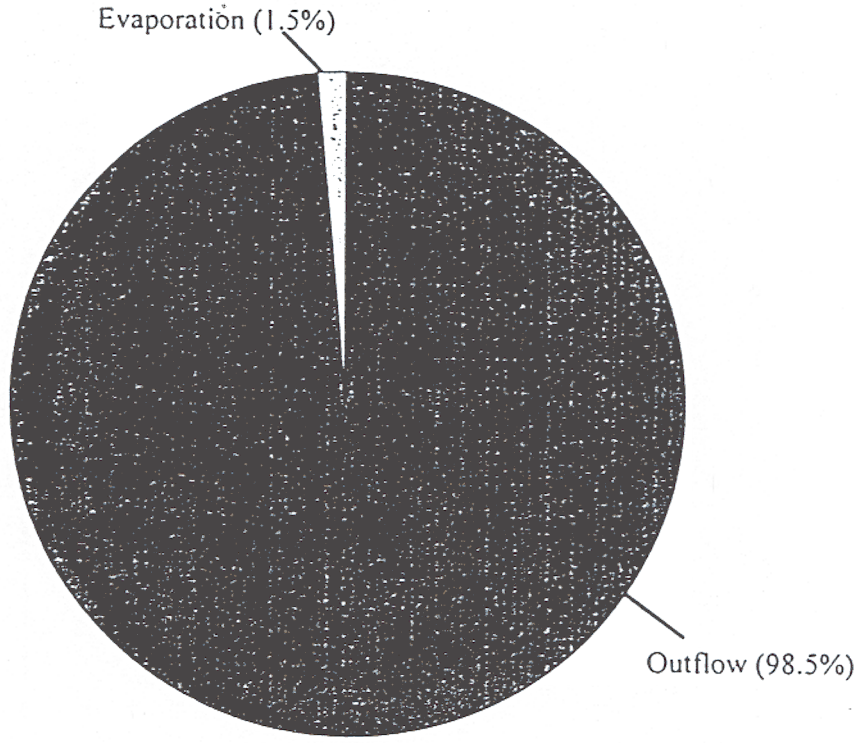
## Inflow: May 1992 to November 1992




## Outflow: May 1992 to November 1992

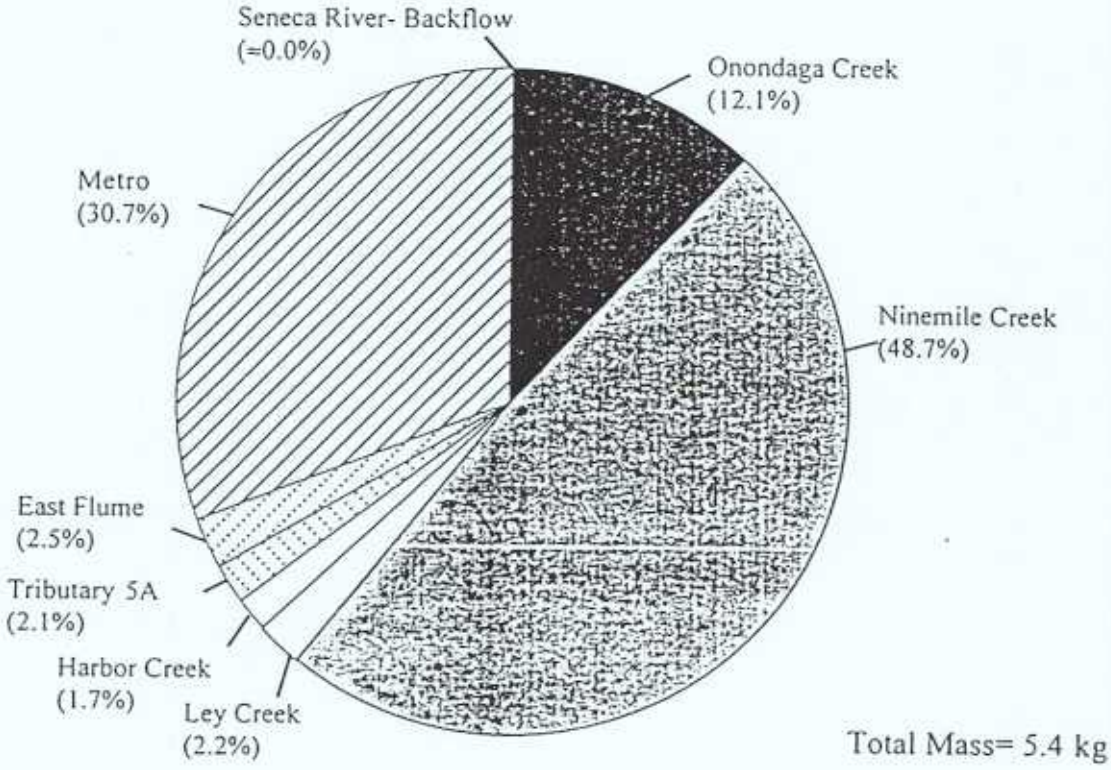



Source: PTI. 1997; OLMM: "CALIB.OUT" File

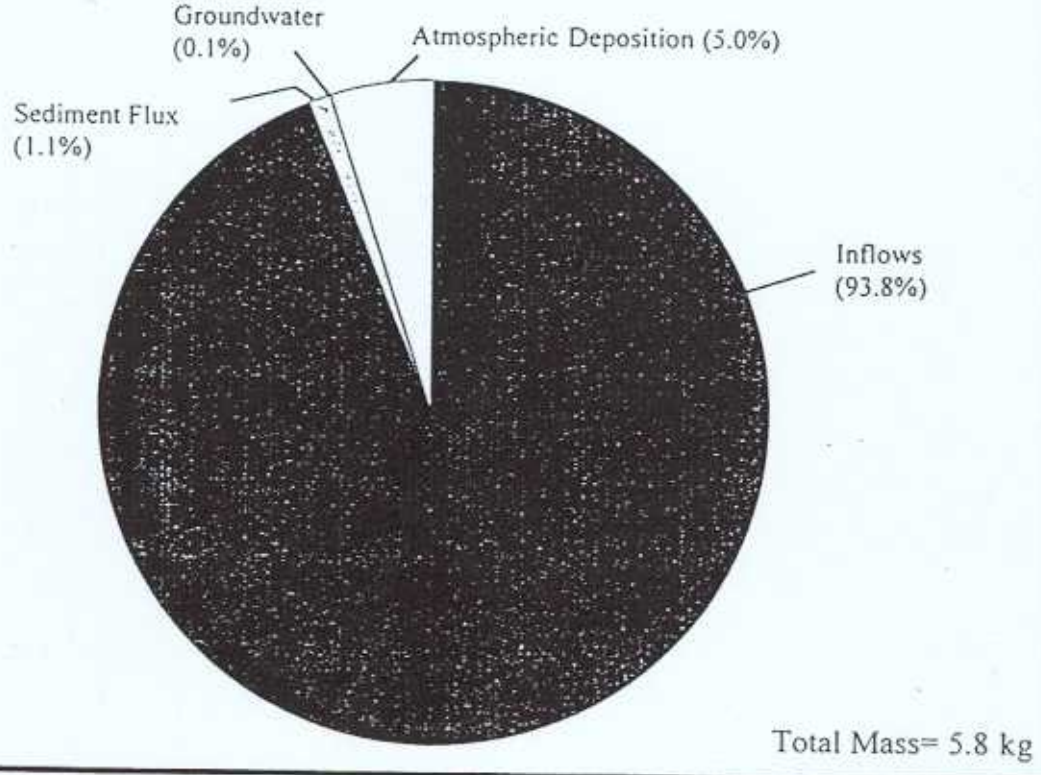
TAMS

**Figure 4-2**
**OLMM Inflow and Outflow Volumes from May 1992 to November 992**

## Inflows: Total Mercury (May 1992 - November 1992)




## All External Sources: Total Mercury (May 1992 - November 1992)




Source: PTI, 1997; OLMM; "CALIB.OUT" FILE

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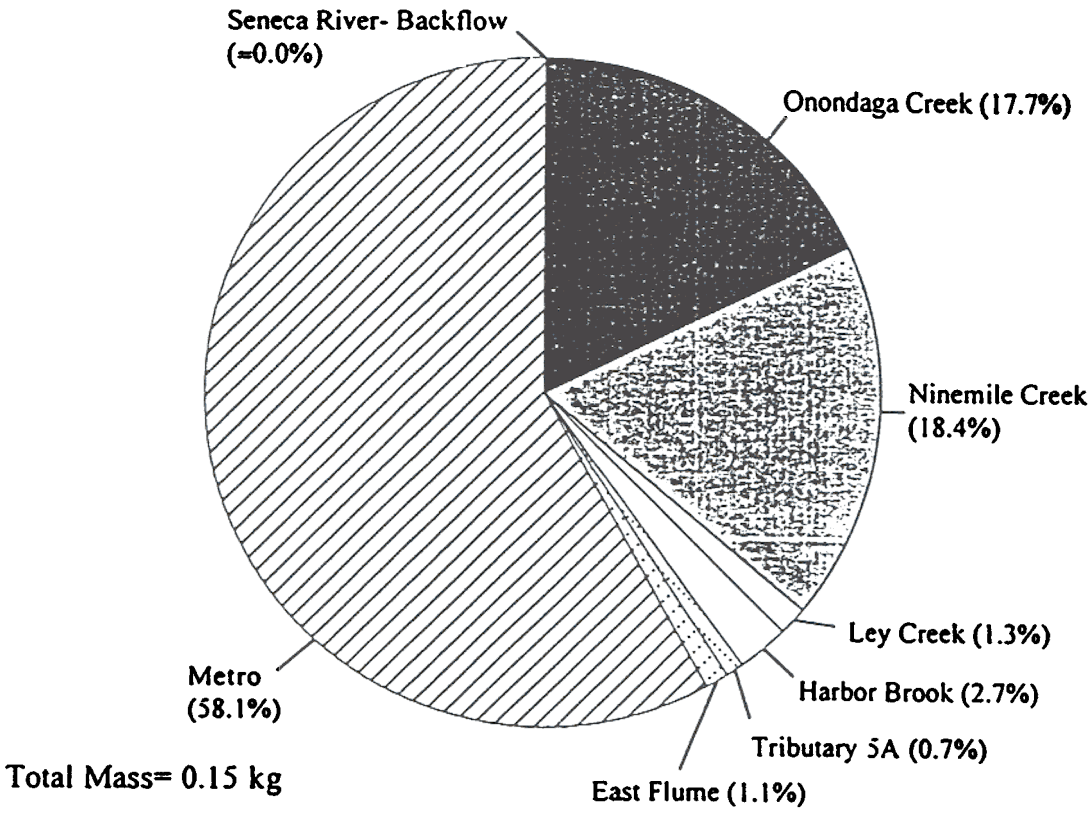
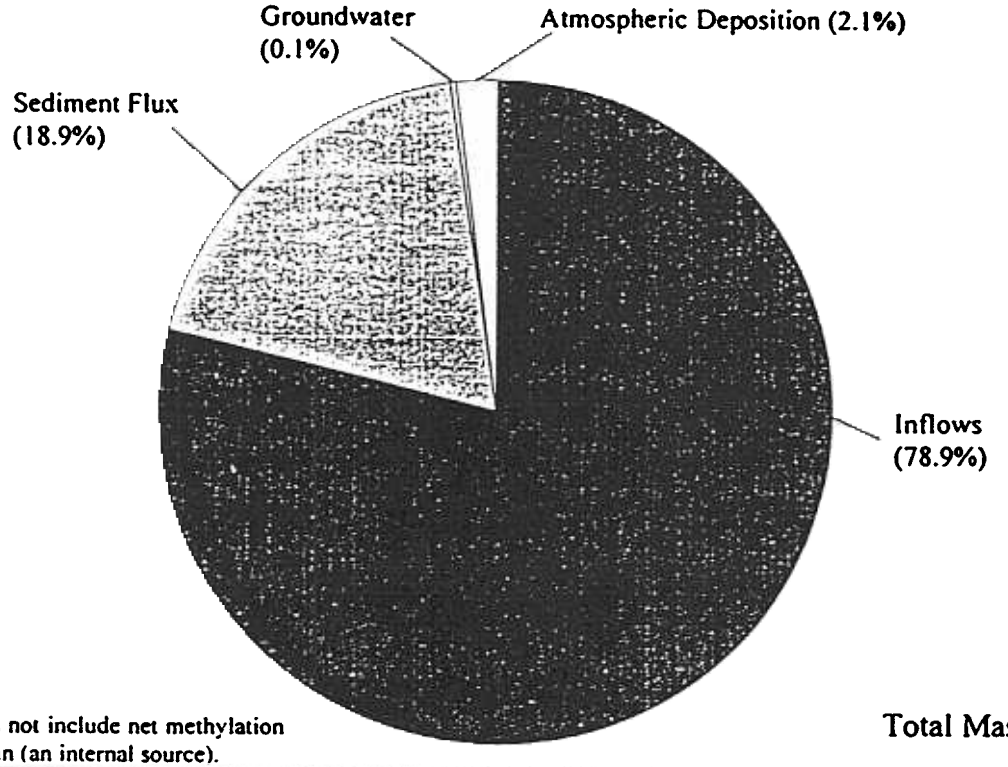
## Inflows: Methyl Mercury (May 1992 - November 1992)




## All External Sources: Methyl Mercury (May 1992 - November 1992)




Note:
1. Bottom chart does not include net methylation in the water column (an internal source).

