Appendix H

Estimation of Mercury Loads to Onondaga Lake from Tributaries and Metro

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One of the objectives of the remedial investigation (RI) was to quantify sources of chemical parameters of interest (CPOIs) – in particular, mercury – to Onondaga Lake. Mercury may be introduced to the tributaries by overland runoff, groundwater seepage, urban stormwater runoff, combined sewer overflow (CSO), and sediment resuspension during high-flow events. In 1992, concentrations of total mercury and methylmercury were obtained by Honeywell for the tributaries of the lake and the Metropolitan Syracuse Sewage Treatment Plant (Metro) effluent (PTI, 1993). These concentrations were used, along with the available flow data (addressed below), to investigate the relationship between concentrations of mercury and flow rate and to develop loading estimates.

The accuracy and precision of contaminant load calculations for rivers are significantly influenced by the sampling frequency and the scale of the drainage basin (Phillips et al., 1999). Because mercury binds strongly to particulate matter, it is important to sample during high-flow periods, especially during storm events. For example, Mason and Sullivan (1998) documented a three- to five-fold increase in mercury concentrations in an urban, impacted river in Washington, DC, and reported that mercury loads could be significantly underestimated by not sampling during storms.

H.1 Approach

The general approach for estimating mercury loads to Onondaga Lake from its tributaries and Metro was as follows:

- Characterize flow rates.
- Sample under a variety of flow conditions for concentrations of total mercury and methylmercury.
- Develop concentration versus flow relationships.
- Estimate mercury and methylmercury loads.
- Estimate confidence intervals for mercury and methylmercury loads.

Data from the eight tributaries that discharge directly to the lake (i.e., Ninemile Creek, Onondaga Creek, Ley Creek, Harbor Brook, Tributary 5A, the East Flume, Bloody Brook, and Sawmill Creek) and from Metro were used to estimate the mercury loads to Onondaga Lake (see Figure H-1). In the following sections, daily flow rates for 1992 are presented, followed by a description of concentration versus flow rate relationships for total mercury and methylmercury. Finally, loadings of total mercury and methylmercury from the tributaries and Metro discharge to Onondaga Lake were estimated for May 25 through

September 21, 1992. This time period was selected because all of the data necessary for calculating a mass balance (e.g., sediment traps and high flows for that period) were available.

H.1.1 Characterization of Flow Rates

The US Geological Survey (USGS) monitors water elevations and develops flow rates for the four largest tributaries to Onondaga Lake: Ninemile Creek, Onondaga Creek, Ley Creek, and Harbor Brook (USGS, 2002). These four tributaries are also referred to herein as "gauged" tributaries.

Flow rates at the remaining four tributaries, which are not monitored by the USGS, were measured using other means. These tributaries are also referred to herein as "non-gauged" or "ungauged" tributaries. For Tributary 5A, Bloody Brook, and Sawmill Creek, flow rates were determined using the predictive expressions for non-gauged discharges to Onondaga Lake provided by Effler and Whitehead (1996). These predictive expressions are linear regression relationships obtained between the non-gauged tributaries and gauged discharges using 16 instantaneous flow measurements. Flow rates estimated by PTI (1994) in the East Flume were used in load calculations for that tributary. Flow rates for Metro are monitored on a daily basis by the Onondaga County Department of Drainage and Sanitation (OCDDS) (OCDDS, 2002, pers. comm.).

The 1992 flow profiles for the tributaries and Metro discharge (see Figures H-2, H-3a, and H-3b) indicate that the peak flow occurred in March. Onondaga Creek, Ninemile Creek, and Metro combined contributed 81.5 percent of the hydraulic loading to Onondaga Lake, based on annual average flow rates for 1992. Ley Creek and Harbor Brook combined contributed 10.2 percent, and the four non-gauged tributaries (Tributary 5A, the East Flume, Bloody Brook, and Sawmill Creek) together contributed 8.3 percent of the hydraulic loading.

The mean flow rates for the period of loading calculation (between May 25 and September 21, 1992) are similar to or only slightly lower than (<13 percent) the overall annual average for the tributaries and Metro. The average flows for the gauged tributaries in 1992 are also comparable to the long-term average flows from 1973 to 2000 (Table H-1).

H.1.2 Concentrations of Total Mercury and Methylmercury

Concentrations of total mercury and methylmercury (whole-water basis) were measured by PTI in each tributary and Metro once a month from April through July and twice a month from August through December 1992 (PTI, 1993). Because the sampling started in April, the high spring flows of March were missed and, thus, annual loadings were not calculated.

When flows were relatively low, a single grab sample was collected each month. Under high-flow conditions, from August through December, an initial grab, followed by a flow-weighted composite, was collected. For this analysis, the concentrations from the composite samples were used when both grab and composite sample results were reported for the same day at the same station. In addition to the field data collected by PTI in 1992, total mercury concentrations (whole-water basis) were periodically measured in Ninemile Creek, Onondaga Creek, Ley Creek, and Metro from February through August 1992 by Driscoll (1995). The results from all of these samples were paired with the available daily mean flow rates to develop the relationship between concentration and flow.

Figures H-2 through H-5b present the measured mercury and methylmercury concentrations and flow rates for the tributaries and Metro to Onondaga Lake for 1992. Sawmill Creek and Bloody Brook were excluded from further load estimation because of limited mercury concentration data (only two samples were collected) and the relatively low flow rates in these two tributaries. For other tributaries and Metro, it is shown that measurements of total mercury and methylmercury concentrations were made over a range of flow conditions that represented changes on the order of five or less, and since the high spring flows were missed, the highest flows that were sampled were roughly one-third to one-fifth of the highest flow for the year. There are combined data sets for total mercury for 11 months of the year, and methylmercury data for nine months. There were no seasonal patterns observed in the tributary and Metro mercury and methylmercury concentrations.

H.1.3 Concentration versus Flow Rate Relationships

In order to estimate the mercury and methylmercury concentrations on the days when no sample was collected, the relationship between flow and concentration was investigated for each station using all the samples collected in 1992, as shown in Figures H-6 and H-7. These figures depict linear regression plots of log-transformed concentrations and flow. If a relationship between concentration and flow was established, then the continuous flow measurements were used to predict the mercury and methylmercury concentration for the time period between samples.

For total mercury, moderate relationships with significant slopes (p-value <0.05) were obtained for Harbor Brook and Tributary 5A. For methylmercury, moderate relationships with significant slopes (p-value <0.05) were also obtained for Ninemile Creek, Harbor Brook, Ley Creek, and Tributary 5A. No relationship between mercury concentration and flow was established for the other tributaries and Metro.

