



## Technical Memorandum

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**To:** Richard Clark, MPCA  
**From:** Cliff Twaroski, Jay Smith and Neal Hines, Barr Engineering  
**Subject:** Results from the Additional Baseline Monitoring for Sulfate and Methylmercury in the Embarrass River Watershed (July – November 2009)  
**Date:** April 9, 2010  
**Project:** PolyMet Mining, NorthMet Project (23/69 0862 015 074)  
**c:** Ed Swain, MPCA; Mike Berndt, MDNR; Travis Bavin, MDNR; Stuart Arkely, MDNR; Ann Foss, MPCA; Jim Scott PolyMet, Kevin Pylka PolyMet; Barr Engineering Project Team

Additional baseline monitoring for sulfate, methylmercury (MeHg) and total mercury (HgT) was conducted by PolyMet in the Embarrass River watershed from July through early November 2009. This monitoring included sampling at sites located in the Embarrass River and selected tributaries, and in the chain of lakes downstream of the former LTV Steel Mining Company (LTVSMC) tailings basin (hereafter identified as “tailings basin”). The monitoring was initially discussed with staff from the Minnesota Pollution Control Agency (MPCA) and the Minnesota Department of Natural Resources (MDNR) in May 2009, with several follow-up discussions to refine the sampling plan and to provide updates on progress. The work plan for the additional monitoring was submitted to the MPCA and MDNR staff for review and comment (initial draft submittal on June 3, 2009; revised work plan submitted on June 26, 2009; updated work plan submitted on October 14, 2009) (Attachment A).

Summarized in this memorandum are the results from the 2009 baseline monitoring for sulfate, MeHg and HgT in the Embarrass River and selected tributaries. As stated in the Work Plan, the main goal of the additional baseline monitoring is to further characterize background conditions with regard to sulfate loading from the existing tailings basin and its effect on MeHg concentrations within two aquatic environments. The first consists of the large wetlands that lie north and west of the tailings basin. The second consists of the chain of lakes in the lower Embarrass River. A Table of Contents is provided below for the discussion of the results from the additional baseline monitoring conducted in 2009.

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**Attachments**

- Attachment A Work Plan for Additional Baseline Monitoring for Sulfate and Methylmercury in the Embarrass River Watershed, Revised (Updated October 2009)
- Attachment B Hydrologic Data Summary - Streams  
Hydrologic Information for Sabin and Wynne Lakes
- Attachment C Listing of Data from Additional Baseline Monitoring in 2009 by Sample Location and Sampling Date
- Attachment D Statistical Analysis Results

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## Study Approach; Hypotheses

The 2009 monitoring of the Embarrass River and tributary streams is a follow-up action to an initial assessment of the relationship of sulfate and MeHg in baseline stream monitoring data collected for three proposed mining projects (Minnesota Steel, near Nashwauk; PolyMet, NorthMet Project, near Hoyt Lakes; Franconia, near Birch Lake and Babbitt) (Barr Engineering, Technical Memorandum, April 2008). The baseline datasets evaluated in the April 2008 analysis were generally lacking in storm-event data. In addition, MPCA and MDNR staff expressed their concerns that PolyMet's previous baseline sampling efforts did not include sufficient data to determine if the wetlands to the north and west of the tailings basin are capable of releasing elevated levels of MeHg into the tributaries of the Embarrass River during storm events. Other studies have suggested that flooding events may serve to flush MeHg from wetland landscapes, particularly during larger rain events when overtopping of river channels may flood and "flush" surrounding peatlands (Balogh et al., 2005; Balogh et al., 2006). Therefore, the additional baseline monitoring in 2009 included specific requirements for sampling streams to assess the flushing of MeHg from the watershed following relatively large rain storm events (storm event greater than 0.75 inches in a 24-hour period).

Concerns have been expressed to PolyMet that 1) sulfate from the tailings basin may be enhancing mercury methylation in the wetlands to the north/northwest of the basin and contributing to higher fish mercury concentrations in downstream lakes, and 2) that sulfate from the tailings basin may be enhancing mercury methylation in the chain of lakes on the Embarrass River and causing the relatively high fish mercury concentrations in those lakes. Fish mercury concentrations for walleye and northern pike in the MPCA/MDNR database for the Embarrass River chain of lakes range from 0.75 ppm to 1.02 ppm (normalized to a 40 cm walleye) and 0.52 to 0.69 ppm (normalized to a 55 cm northern pike), respectively. These fish mercury concentrations are high compared to some lakes in northeast Minnesota, but are similar to concentrations in other lakes in the region that have dark-colored water (Barr Engineering, Technical Memorandum on fish mercury concentrations, July 2008). To address the agency concerns regarding the potential enhanced methylation of mercury in the lakes due to sulfate additions from the tailings basin, two of the lakes in the chain of lakes were included in the 2009 additional baseline monitoring.