Source: PTI. 1997; OLMM: "CALIB.OUT" FILE

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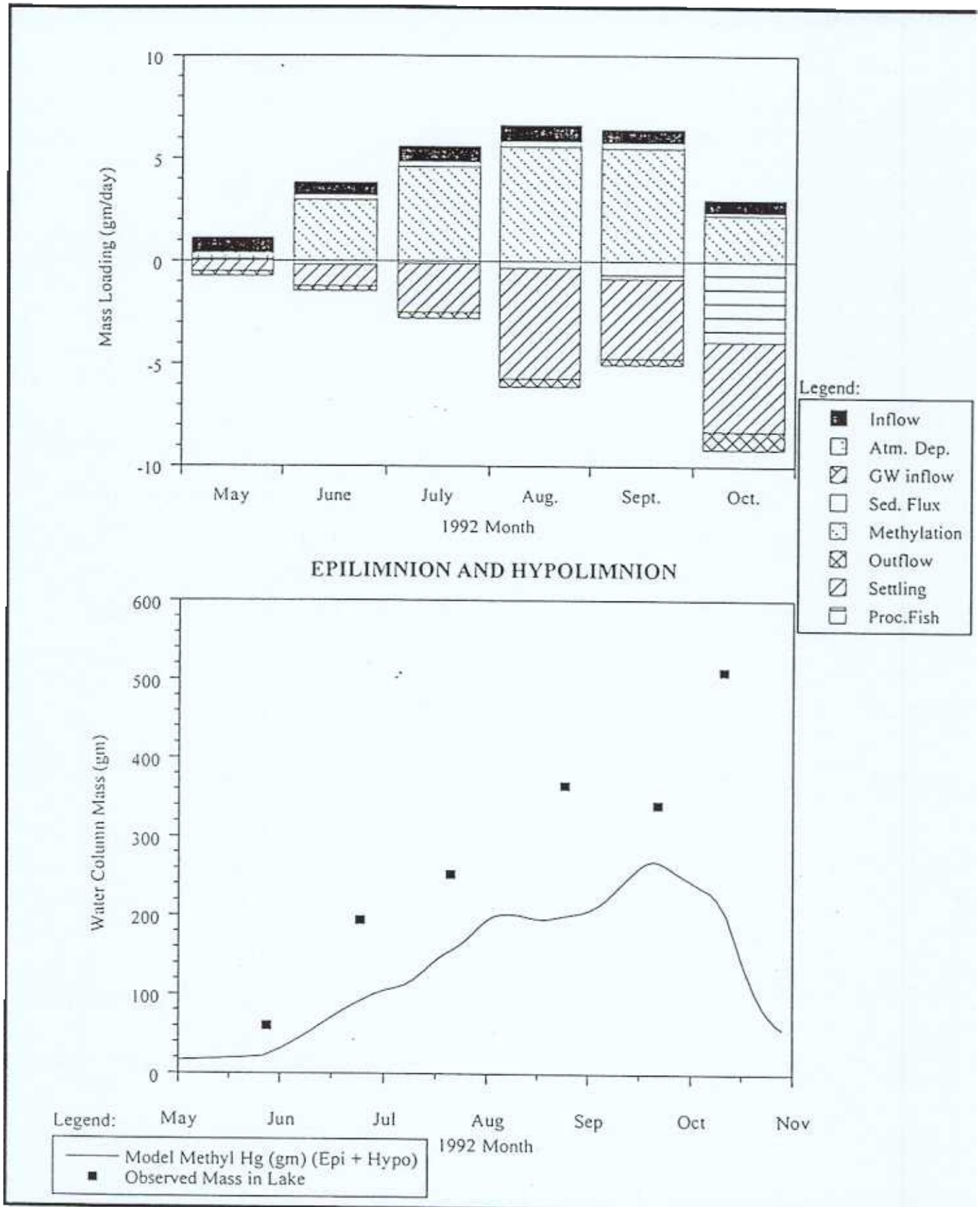
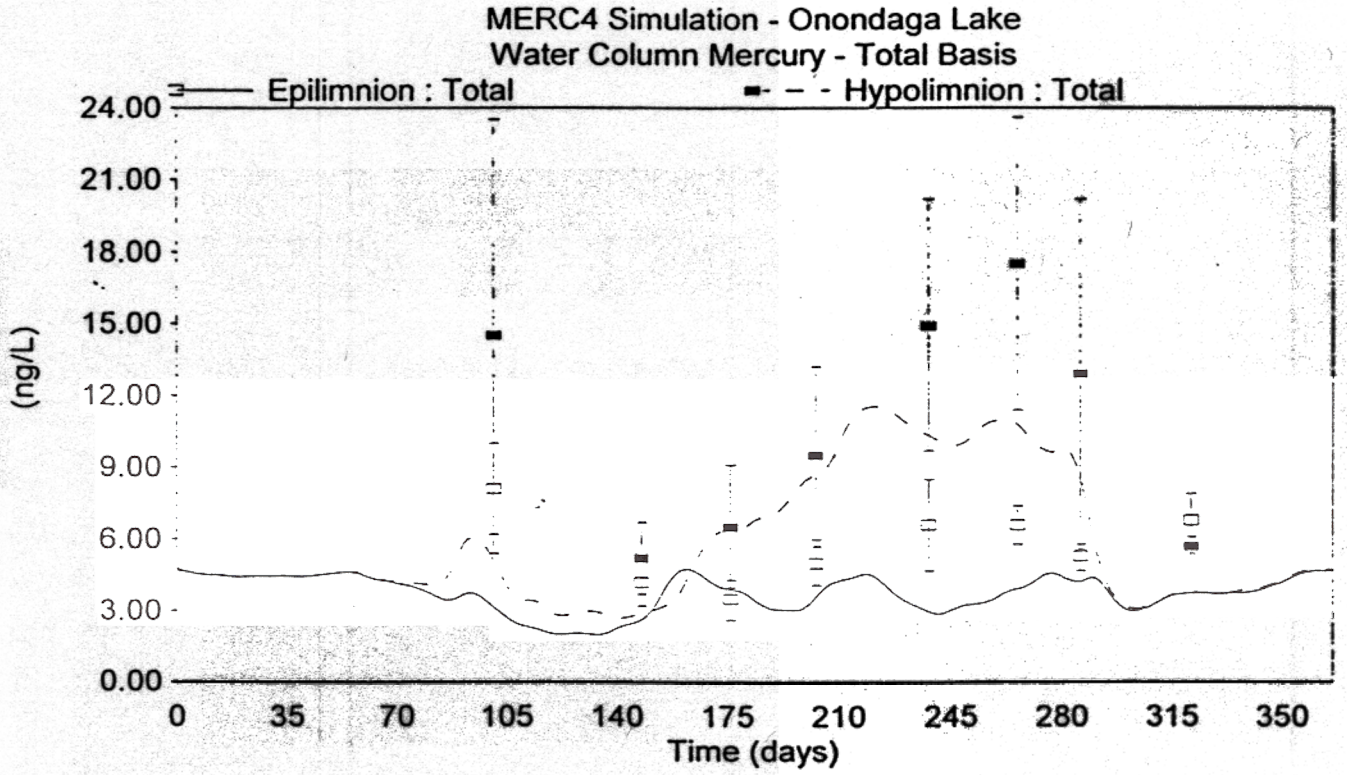
**Figure 4-4**
**OLMM Methyl Mercury Loads for May 1992 to November 1992**




Source: PTI. 1997: OLMM "CALIB.MBT", "CALIB.MDF" and "LAKE.OBS" Files

TAMS

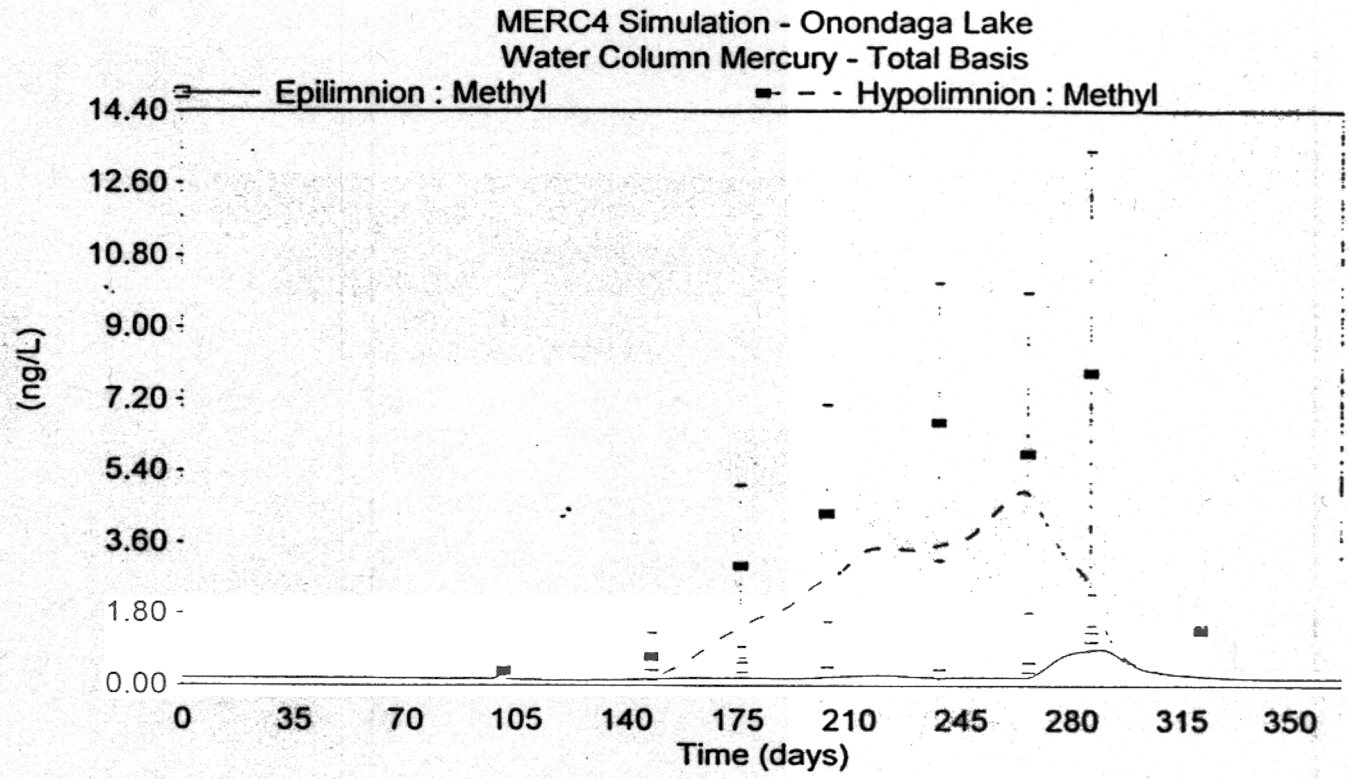
**Figure 4-5**
**Methyl Mercury Mass Balance and Inventory**