The presence or absence of total mercury relationships is consistent with an understanding of the sources of total mercury to the tributaries. Only Harbor Brook and Tributary 5A have major sources of mercury (i.e., the Wastebed B and Willis Avenue sites) along a large portion of their drainage basin. While Ninemile Creek does have a major source of mercury (i.e., the LCP Bridge Street site) in its drainage basin, that site is on a very small tributary to Ninemile Creek (i.e., the West Flume), and there is no reason to expect the mercury loads from the LCP Bridge Street site to be related to the flow response of the main stem of Ninemile Creek. Similarly, flow to the East Flume in 1992 was predominantly from stormwater from non-source areas.

H.1.4 Estimation of Loads

Using the FLUX model (Walker, 1987), loading of total mercury and methylmercury to Onondaga Lake was estimated for May 25 through September 21, 1992. Six mathematical methods are provided by the FLUX model for relating measured analyte concentration to stream flow rate, with subsequent load estimation, as follows:

- Method 1 calculates the average daily load directly from the concentration and flow data on the days that samples were collected. The long-term flow-rate record is not used in this method.
- Method 2 calculates a flow-weighted mean concentration and calculates the daily load using this weighted mean concentration and the daily mean flow rate.
- Method 3 modifies Method 2 by accounting for the variability in both the mean load estimate and mean flow rate of the sampling data.
- Method 4 develops a first-order linear regression of the $\log_{10}$ of the sampling data.
- Method 5 modifies Method 4 by accounting for the variability in the mean sample and flow rate and the mean long-term flow rate for the period of interest.
- Method 6 performs a first-order linear regression of the natural log of the sampling data. The model then uses this relationship to estimate daily concentrations. Daily loads are then calculated using the estimated concentrations and the mean daily flows.

Depending on the characteristic of the data sets, one method was selected for each tributary and Metro and used to estimate analyte loading rates.

When a significant correlation between concentrations and flow was observed ($p\text{-value} < 0.05$), this relationship was used to derive daily concentrations based on daily flow values. This corresponds to Method 6 of the FLUX model. The model also corrects the inherent underestimation bias that occurs during back transformation of regression values by applying the correction proposed by Ferguson (1986).

An exception to the above was the methylmercury load estimate for Ley Creek, where the slope of the regression was negative. Method 1 was used in this instance, as per Walker (1987), who specified that Method 1, which is a direct load averaging technique, is more appropriate for situations in which concentration tends to be inversely related to flow.

When the correlations between flows and concentrations were not significant ($p\text{-value} > 0.05$), an averaging strategy was used to estimate loads. Method 2 of the FLUX model, which is a flow-weighted average method, was used in these cases. This method, which amounts to a ratio-estimate, has a relatively small bias and lower variance than other comparable methods of estimation (Littlewood, 1995; Walker, 1987; Walling and Webb, 1985).

Loads were estimated for the period from May 25 to September 21, 1992 (Tables H-2 and H-3). FLUX uses a jackknife procedure to estimate error variance, reflected by the CV, or coefficient of variation, estimate. Error variances were sometimes reduced by stratifying the samples into groups of relatively low and high flows. The variances were not used to develop confidence intervals because an assumption about the form of the distribution will be required (see Section H.1.5 below).

The mean mass of total mercury discharged to Onondaga Lake in this four-month period in 1992 was estimated to be approximately 2,500 g. Approximately 51, 24, and 14 percent (a total of 89 percent) of the estimated total mercury input from the tributaries and Metro was discharged by Ninemile Creek, Metro, and Onondaga Creek, respectively. The remaining 11 percent of tributary and Metro input was attributed to Ley Creek, Harbor Brook, Tributary 5A, and the East Flume.

The mean mass of methylmercury discharged to Onondaga Lake in this four-month period in 1992 was estimated to be 116 g. Approximately 42, 36, and 18 percent (a total of 96 percent) of the estimated methylmercury input from tributaries and Metro was discharged by Ninemile Creek, Metro, and Onondaga Creek, respectively. The remaining 4 percent of tributary and Metro input was attributed to Harbor Brook, the East Flume, Ley Creek, and Tributary 5A.

Reductions in mercury and methylmercury concentrations in Metro effluent since 1992 have resulted in reduced loadings from this source (OCDDS, pers. comm., 2002). Sampling and analysis of low-level mercury in all of the tributaries have not been performed by Honeywell since 1992, so it is not known if tributary loads have increased or decreased since 1992.

It was assessed whether mercury loading from Onondaga Creek was overestimated in this analysis due to backwater effects from Onondaga Lake, a possibility that was raised due to increased chloride levels in Onondaga Creek through the Barge Canal. Observations of these increased chloride concentrations are discussed extensively in Effler and Whitehead (1996). There are two possible sources of chloride to the Barge Canal: discharge of saline groundwater from the Niagara Mohawk Power Corporation facility (from 1960 to 1991), and discharge of chloride- and sodium-enriched brine to Onondaga Creek via groundwater.

Data collected in 1992, and reported in Effler and Whitehead (1996), suggested both point source (shown by a sharp increase in concentration) and diffuse loading of chloride to Onondaga Creek downstream of Spencer Street. Bubbles indicating entry of groundwater were also encountered at several locations (Effler and Whitehead, 1996). In addition, there are no significant differences between mercury concentration in samples collected at Hiawatha Boulevard, downstream of the Barge Canal, by PTI in 1992 and concentration in samples collected at Spencer Street, upstream of the Barge Canal, in 1992 (Driscoll, 1995) and 1995 to 1996 (Gbondo-Tugbawa, 1997). Based on these findings, the backflow effect was not considered, and the PTI concentrations were not modified in the calculation of mercury loads from Onondaga Creek.

H.1.5 Confidence Interval Estimation

The 95 percent confidence intervals for the estimated tributary loads were calculated by the bootstrap resampling technique (Efron, 1982). This technique does not require knowledge of or make assumptions about the distribution of the statistic of interest. The bootstrap procedure is summarized as follows:

- For each tributary, a bootstrap resample was created by randomly selecting a set of "n" pairs (concentration and flow), with a replacement. For example, for a tributary with ten observations, ten random selections of flow/concentration pairs were made.

- The mean load of the bootstrap resample was estimated.

- The previous two steps were repeated 10,000 times.

- The 10,000 mean loads obtained were sorted and the 95 percent confidence intervals were selected as the 2.5^{th} and 97.5^{th} percentiles.

Since the FLUX model develops estimates of concentrations for days on which samples were not collected, the bootstrap technique was also performed on the 120 flow and concentration pairs from FLUX. The results were consistent with the simulations that used only the sampled data. Tables H-2 and H-3 present the 95 percent confidence intervals for total mercury and methylmercury loads from the various tributaries and Metro. For the stratified period, total mercury input from the tributaries and Metro ranged from about 2,100 to 3,000 g, while methylmercury input ranged from about 95 to 141 g.

H.2 References

Driscoll, C. T. 1995. Data diskette to E. A. Henry, PTI Environmental Services, Waltham, MA, transmitted at meeting regarding Onondaga Lake tributary sampling in 1996 in Solvay, NY. Syracuse University, Syracuse, NY. November 3.