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The objectives and hypotheses associated with the monitoring the two aquatic environments are provided below.

**Streams that Drain Wetlands:**

Objective: Compare stream flow and chemistry from watersheds that receive seepage water with elevated sulfate from the tailings basin with stream flow and chemistry from background watersheds (background watersheds not affected by mining related discharges).

Initial Hypothesis: methylmercury concentrations in drainage water and the flux\* of methylmercury from wetlands receiving sulfate from the LTVSMC tailings basin are not different from concentrations or flux from background wetlands.

Revised Hypothesis (based on November 3, 2009 site visit with MPCA, MDNR and Tribal representatives): methylmercury concentrations in drainage water from wetlands receiving sulfate from the LTVSMC tailings basin are not different from concentrations in drainage water from background wetlands.

\*flux = export of methylmercury per unit area of watershed; in micrograms per square meter per year ( $\mu\text{g}/\text{m}^2/\text{yr}$ )

The change in the hypothesis for the streams portion of the study is based on discussions with MPCA/MDNR staff during the November 3, 2009 site visit that identified the uncertainty in delineating a wetland watershed and the corresponding uncertainty in estimating wetland watershed flux of mercury. Based on the November 3, 2009 discussion, the estimates of MeHg export (i.e., flux) from the respective watersheds are not included in this technical memorandum. Therefore, the data analysis focuses on comparing concentrations of MeHg and the fraction of MeHg to total mercury from the low sulfate (background) streams to the streams with elevated sulfate.

**Lakes Downstream of the Tailings Basin:**

Objective: develop methylmercury budgets for two study lakes receiving sulfate loading from mining features and determine the predominant source of water-column methylmercury in the lakes: from upstream production in the watershed versus in-lake production.

Hypothesis: methylmercury concentrations the in water column of Wynne and Sabin Lakes are primarily from upstream watershed contributions and not from in-lake processes.

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## Site Description

### Embarrass River and Selected Tributaries

Five stream monitoring sites were identified for this study. Two of the sites are in the main channel of the Embarrass River (PM12, upstream of mining features; PM13, downstream of mining features). Three of the sites are in tributaries to the Embarrass River (sites PM11, PM19, PM20). Approximate monitoring locations are shown in Figure 1.

Sites PM12 (Embarrass River upstream of mining features) and PM20 (in Bear Creek at the confluence with the Embarrass R. (Figure 1), are considered to be background sites and are not affected by mining features (i.e., not affected by tailings basin seepage water). Although there is a wastewater treatment facility in Babbitt that discharges to the flowage that becomes the Embarrass River, there is little other development upstream of site PM12 and therefore it is considered a background site. In comparison, sites PM11 and PM19 are located on streams that drain wetlands near the tailings basin and are receiving sulfate from tailings basin seep water. Site PM13 is downstream of all of these sites (Figure 1) and provides an opportunity to collect samples that reflect the mixing of waters from the respective background (non-mining) portions and mining portions of the watershed and investigate the significance of mining related features to the overall chemistry of the Embarrass River. Site PM23, further downstream of PM13 (Figure 1), at the entrance of the Embarrass River into Sabin Lake, is associated with the lake sampling portion of this study and provides additional data on chemical concentrations in the Embarrass River downstream of mining features.

### Sabin and Wynne Lakes

A chain of lakes is present on the Embarrass River, located northeast of Biwabik, MN, that is downstream of the tailings basin. The first two lakes in this chain of lakes are Sabin and Wynne Lakes. Both are narrow and relatively deep lakes (~12m), oriented in a north-south direction, that stratify and support sport fish populations. Each lake has a deep basin. A mid-basin monitoring location near the deepest portion of each was established; PM21, Sabin Lake; PM22, Wynne Lake (Figure 1). The Embarrass River flows into the northern tip of Sabin Lake (monitoring site PM23) and exits the lake at its southern tip. The two lakes are connected together by the narrows (~150m long), which has active flow and is not navigable even by canoe. On calmer days, flow was visible

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in the surface water of Sabin Lake, but not in Wynne Lake. There is a major inlet to the chain of lakes at the narrows between Sabin and Wynne Lakes that drains wetlands north of the Giants Ridge resort and provides additional inputs to Wynne Lake (site PM24; Figure 1). Wynne L. has one other minor inlet (intermittent stream) on its southeast shoreline that was also sampled for this study when it was flowing (site PM25; Figure 1).