Source: OLMM "CALIB.INP" File

TAMS

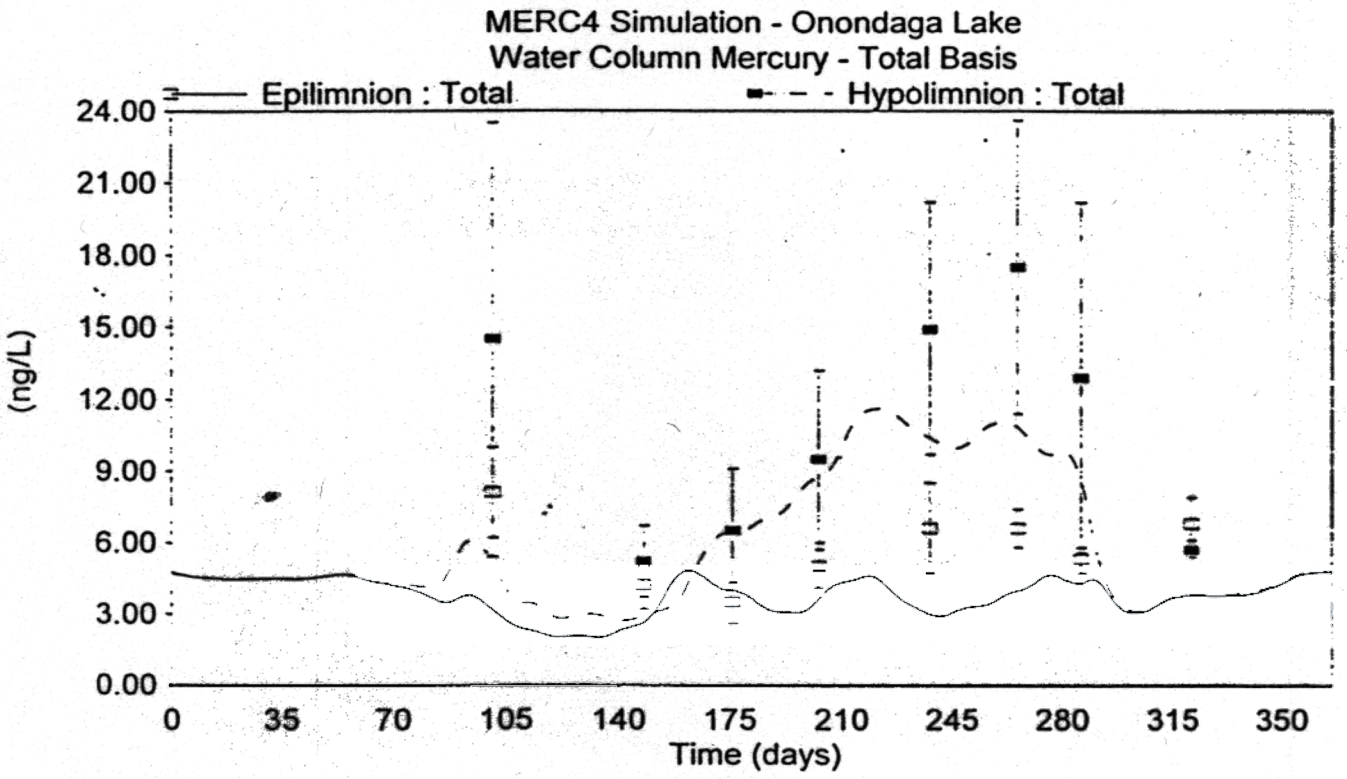
**Figure 5-1**
**PTI's Model Calibration - Total Mercury**




Source: OLMM "CALIB.INP" File

TAMS

**Figure 5-2**
**PTI's Model Calibration - Methyl Mercury**




Source: OLMM "TAMS 01.INP" File

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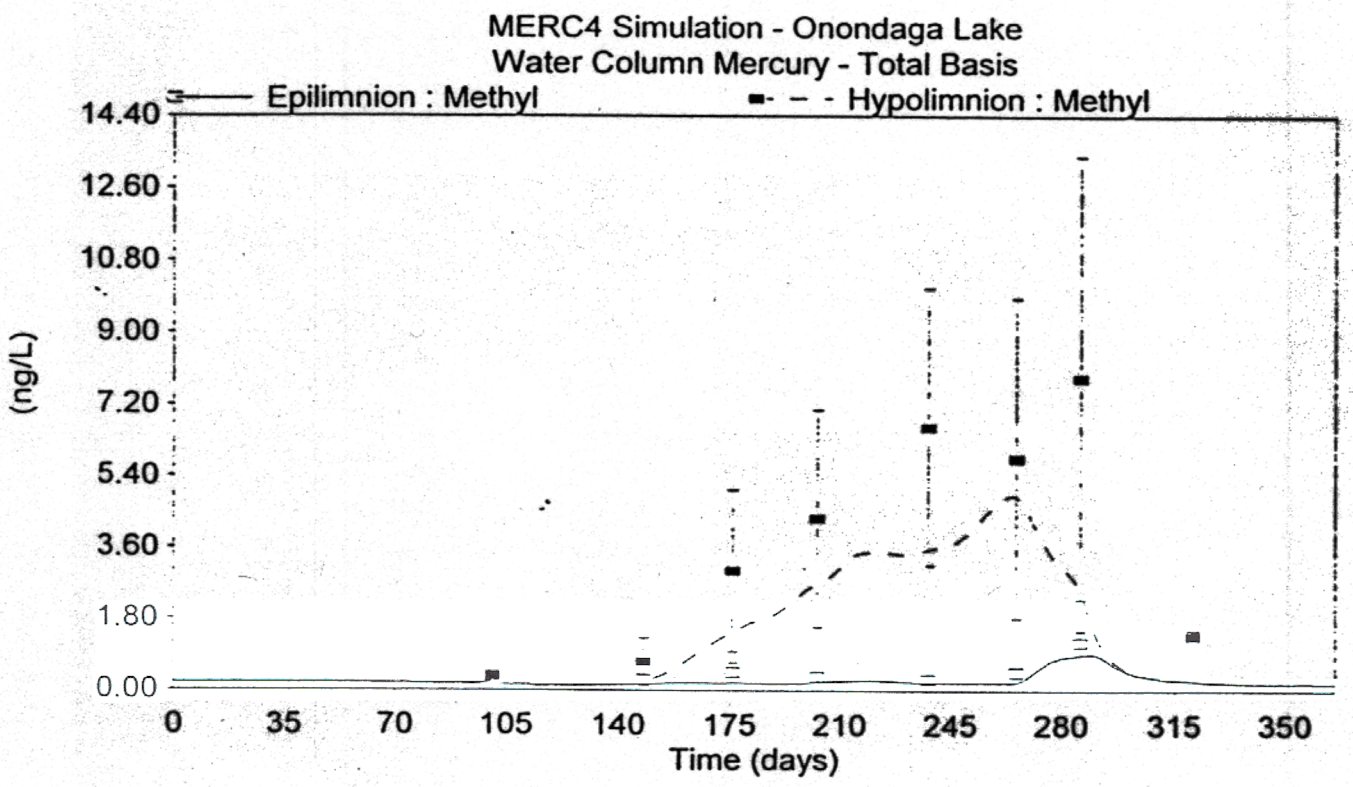
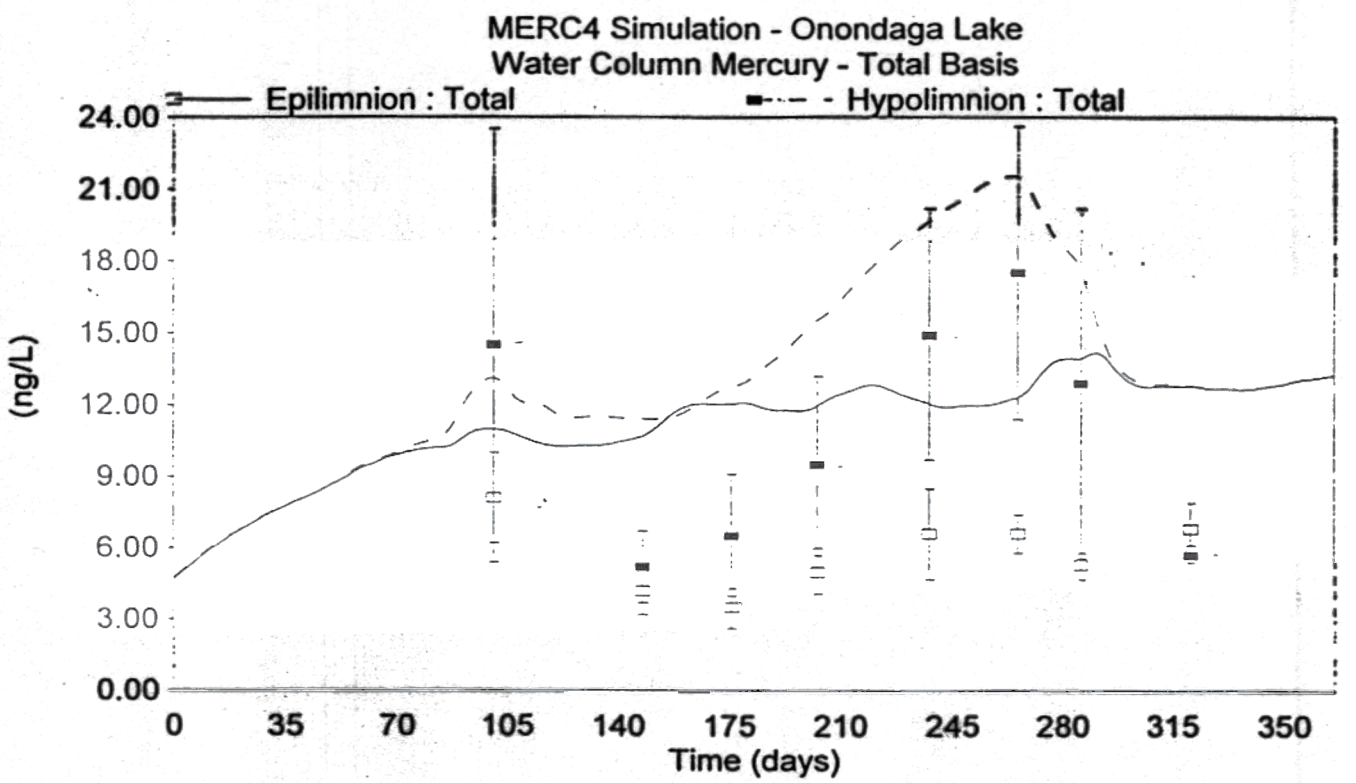
**Figure 5-3**
**Model Run 1 - Total Mercury**