Effler, S. W. and K. A. Whitehead. 1996. Tributaries and discharge. In: Limnological and Engineering Analysis of a Polluted Urban Lake. S. W. Effler (ed). pp. 97-199. Springer-Verlag, New York, NY.

Efron, B. 1982. The jackknife, the bootstrap and other resampling plans. J.W. Arrowsmith, Ltd., Bristol, England.

Ferguson, R. I. 1986. River load underestimation by rating curves. Water Resources Research, 22: 74-76.

Gbondo-Tugbawa, S. 1997. Concentrations and Fluxes of Total and Methyl Mercury to Onondaga Lake, Syracuse, New York. Masters' Thesis, Syracuse University, Syracuse, NY.

Littlewood, I. G. 1995. Hydrological regimes, sampling strategies and assessment of errors in mass load estimates for United Kingdom rivers. Environmental International, 21:211-220.

Mason, R. P. and K. A. Sullivan. 1998. Mercury and methylmercury transport through an urban watershed. Water Research, 32(2):321-330.

Onondaga County Department of Drainage and Sanitation (OCDDS). 2002. Personal communication via e-mail to R. Montione, TAMS Consultants, Inc. March 19.

Philips, J. M., B. W. Webb, D. E. Walling, and G. J. L. Leeks. 1999. Estimating the suspended sediment loads of rivers in the LOIS study area using infrequent samples. Hydrological Processes, 13:1035-1050.

PTI Environmental Services (PTI). 1993. Onondaga Lake Remedial Investigation/Feasibility Study Mercury and Calcite Mass Balance Investigation Data Report. Prepared for AlliedSignal, Inc., Solvay, NY. PTI, Bellevue, WA.

PTI. 1994. Onondaga Lake Remedial Investigation/Feasibility Study Tributary and Sewer Flow Rate Data Report. Prepared for AlliedSignal, Inc., Solvay, NY. PTI, Bellevue, WA.

US Geological Survey (USGS). 2001. United States NWIS-W data retrieval. US Geological Survey, Washington, DC. Web site: http://waterdata.usgs.gov/nwis/sw. Accessed May 2002.

Walker, W. W. 1987. Empirical methods for predicting eutrophication in impoundments. Report 4: Phase III: Applications Manual. Technical Report E-81-9. US Army Corps of Engineers Waterways Experiments Stations, Vicksburg, MS.

Walling, D. E. and B. W. Webb. 1985. Estimating the discharge of contaminants to coastal waters by rivers: some cautionary comments. Marine Pollution Bulletin, 16:448-492.

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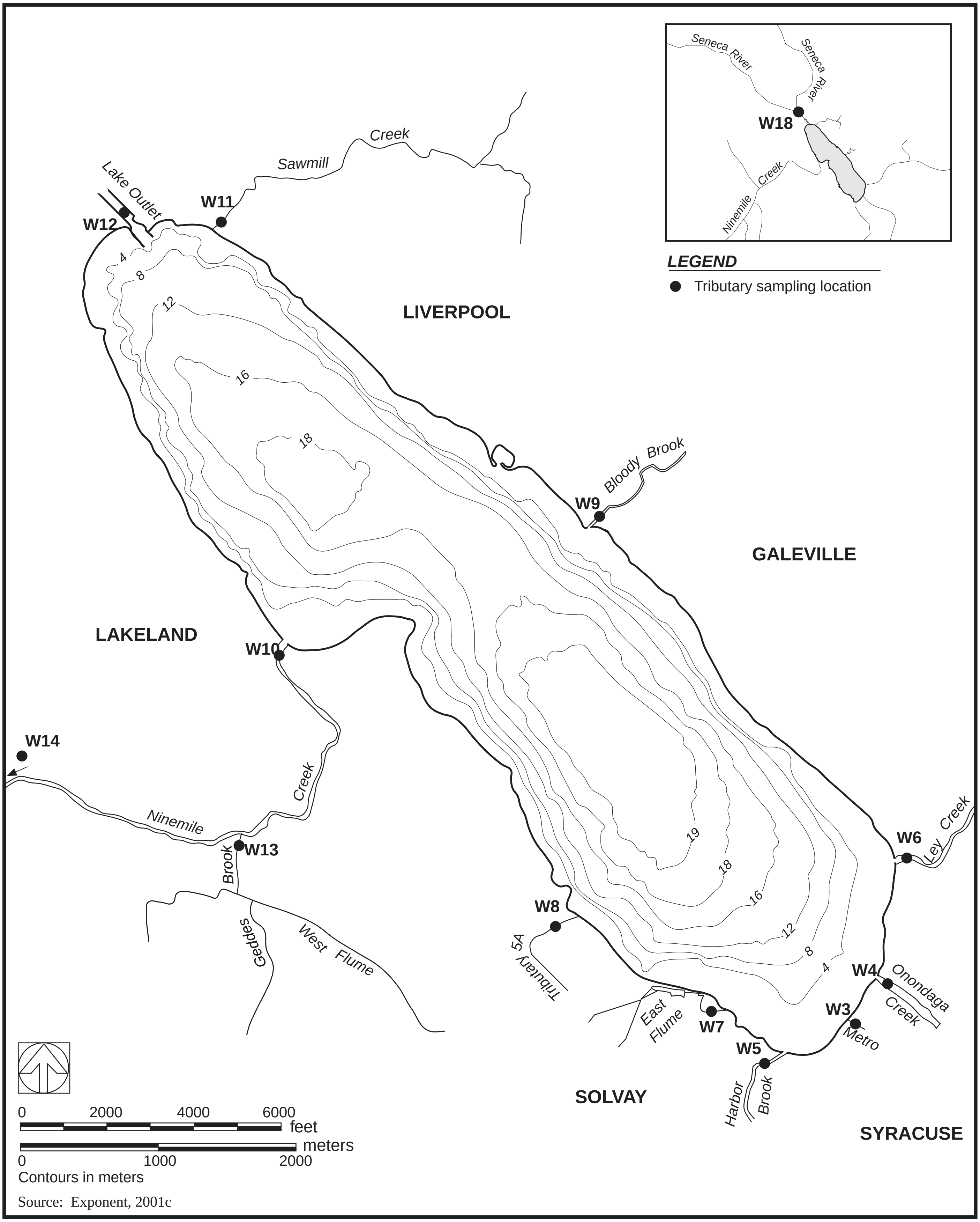
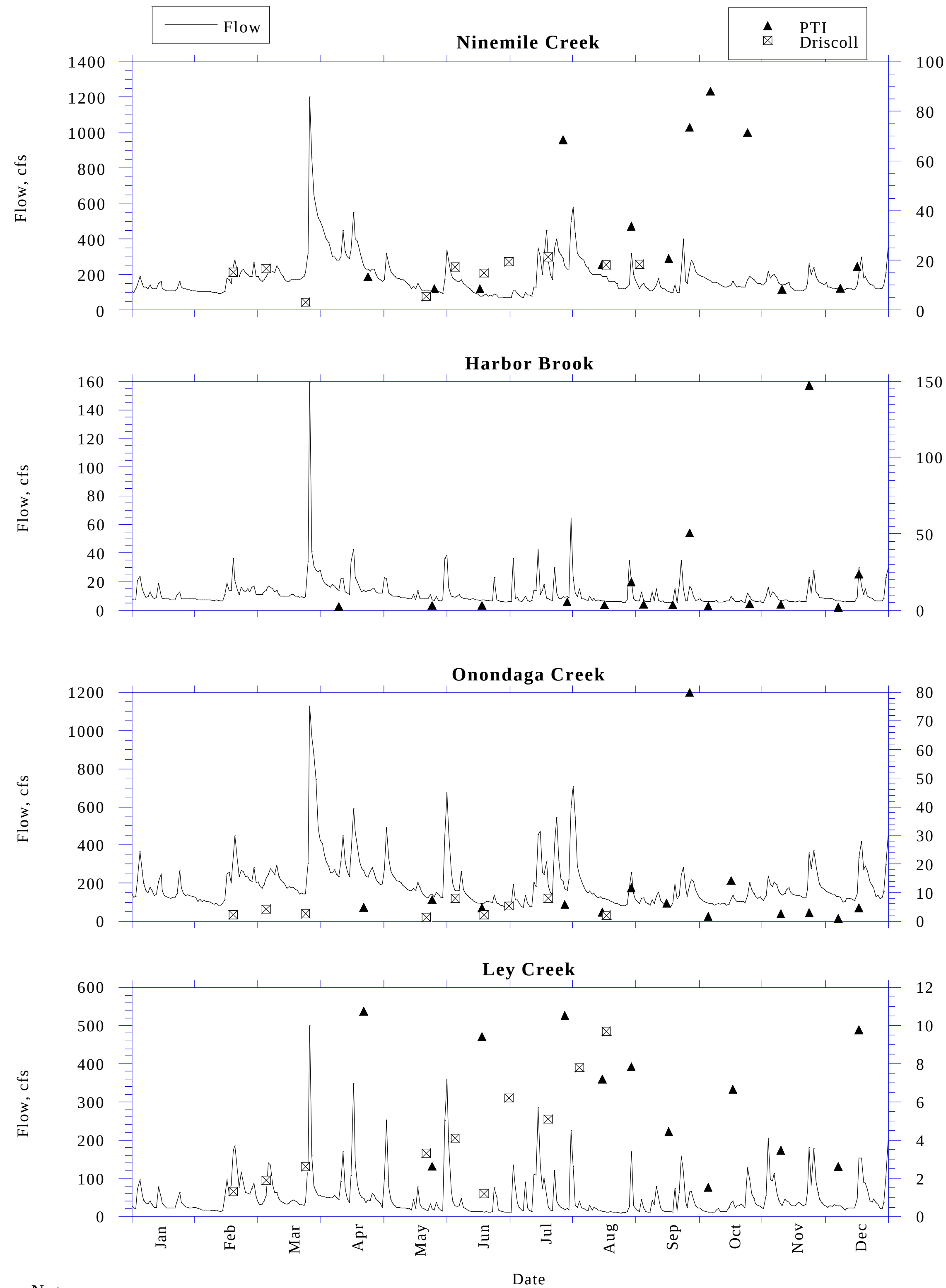