Both lakes are affected by development. Cabins are present, particularly on Wynne Lake, and Giants Ridge golf and ski resort is located on the west side of the lakes at the narrows. Of the two lakes, Sabin tends to have higher chlorophyll concentrations and higher total suspended solids concentrations. Both lakes are tea-colored from dissolved organic matter.

## **Data Collection – Summary**

### **Sampling Frequency and Locations; Parameter List**

#### **Embarrass River and Selected Tributaries**

The frequency of monitoring for the stream portion of the study as outlined in the work plan was met for the two flow regimes: 1) rain storm events (or “flush events”), and 2) non-rain events (or “routine monitoring”):

- 1) Three rain storm events (>0.75 inches of rainfall) were sampled at each of the stream sites within seven days after the respective rain event occurred (sample collections on July 21, July 28, and August 26).

Following the recommendations of MPCA and MDNR staff for storm event sampling, the work plan was designed to assess the flushing of the landscape, targeting the falling portion of the hydrograph. The actual timing of sampling is revealed by the hydrographs presented in Attachment B (Hydrologic Data Summary, Figures 3, 4, 5, 8, and 11, respectively).

Sampling coincided generally with the falling portion of the hydrograph and in some cases, due to sequential rain storms, the rising portion of the hydrograph was also sampled (see PM12, PM13, and PM20 for July 21 and August 20 sampling events; Attachment B).

- 2) Non-storm events were sampled approximately monthly and included 5 dates from July to November, 2009.

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Sample collection is briefly summarized here and in full detail in the updated work plan (Barr, October 14, 2009). All samples were collected employing the clean hands technique from USEPA Method 1631 for the collection of surface water samples for low-level mercury analysis. All samples were collected by hand away from the stream bank and beneath the surface of the water to minimize potential influence from vegetation, sampling-related activities occurring on the stream bank and potential influences from material present on the water surface. Filtering of samples was conducted on the stream bank following the methodology used by the MNDR in their recent study of the St. Louis River (Berndt and Bavin, 2009). Unfiltered samples were collected directly in the bottles to be transported to the respective laboratories.

***Parameters; Laboratory Analysis***

The following list of parameters was analyzed for the stream samples based on recommendations and discussions with the MPCA and MDNR staff.

- 1) Filtered: Samples from the stream sites (PM11, PM12, PM13, PM19, PM20) were filtered for methylmercury (MeHg), total mercury (HgT), total iron, organic carbon, and total phosphorus using Nalgene 0.45 $\mu$ m (#166-0045) hand-vacuum pumped canisters.
- 2) Unfiltered: Sulfate, <sup>34</sup>S (isotope 34 sulfur), acid volatile sulfide (AVS), chloride, color, total suspended solids (TSS), and ortho phosphorus were submitted to laboratories as unfiltered samples.

Sample analysis was conducted at three laboratories for this study.

- Northeast Technical Services (NTS), Virginia, MN
- Columbia Analytical Services, Kelso, WA (methylmercury and sulfide only)
- Isotech Laboratories, Inc., Champaign, IL (sulfur isotope, <sup>34</sup>S, only)

All samples were placed on ice as soon as practical after collection. Samples were hand delivered to Northeast Technical Services. Samples were shipped by Federal Express to Columbia Analytical Services and to Isotech Laboratories in order for samples to be analyzed within the specified holding times as specified by the analytical methods.

Duplicates, equipment blanks, and filter blanks were collected during each sampling event and are described in the section below entitled “Data Quality Assurance”.



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The June 26, 2009 work plan identified that chloride and sulfate would be analyzed from filtered samples but were collected as unfiltered samples (summarized in the October 14, 2009 work plan). Both chloride and sulfate are found in the dissolved phase and analysis of both filtered and unfiltered samples (9/23/09) yielded very similar results (Attachment C).