Source: OLMM "TAMS 01.INP" File

TAMS

**Figure 5-4**
**Model Run 1 - Methyl Mercury**




Source: OLMM "TAMS 02.INP" File

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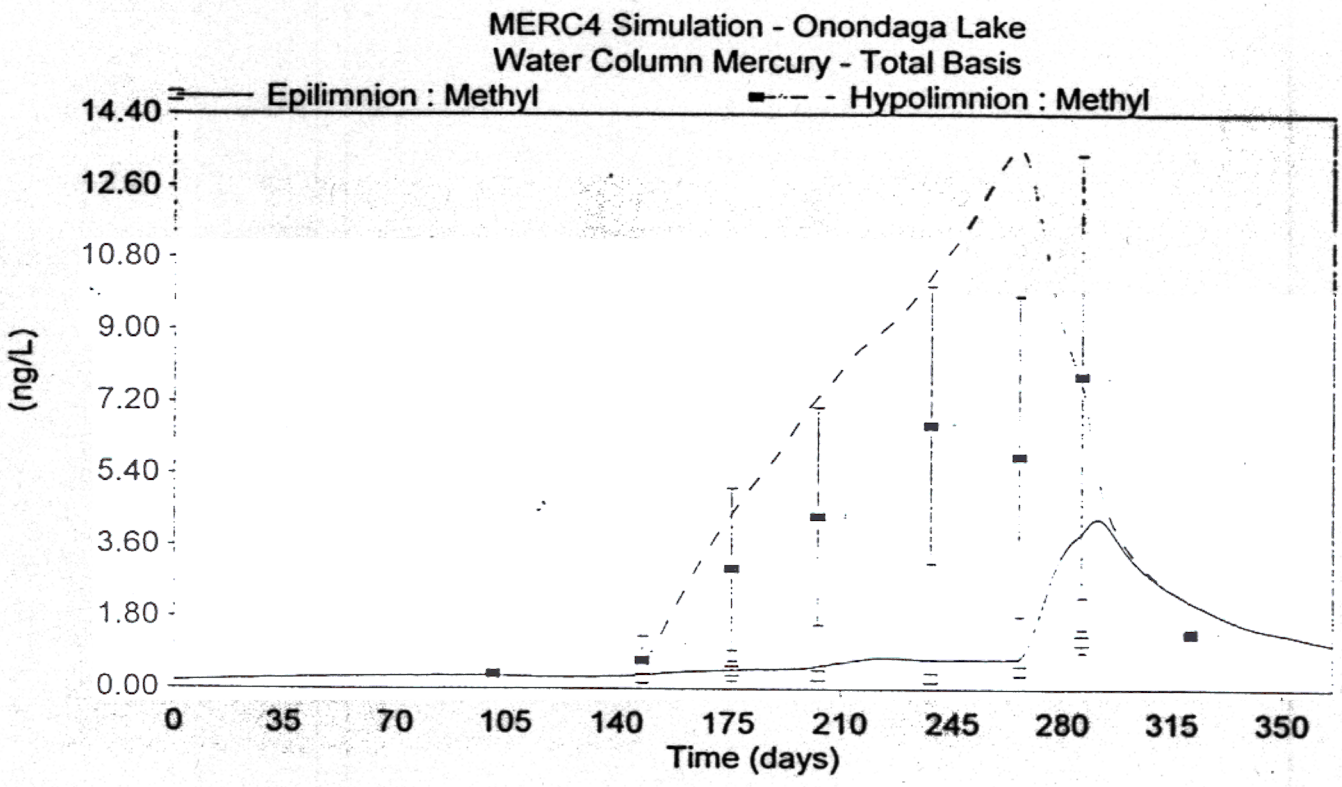
**Figure 5-5**
**Model Run 2 - Total Mercury**




Source: OLMM "TAMS 02.INP" File

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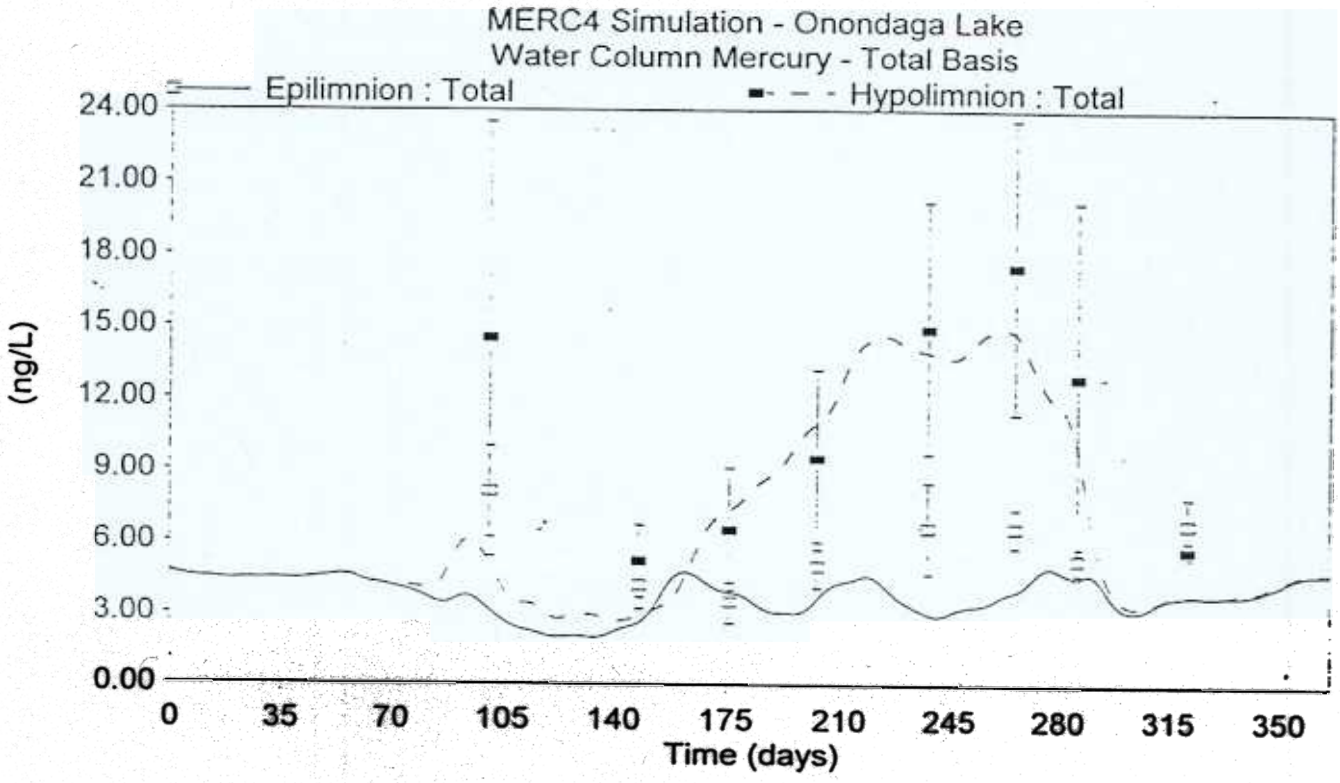
**Figure 5-6**
**Model Run 2 - Methyl Mercury**