Figure H-1. Locations of Metro Discharge and Tributary Sampling Stations for the Onondaga Lake RI

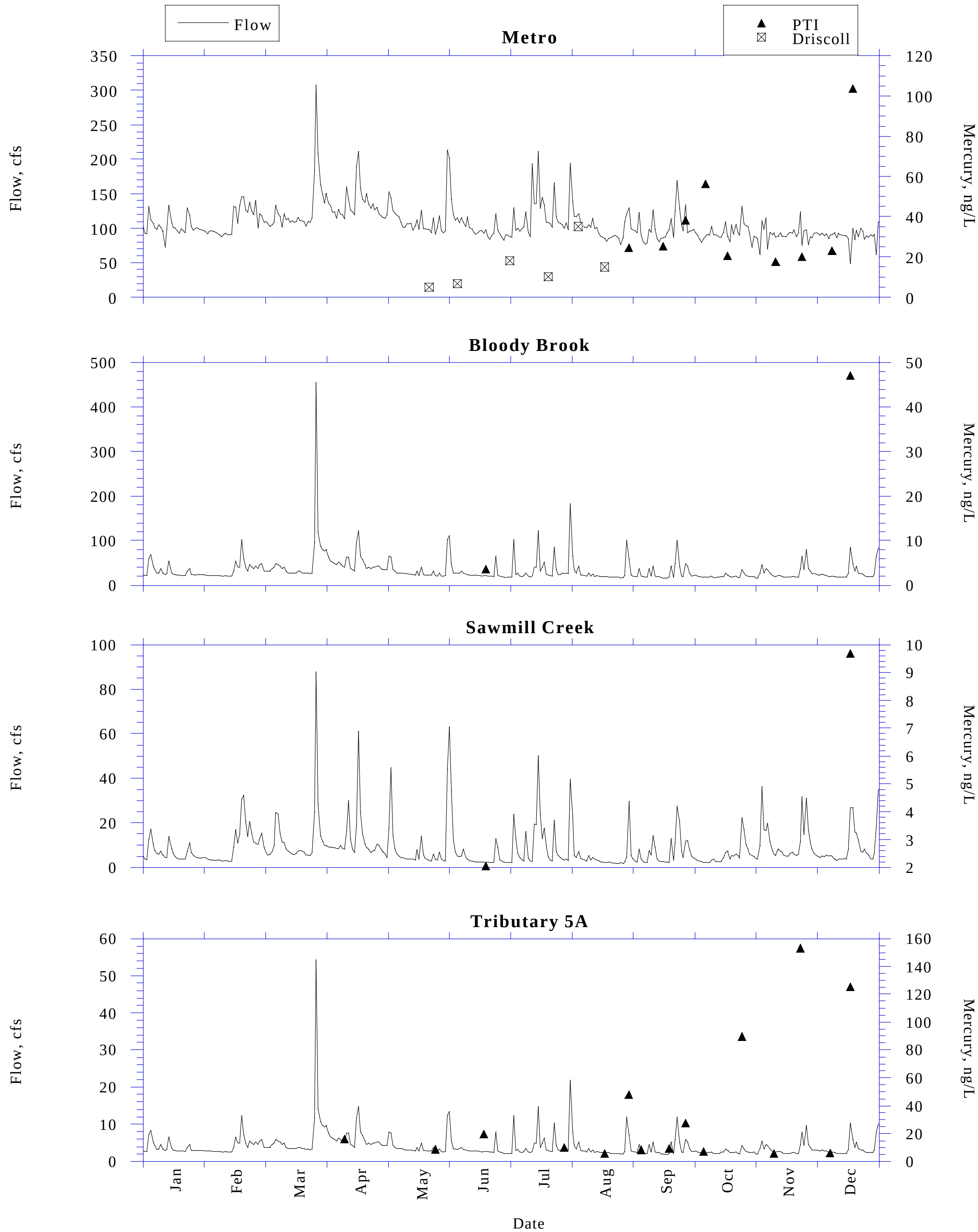


Note:
Flow rates at these four stations are monitored and reported by USGS (2002).