***Parameters; Measured in the Field:***

During each sampling event, the following data were collected using field instruments:

- 1) Temperature, dissolved oxygen, pH, specific conductivity, and oxidation-reduction potential (ORP) using a calibrated (daily) YSI water quality meter (MPS 556).
- 2) In-situ sulfide (Cole Parmer ion specific electrode) but calibration could not be held over the course of sampling, data not collected after 7/29/09.

**Sabin and Wynne Lakes**

The deepest part of each lake was determined from available bathymetric maps and a mid-basin sampling location was established; site PM21 in Sabin Lake and site PM22 in Wynne Lake (Figure 2). Maximum depths were checked in the field during each sampling event. At each mid-basin location, water samples were collected at the lake surface, one meter off the bottom and at one or more intermediate depths according to the temperature and dissolved oxygen profile. The temperature and oxygen profiles were used to determine the location of the metalimnion. Because the metalimnion is a critical interface where potential production of MeHg may be observed (sulfate/sulfide cycling), this boundary was sampled during each sampling event.

As part of the mass balance sampling, streams entering each lake were also sampled. Besides site PM23, there are no other stream inlets to Sabin Lake. Site PM24 is a major inlet to the chain of lakes at the narrows between Sabin and Wynne Lakes and drains wetlands north of Giants Ridge resort. Wynne Lake has one minor inlet towards the southeast that had intermittent flow (site PM25, Figure 1). While the channel was too small to quantify the flow rate, water samples were collected when there was visually observable flow.

Samples collected at the mid-basin locations and inlet stream sites were unfiltered for all parameters. Additional data were collected in the field as listed above for the streams portion of the study (temperature, dissolved oxygen, pH, etc.) in addition to secchi disk readings.

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Duplicates and equipment blanks (Kemmerer sampler) were collected during each outing and are described in the section below entitled “Data Quality Assurance”.

The June 26, 2009 work plan identified that dissolved organic carbon would be analyzed from filtered surface samples for lakes but was collected as an unfiltered sample (total organic carbon). This analytical change was included in the October 14, 2009 work plan and discussed with MPCA and MDNR staff who recommended collecting both filtered and unfiltered samples for comparison. The collection of duplicate samples for DOC (filtered sample) and TOC (unfiltered sample) analysis was done on November 4<sup>th</sup>, 2009 and the laboratory data revealed similar concentrations for both (Attachment C).

### **Data Quality Assurance**

A quality assurance and quality control review was conducted to assess the monitoring performance. This review was performed in accordance with Barr Engineering Standard Operating Procedure for data validation, which is based on *The National Functional Guidelines for Inorganic and Organic Data Review* (EPA 2004/2005). Both laboratory and field sampling procedures were examined in the review of the data for the respective sampling events. Field sampling procedures were examined utilizing field blank and equipment blank analysis and blind field duplicate data. Laboratory procedures were evaluated by examining recommended holding times and preservation, laboratory blank analyses, laboratory control sample (LCS) and laboratory control sample duplicates (LCSD), duplicate analysis, matrix spike (MS) and matrix spike duplicates (MSD), and laboratory duplicate data.

The laboratory completed all analyses within recommended holding times. As previously mentioned, samples were delivered to the respective laboratories as soon as possible after collection. There were generally no issues associated with the sample delivery except for one sampling event. During the July 28/29, 2009 sampling event (chain-of-custody 27947 and 27949), one cooler with lake and stream samples on ice was received by Northeast Technical Services on the morning of July 30 having a temperature of 8.3 degrees Celsius (8.3° C), slightly above the recommended receiving temperature of 4° C but below the maximum allowed temperature of 10° C. This slightly elevated temperature of the cooler was considered a minor deviation and no qualification was applied to the parameters analyzed from those samples since the laboratory received the samples within 24 hours of collection.

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Associated project field blank samples were non-detect for target parameters. For the streams portion of the study, a "total Hg field filter blank" was collected during each sampling event and involved filtering NTS laboratory water through a blank filter. All the data for the "total Hg field filter blank" were non-detect, with a reporting limit of 0.5 ng/L (data reported as <0.50 ng/l). For two sampling events, the "total Hg field filter blank" was analyzed for all parameters (e.g., DOC, iron, etc.) and provides data equivalent to a trip blank or a field blank. Associated laboratory blank samples were non-detect for target parameters.