Source: OLMM "TAMS 03.INP" File

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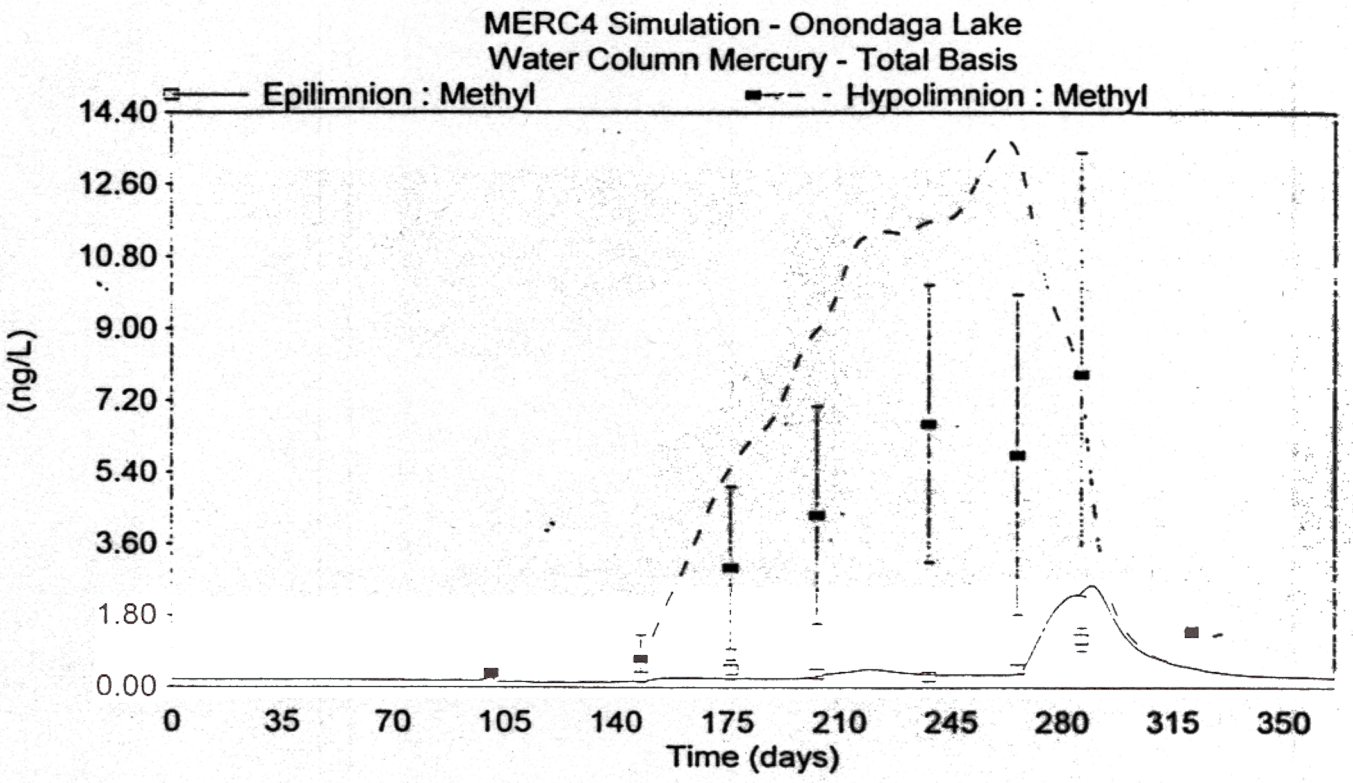
**Figure 5-7**
**Model Run 3 - Total Mercury**




Source: OLMM "TAMS 03.INP" File

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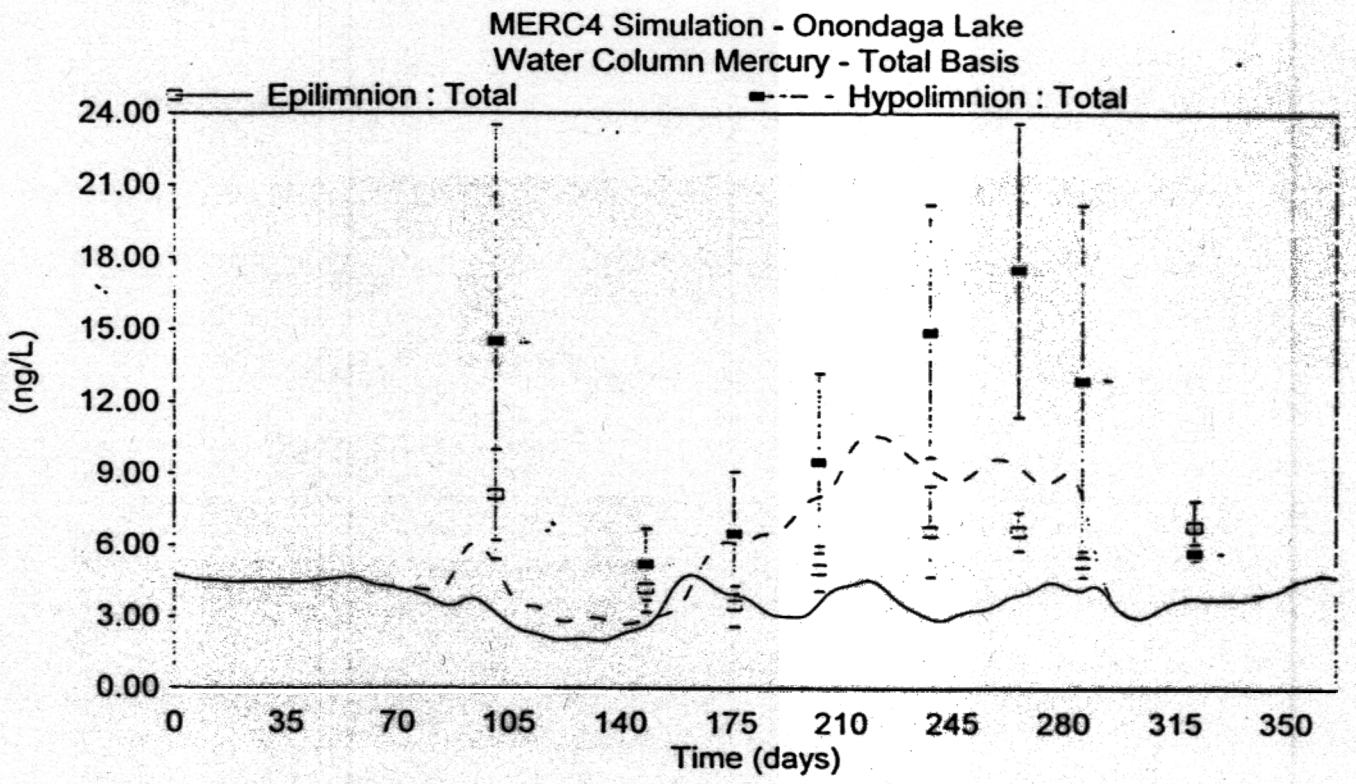
**Figure 5-8**
**Model Run 3 - Methyl Mercury**