TAMS

Figure H-2

Flow Rate and Total Mercury Concentration for Gauged Tributaries in 1992



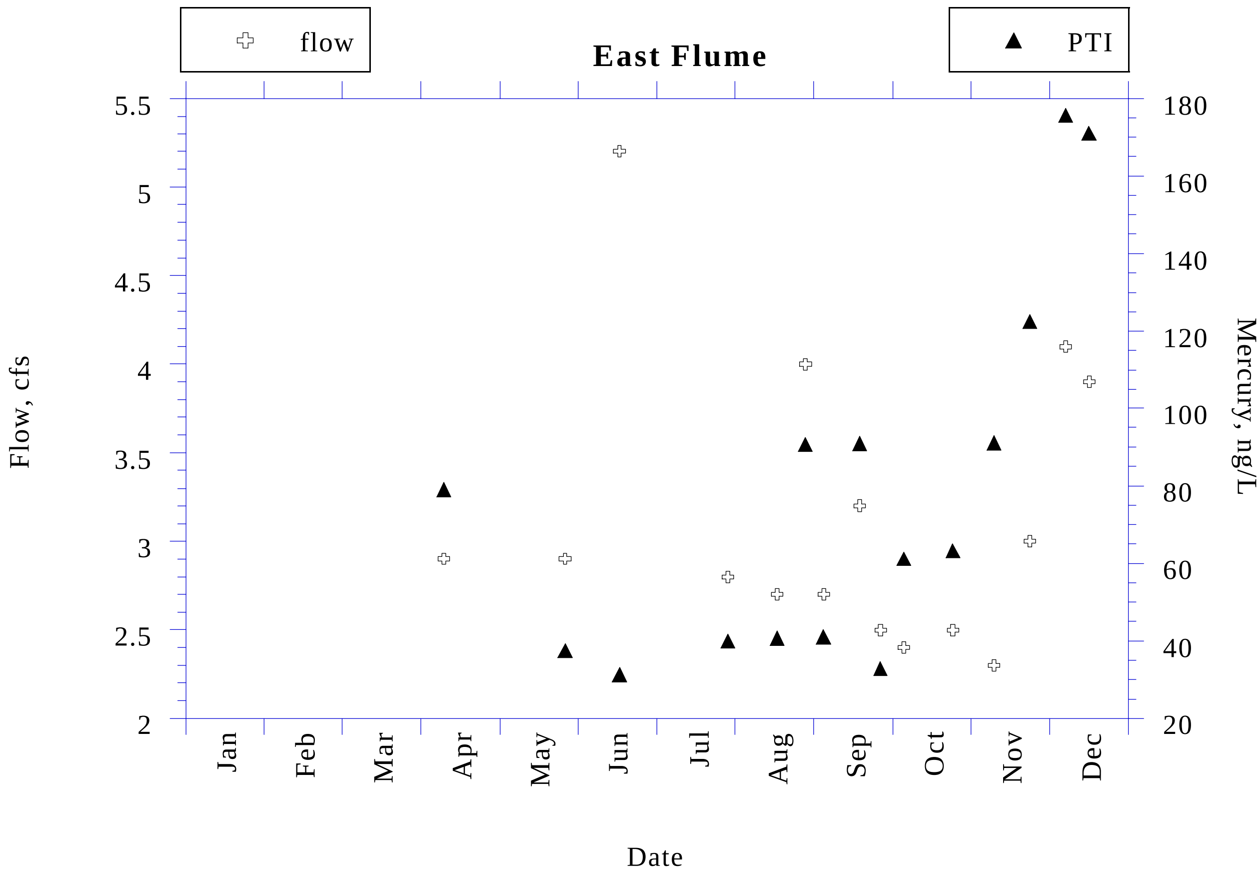
Note:

Flow data at Metro were provided by Onondaga County (OCDDS, 2002). Flows at the other three tributaries were calculated based on relationships developed by Effler (1996).

TAMS

Figure H-3a

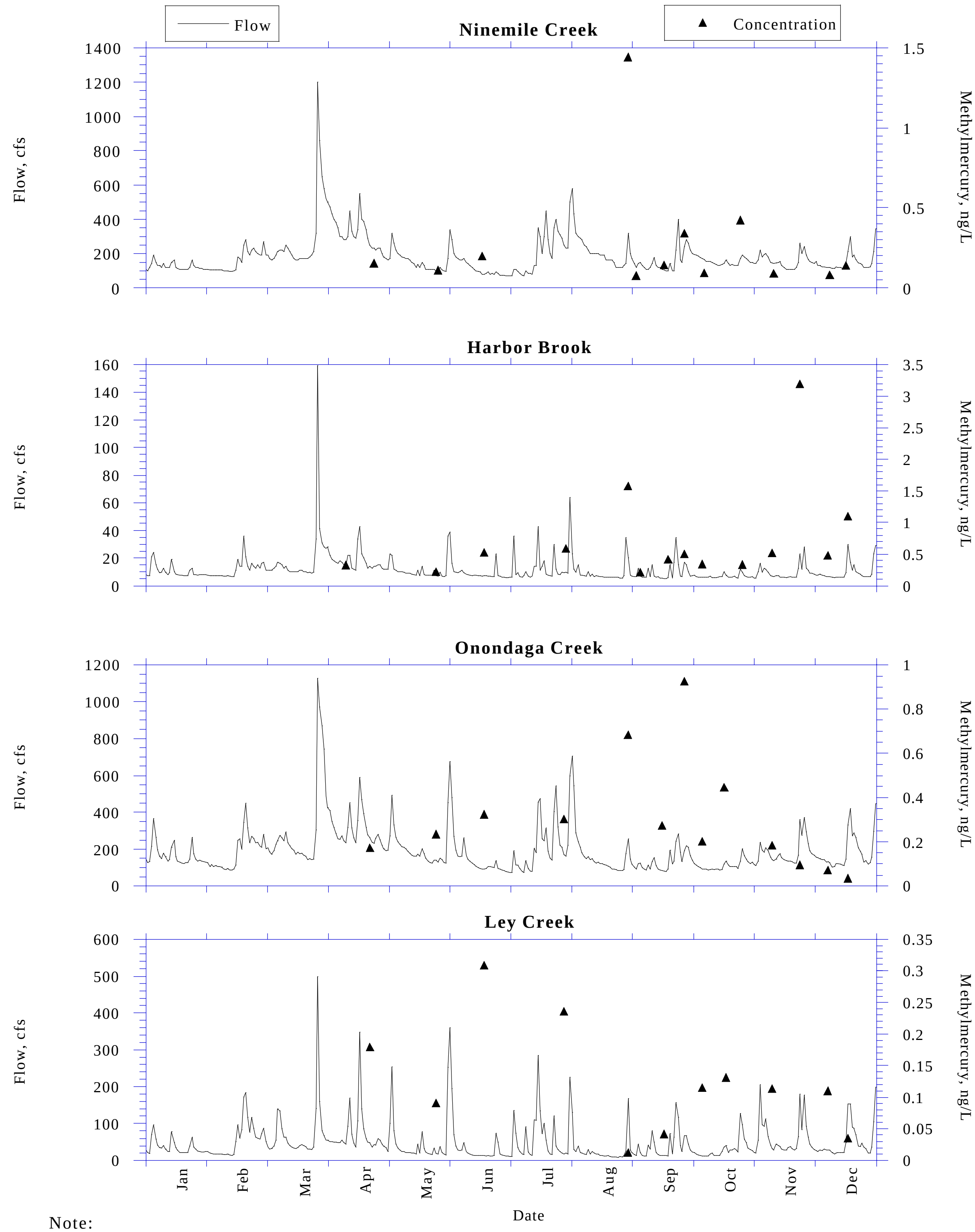
Flow Rate and Total Mercury Concentration for Metro Discharge and Ungauged Tributaries in 1992