Multiple equipment field blank samples using the Kemmerer sampler (lake sites at depth - PM21, PM22 only) had detections for low level mercury (total mercury concentrations) above the reporting limit (RL). Following USEPA guidance, the associated lake samples whose total mercury concentrations were within five times the field blank sample concentrations were "b" qualified and are considered potential false positive concentrations. This data qualifier for total mercury concentration in the respective lake samples is identified in Table 2 in Attachment C. The use of the Kemmerer sampler only affected total mercury concentrations at depth (> 0 - 0.1 m); other parameter concentrations, including MeHg concentrations, were not affected by the Kemmerer sampler. Because the lake study focused on MeHg concentrations and not total mercury concentrations, the Kemmerer sampler issue is not considered significant for this study.

Accuracy and precision are determined through the evaluation of LCS/LCSD and MS/MSD recoveries and by calculating the relative percent differences (RPDs) values. The LCS/LCSD recoveries and associated RPDs met laboratory acceptance criteria. With one exception, the MS/MSD recoveries and associated RPDs met laboratory acceptance criteria for the monitoring events, indicating an acceptable level of accuracy and precision. For the sampling event on 11/04/2009, the MS/MSD sample (site PM21- 0 m, surface sample; K0910797-001) displayed lower percent recovery for MeHg but no qualification was applied due to the recovery being a minor deviation (<5%).

The RPD values between the original sample and its corresponding blind field duplicate sample, and between the respective laboratory duplicate samples, demonstrated good laboratory precision except in the following cases.

- For the sampling event on 11/03/2009, the original sample from site PM11 (NTS sample #388754) and its blind field duplicate M21, (NTS 388770) displayed higher RPDs for total suspended solids (TSS), total iron, and MeHg. The RPD for total iron (41%) was above

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acceptance criteria and the corresponding data point for total iron was denoted with an asterisk (“\*”) and qualified as an estimated concentration for the original sample and field duplicate from site PM11 (Attachment C, Table 1, sampling date = 11/03/2009).

Note: Higher RPDs are expected when concentrations are close to the Reporting Limit (RL) and are not always indicative of poor precision. Because the original and blind field duplicate sample concentrations for TSS and MeHg were close to the RL, exaggerating the RPD, no data qualifiers have been applied to the concentrations for these two parameters (Attachment C, Tables 1 and 2).

- For the sampling event on 08/21/2009, the original sample from site PM23 (Isotech #169394) and its blind field duplicate (sample number M10, Isotech number 169395) showed varying results for the sulfur isotope (<sup>34</sup>S) analyses. For the original sample the laboratory reported “NA” results while for the blind field duplicate the laboratory reported a concentration of 13.2 per mil. Barr Engineering staff have denoted the concentrations for both samples (original and field duplicate) with an asterisk (“\*”) and qualified the respective concentration as an estimated value (Attachment C).

With regard to MeHg laboratory analytical data, the relative percent difference (RPD) is considered high (~30.3% for all comparisons of original sample concentration to duplicate sample concentration for this study). However, this relatively high RPD is typical for MeHg analysis because 1) most environmental concentrations are very small (tenths of a ng/L) and 2) the method itself, particularly the distillation step. A relatively small difference in concentration between the original sample and a field duplicate can have a relatively high RPD. Therefore, differences on the order of 0.1 to 0.2 ng/L for MeHg are not significant between two data points (original sample versus duplicate sample) and the MeHg concentration data are not typically identified with data qualifiers.

The final quality assured concentration data reported by the respective laboratories are provided in Attachment C, Table 1 (streams, sites PM11, PM12, PM13, PM19, PM20) and Table 2 (lakes, sites PM21, PM22; tributary streams, PM23, PM24, PM25), respectively. Several values are reported as being less than the reporting limit (e.g., MeHg concentration for site PM11 on sampling date 7/21/2009; Table 1 in Attachment C). If a parameter’s concentration was below the reporting limit, an estimate of the concentration for the specific sampling time was made by using one-half of the reporting limit. For example, for a MeHg value reported as < 0.1 ng/L, the estimated value for that sampling date was 0.05 ng/L. Only a few values in the dataset were estimated values.

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- MeHg: non-detect at site PM19, fall samples, and site PM11 for one of the duplicates on 7/21/09.
- $\text{SO}_4^{-2}$ : three non-detects at site PM12 and one non-detect at site PM20.