Source: OLMM "TAMS 04.INP" File

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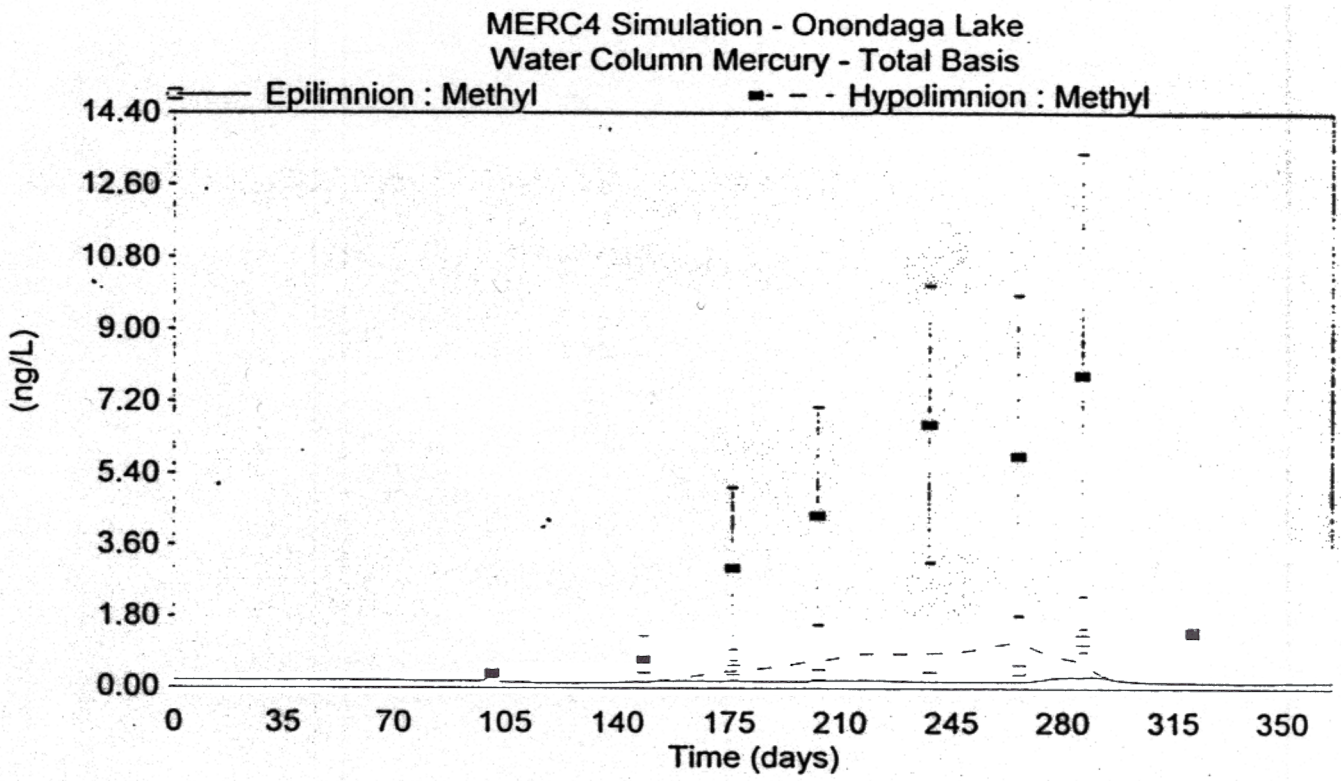
**Figure 5-9**
**Model Run 4 - Total Mercury**




Source: OLMM "TAMS 04.INP" File

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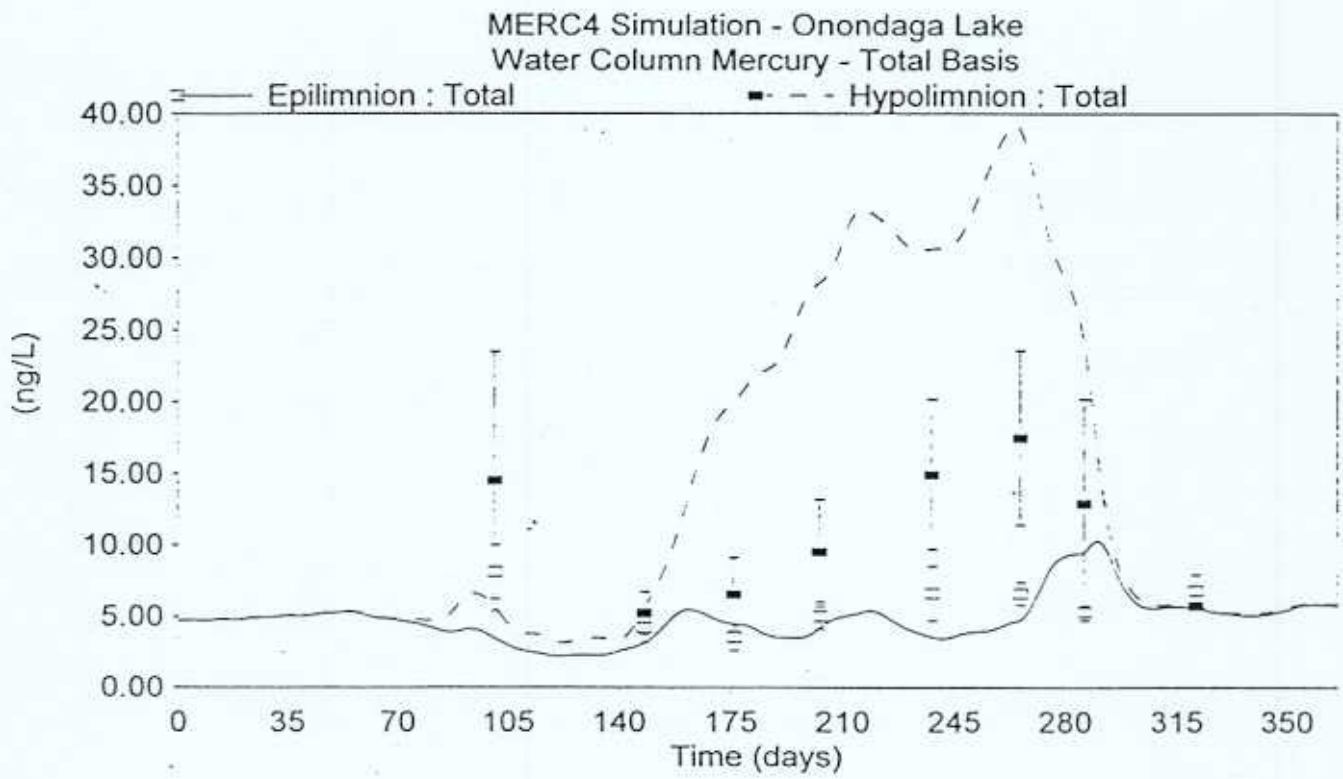
**Figure 5-10**
**Model Run 4 - Methyl Mercury**




Source: OLMM "TAMS 05.INP" File

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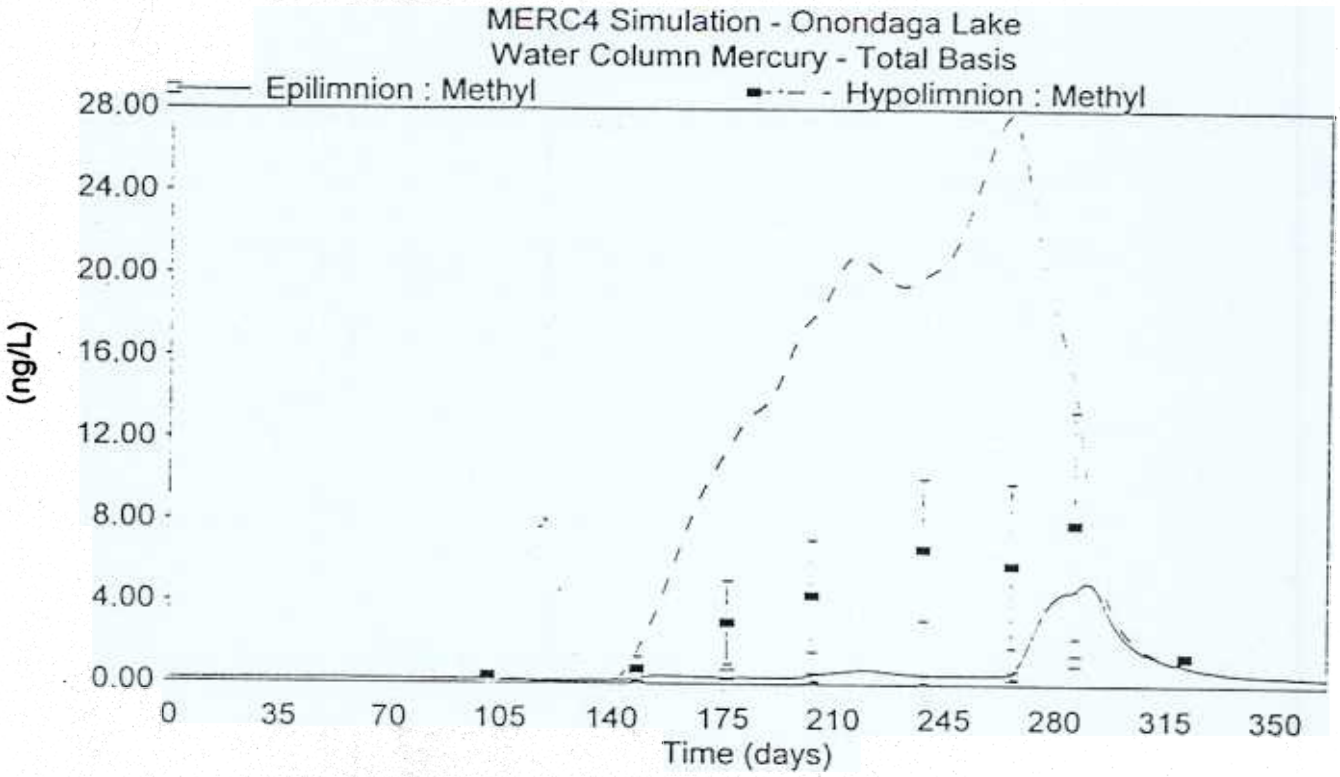
**Figure 5-11**
**Model Run 5 - Total Mercury**