Note:
Flow rate at East Flume was measured intermittently by PTI in 1992.

TAMS

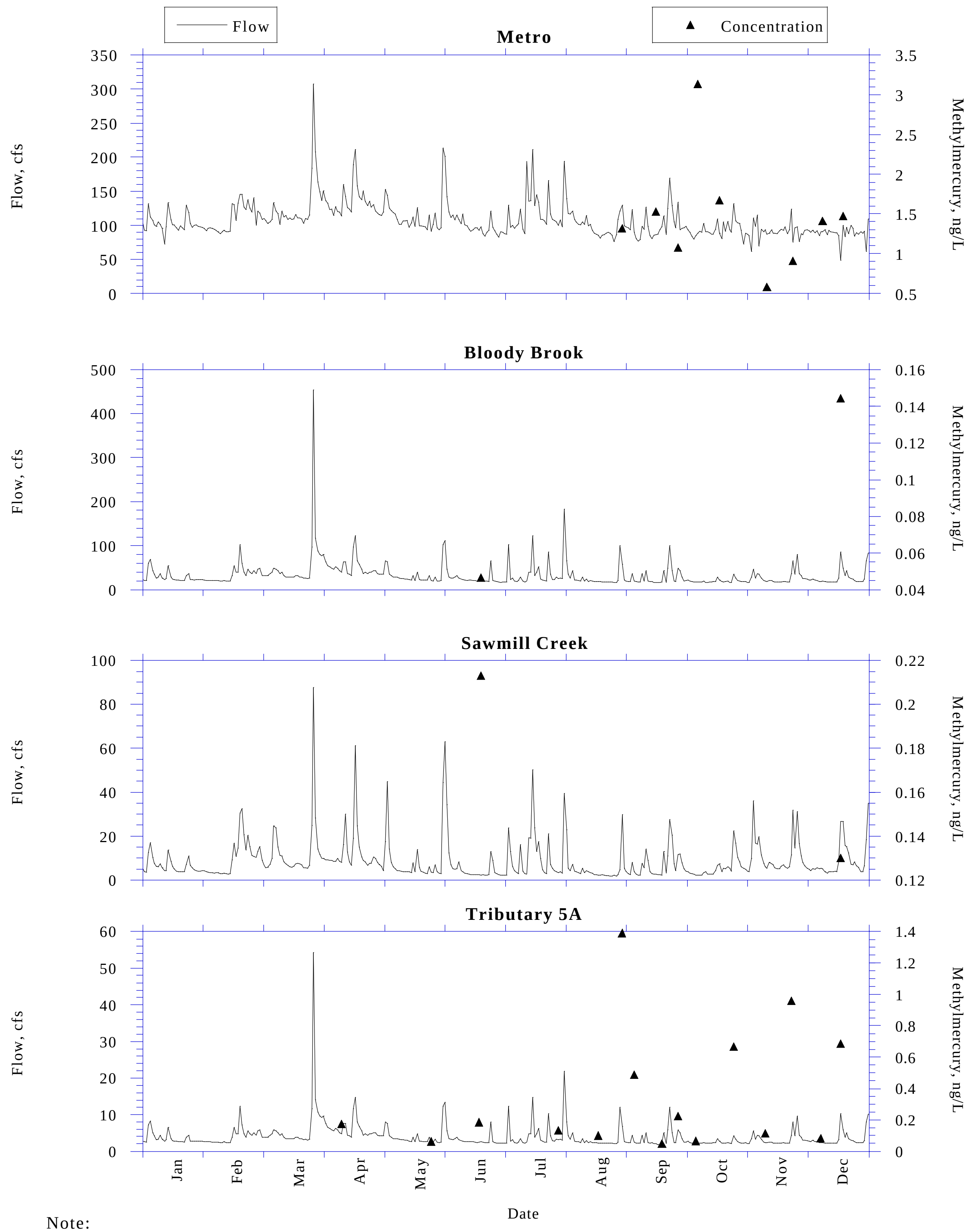
Figure H-3b
Flow Rate and Total Mercury Concentration for Ungauged Tributaries in 1992



Note:
Flow rates at these four stations were monitored and reported by USGS (2002).

TAMS

Figure H-4
Flow Rate and Methylmercury Concentration for Gauged Tributaries in 1992



Note:
Flow data at Metro were provided by Onondaga County (OCDDS, 2002). Flows at the other three tributaries were calculated based on relationships developed by Effler (1996).