## Hydrologic Data

### Streams

For the five stream monitoring locations (sites PM11, PM12, PM13, PM19, PM20) and the inlet streams to the lakes (PM23, PM24), stream flow was estimated using a Marsh McBirney dynamic velocity flow meter (Model 2000, Loveland, CO, tolerance  $\pm 2\%$ ). Flow measurements were taken at 10 or more locations across the respective stream channels. Velocity was measured at 60% of the total stream depth. The first set of flow measurements (6/25/2009) was collected during sampling site reconnaissance but no samples were collected for chemical analysis at that time. Chemistry samples were collected starting July 9, 2009. Continuous stage height was measured for each of the five stream locations using data loggers (In-Situ aqua troll 200) (but the inlet streams to the lakes (PM23, PM24, PM25) did not have continuous recording instrumentation). The time series of stage height was evaluated relative to measured flow using the Marsh McBirney field meter and sufficient data was used to develop preliminary stage – flow curves for sites PM13, PM19 and PM20 (Attachment B).

### Lakes

Lake level was monitored continuously in both Sabin and Wynne lakes to evaluate hydrologic bounce (PM21, PM22). Figure 3 shows the relative lake levels for both Sabin and Wynne Lakes and demonstrates that the two lakes respond similarly. Although just over twice the volume of Sabin Lake, Wynne Lake's surface area is a little smaller and its maximum depth is slightly deeper (Figure 2). The available data (bathymetric maps, inflow to Sabin Lake) indicate that the hydrologic residence time in both lakes is short, averaging approximately 43 days over the study period.

## Data Analysis and Statistical Results

Monitoring data summary results and associated statistical analysis and data plots are presented in three sections: A) Embarrass River and Selected Tributaries; B) Sabin and Wynne Lakes; and C) Transect Analysis for Methylmercury Concentrations in the Embarrass River. For this transect analysis, data from the stream portion of the study (sites PM12 and PM13) are combined with data

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from the lake portion of the study (site PM23, Embarrass River entering Sabin Lake; site PM21 in Sabin Lake; site PM22 in Wynne Lake) to assess the MeHg concentrations in the Embarrass River upstream and downstream of the tailings basin discharge area.

## **A) Embarrass River and Selected Tributary Streams**

Hypothesis (revised; based on November 3, 2009 discussion with state agencies and Tribal representatives): methylmercury concentrations in drainage water from wetlands receiving sulfate from the tailings basin are not different from concentrations in drainage water from background wetlands.

### **Initial Data Plots**

Total mercury concentrations, MeHg concentrations, and “% that is MeHg” values for stream sites are presented in Table 1. An initial comparison of the MeHg concentrations from background sites (PM12, PM20) and sites with elevated sulfate (PM11, PM19) is presented in Figure 4 as box and whisker plots. Data for site PM13 (downstream of mining features) is also presented for comparison purposes. Figure 4 suggests that MeHg concentrations (mean, range of values) are similar for the background sites (PM12 and PM20) and for the sites with elevated sulfate concentrations (PM11, PM19) that receive seepage from the tailings basin.

The proportion of MeHg to total mercury (i.e., the “percent (%) that is MeHg”) is also shown in Table 1 and can be viewed as a proxy for methylation of mercury on a net basis (Mitchell et al., 2008a). Figure 5 is a box and whisker plot of the “% that is MeHg” values for all five stream sites and indicates that the mean and range of values is similar for background sites (PM12, PM20) and for the sites with elevated sulfate (PM11, PM19). There does not appear to be increased levels of “% that is MeHg” for the sites with elevated sulfate.

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**Table 1. Mercury concentrations, methylmercury concentrations, and methylmercury as a percent of total mercury for the stream monitoring locations sampled as part of the additional baseline monitoring conducted for the NorthMet Project in 2009 (July – November).**