Source: OLMM "TAMS 05.INP" File

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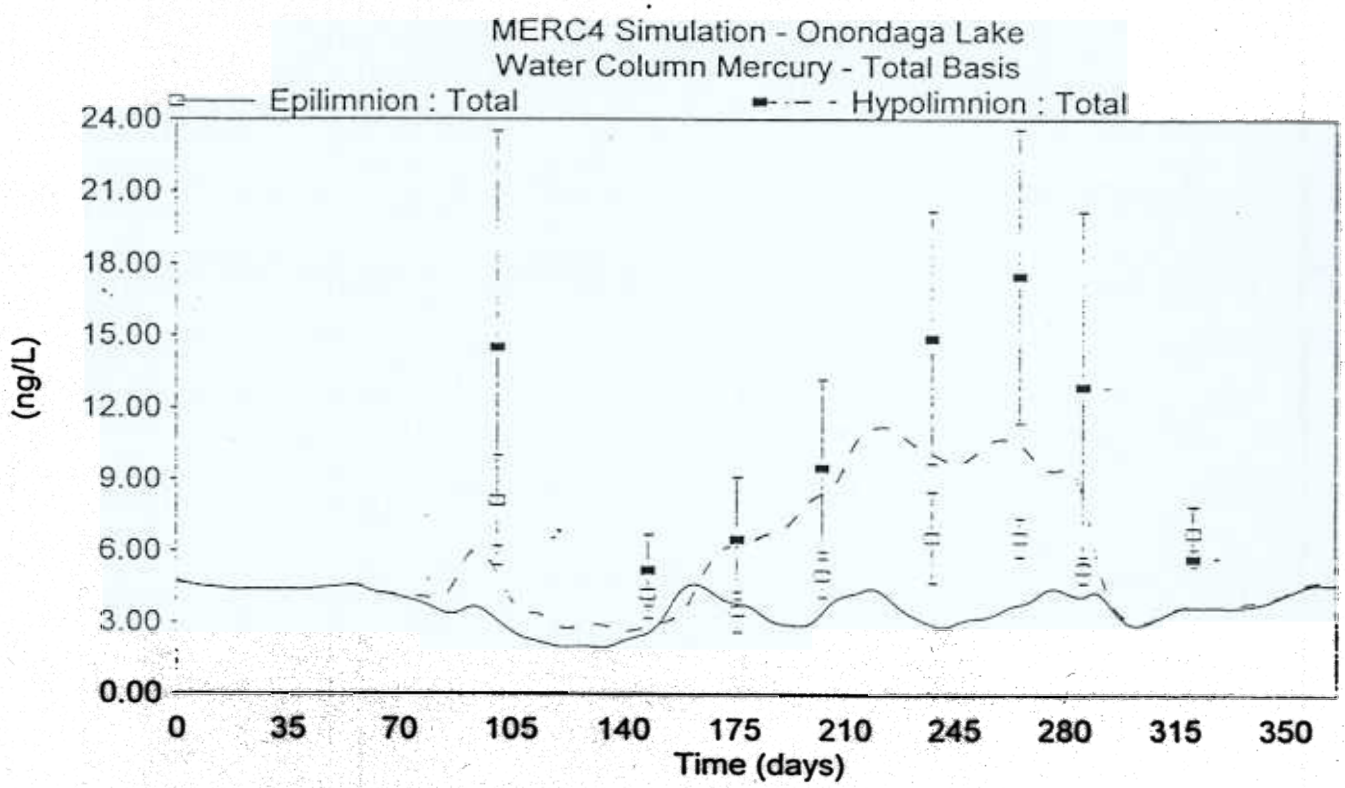
**Figure 5-12**
**Model Run 5 - Methyl Mercury**




Source: OLMM "TAMS 06.INP" File

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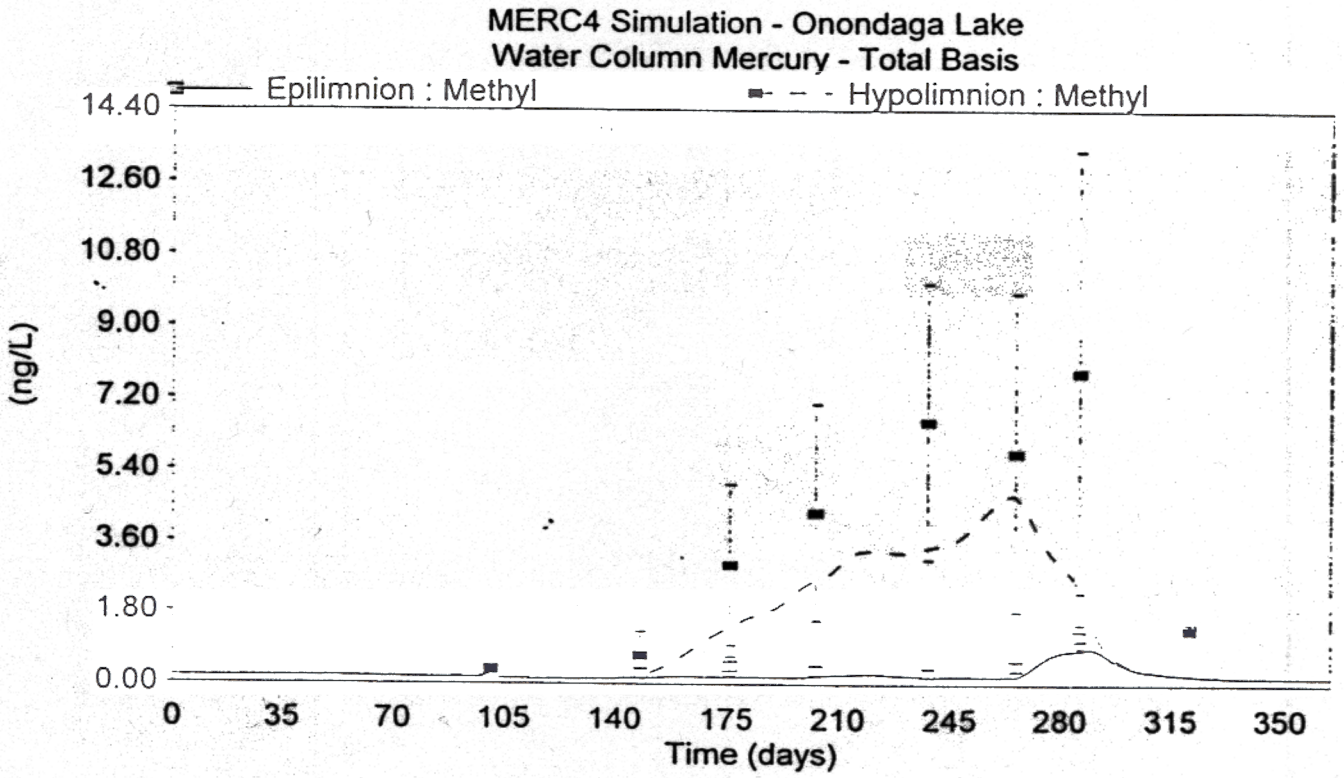
**Figure 5-13**
**Model Run 6 - Total Mercury**




Source: OLMM "TAMS 06.INP" File

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**Figure 5-14**
**Model Run 6 - Methyl Mercury**