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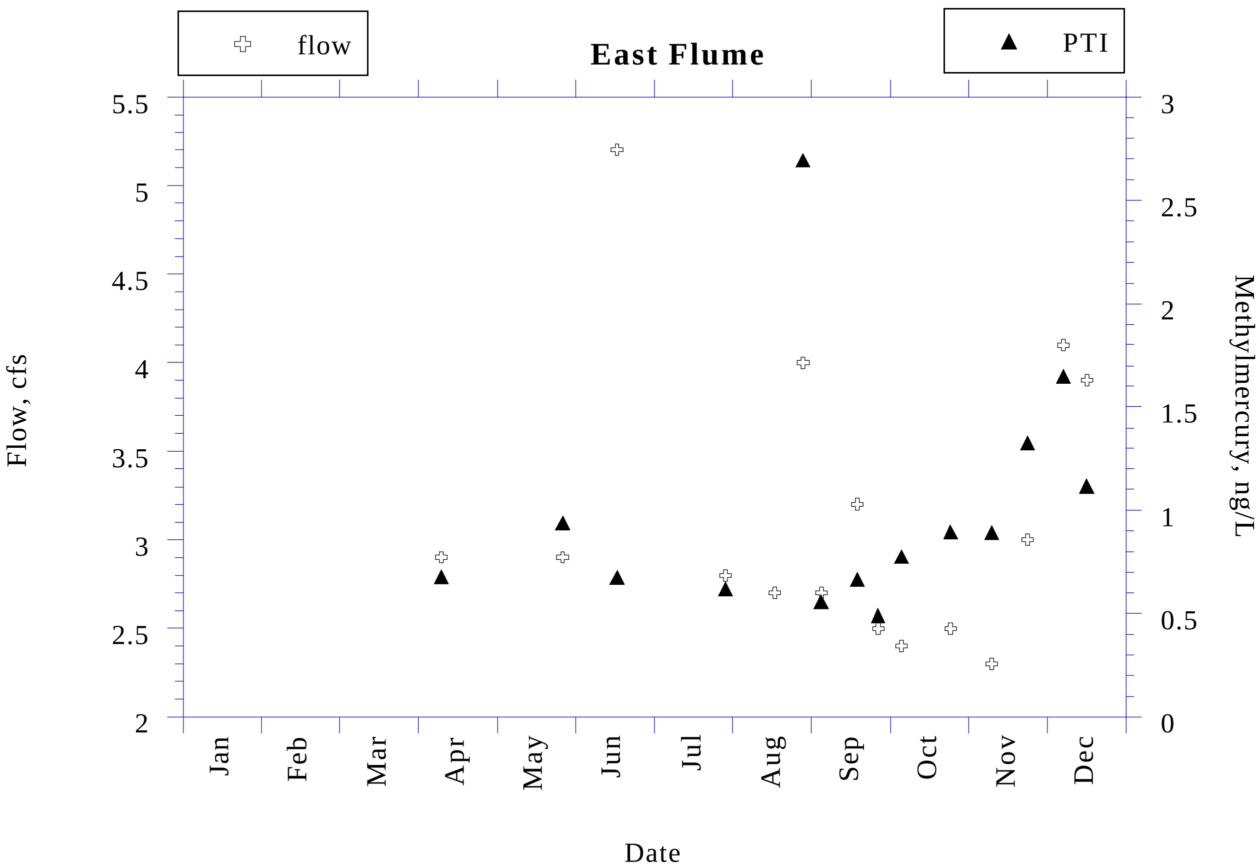
Figure H-5a

Flow Rate and Methylmercury Concentration for Metro Discharge and Ungauged Tributaries in 1992



Note:
Flow rate at East Flume was measured intermittently by PTI in 1992.

TAMS

Figure H-5b

Flow Rate and Methylmercury Concentration for Ungauged Tributaries in 1992

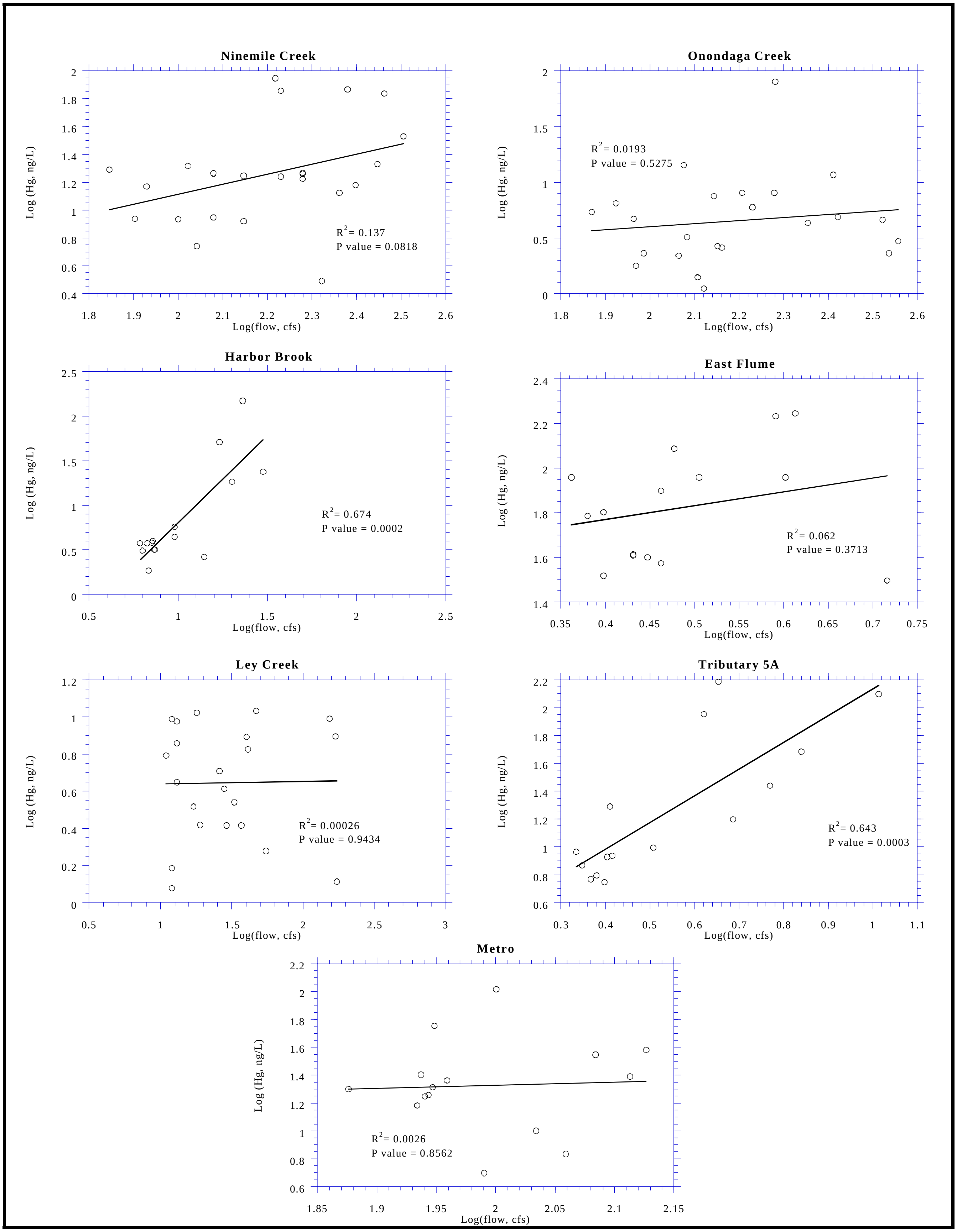


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Figure H-6

Log-Transformed Least-Square Regression Between Flow and Total Mercury Concentration for Metro Discharge and Tributaries to Onondaga Lake in 1992

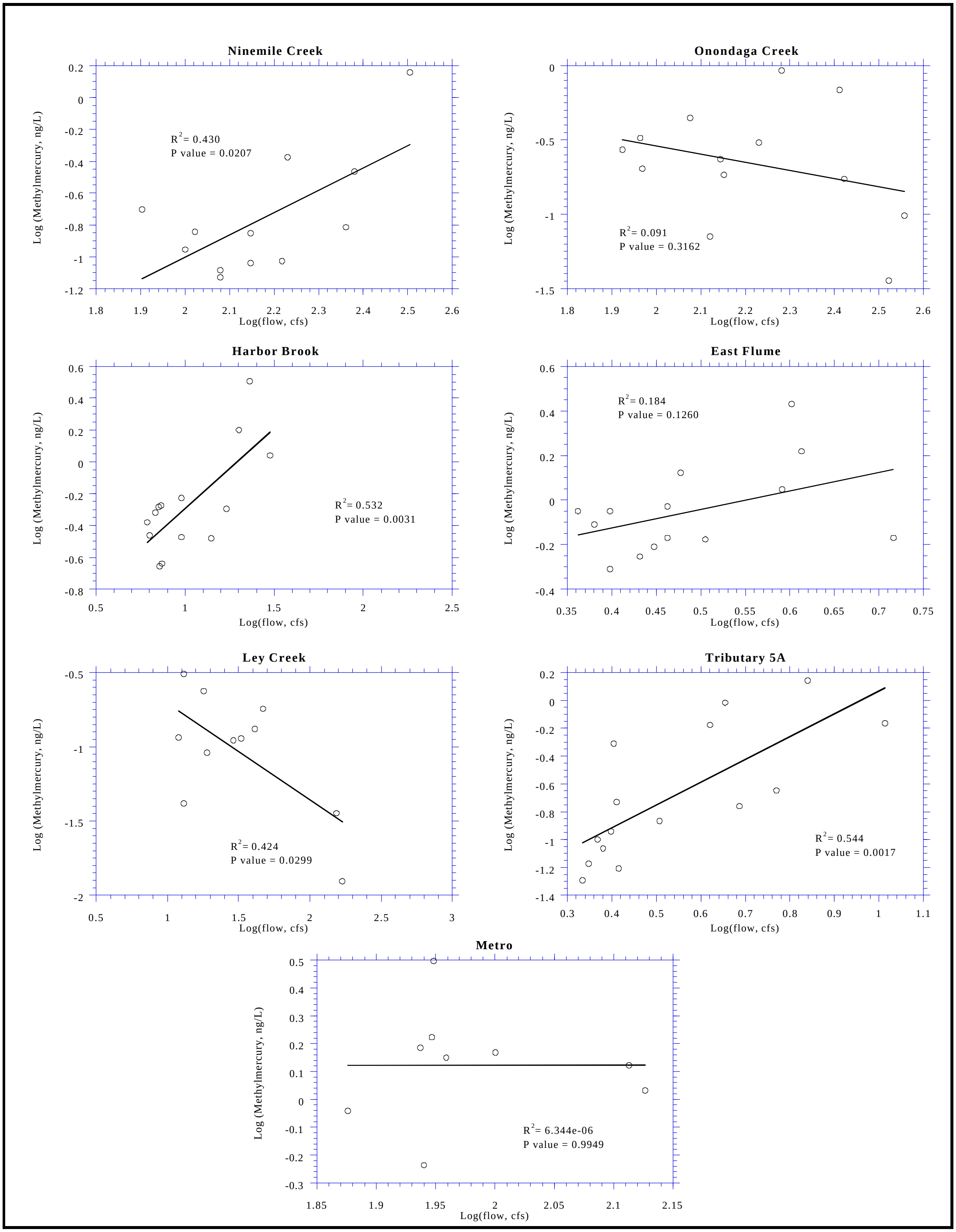

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Figure H-7

Log-Transformed Least-Square Regression Between Flow and Methylmercury Concentration for Metro Discharge and Tributaries to Onondaga Lake in 1992

Table H-1. Tributary and Metro Discharge Flow Rates to Onondaga Lake

Tributary/Metro	Mean Daily Flow Rate in 1992 (cfs) Mean	% Contribution	Mean Flow Rate between May 25 and Sept. 21, 1992	Long-Term Mean USGS Daily Flows (1973 – 2000) (cfs)
Onondaga Creek	193.1	32.5	168.6	175.4
Ninemile Creek	183.7	30.9	168.6	175.9
Metro	107.1	18.0	106.3	
Ley Creek	49.1	8.3	40.9	43.4
Bloody Brook	33.1	5.6	29.8	
Harbor Brook	11.6	2.0	10.5	11.6
Sawmill Creek	8.8	1.5	7.3	
Tributary 5A	4.0	0.7	3.7	
East Flume	3.1	0.5	NA	
Total	**593.7**			

Note: cfs – cubic feet per second

Table H-2. Estimated Mercury Metro Discharge and Tributary Loads to Onondaga Lake, May 25 – September 21, 1992

Tributary[1]/Metro	FLUX Method	Load (g)	CV	Percent of Total	Confidence Interval
Ninemile Creek	2	1,268	0.216	50.8	1,061 - 1,499
Metro	2	611	0.169	24.5	586 - 639
Onondaga Creek	2	346	0.121	13.7	285 - 415
Ley Creek	2	84	0.103	3.4	64 - 109
Harbor Brook	6	81	0.612	2.9	44 - 126
Tributary 5A	6	67	0.401	2.7	37 - 101
East Flume	2	53	0.210	2.1	34 - 76
Total		**2,510**			**2,110 - 2,970**

Notes: CV – coefficient of variation

[1] Sawmill Creek and Bloody Brook were excluded from further load estimation because of limited mercury concentration data and the relatively low flow rates in these two tributaries. Only one sample was collected in the period between May 25 and September 21, 1992.

Table H-3. Estimated Methylmercury Metro Discharge and Tributary Loads to Onondaga Lake, May 25 – September 21, 1992

Tributary[1]/Metro	FLUX method	Load (g)	CV	Percent of Total	Confidence Interval
Ninemile Creek	6	48.6	0.382	41.7	32.5 - 66.6
Metro	2	42.2	0.078	36.2	40.7 - 43.9
Onondaga Creek	2	20.8	0.321	17.8	18.2 - 23.8
Harbor Brook	6	2.59	0.292	2.2	1.82 - 3.58
East Flume	2	0.92	0.363	0.9	0.48 - 1.67
Ley Creek	1	0.86	0.279	0.6	0.80 - 0.92
Tributary 5A	6	0.55	0.294	0.5	0.38 - 0.76
Total		**116**			**95 - 141**

Notes: CV – coefficient of variation

[1] Sawmill Creek and Bloody Brook were excluded from further load estimation because of limited methylmercury concentration data and the relatively low flow rates in these two tributaries. Only one sample was collected in the period between May 25 and September 21, 1992.