Sampling Date	Site PM11 [1] Unnamed Creek (Elevated sulfate)			Site PM19 Trimble Creek (Elevated sulfate)			Site PM12 Embarrass River (Background site)			Site PM20 Bear Creek (Background site)			Site PM13 Embarrass River; (downstream of mining)		
	Hg (total)	MeHg	Percent MeHg	Hg (total)	MeHg	Percent MeHg	Hg (total)	MeHg	Percent MeHg	Hg (total)	MeHg	Percent MeHg	Hg (total)	MeHg	Percent MeHg
	ng/L	ng/L	%	ng/L	ng/L	%	ng/L	ng/L	%	ng/L	ng/L	%	ng/L	ng/L	%
7/9/2009	1.4	0.21	15.0	1.8	0.60	33.3	3.3	0.57	17.3	1.7	0.57	33.5	2.9	0.37	12.8
7/21/2009	1.7	0.080	4.8	1.4	0.35	25.0	2.6	0.54	20.8	1.5	0.19	12.7	3.1	0.27	8.7
7/28/2009	1.5	0.15	10.0	2.1	0.55	26.2	4.3	0.65	15.1	3.4	0.51	15.0	3.3	0.29	8.8
8/20/2009	1.9	0.31	16.5	1.8	0.36	20.0	5	0.63	12.6	2.6	0.23	8.8	3.1	0.62	20.0
8/26/2009	1.4	0.40	28.2	1.8	0.67	37.2	4.3	2.7	62.8	3.1	0.40	12.9	4.1	0.76	18.5
9/10/2009	1.5	0.16	10.7	1.4	0.15	10.7	3.2	0.32	10.0	2.0	0.16	8.0	3.4	0.46	13.5
10/13/2009	0.7	0.13	17.9	0.6	0.05*	8.3	1.5	0.21	14.0	1.3	0.14	10.8	1.5	0.27	18.0
11/3/2009	1.7	0.16	9.4	1.9	0.05*	2.6	3.7	0.12	3.2	4.0	0.13	3.3	3.5	0.23	6.6
Average	1.5	0.2	14.1	1.6	0.45	20.4	3.5	0.7	19.5	2.5	0.29	13.1	3.1	0.41	13.4
St. Dev.	0.5	0.1		0.47	0.19		1.1	0.83		0.98	0.18		0.75	0.19	

Hg = mercury      MeHg = methylmercury      Percent MeHg = methylmercury as a percent of total mercury      ng/L = nanogram per liter

[1] For Site PM11, duplicate sample concentrations for total Hg and MeHg are available and are used to develop an “average” concentration for each sampling event (average of the concentration in the original sample and in the duplicate sample).

\* denotes a concentration that is one-half the reporting limit

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## Statistical Analysis

A number of statistical analyses were conducted for the stream data and Table 2 provides a summary. Output of all statistical results is included in Attachment D. Tests of significance were conducted with the statistical package “R” (R version 2.10.1, The R Project for Statistical Computing, <http://www.r-project.org/>).

The threshold of significance, or critical alpha, for all statistical analyses was set at 0.05, with a secondary cutoff of “marginally significant” set at 0.1. A secondary cutoff was used because of the relatively small datasets being assessed and to balance issues of type I error (a false positive; reject the null hypothesis when it is true) and type II error (false negatives, or accept the null hypothesis when it is false). As shown in Table 2, for the streams dataset, the statistical power to detect a true difference of one standard deviation at the  $p = 0.05$  level for the largest comparison ( $n = 8$ ) is less than 70%; i.e., 70% of the time the analysis would miss a difference that big given the sample size. The use of a secondary cutoff of 0.1 provides a "marginal" confidence interval range that, at the expense of the ability to avoid type I error, increases the statistical power of the comparisons conducted.

A summary of the statistical analyses that were conducted on the 2009 additional baseline monitoring data is provided below, with more details on the paired dataset analyses provided in Table 2. Output from the statistical analyses is provided in Attachment D to this technical memorandum.

- Pair-wise analyses
  - Normality. The differences in concentrations of MeHg and “% that is MeHg” were tested for each paired dataset (data paired by sampling date). The differences, paired by sampling date ( $n_{\text{sampling date}}=8$ ), were tested for normality using the Shapiro-Wilk test. For those paired datasets where the test of normality failed (e.g., comparing site PM12 to site PM13), the non-parametric Wilcoxon signed-rank was used to test for a true difference in the sample central tendencies. Other methods of analysis could have been used, including log-transformations or other forms of data transformation; however, given the small number of data points it was found to be difficult to assume a specific underlying sample distribution. The Wilcoxon signed-rank test makes no generalization about the distributional nature of the sample aside



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from it being symmetrical about the median. This assumption of symmetry is a possible source of error in this analysis; however, it is assumed to be a smaller source of error than the assumption of specific distributional parameters in such a small sample.

- Paired t-test. For the pair-wise comparison of data that passed the test of normality (data assumed to be normally distributed about the mean), a paired t-test was conducted.
- Non-parametric, Wilcoxon signed-rank test (a substitute for the t-test in paired samples). As previously discussed, this non-parametric analysis was used for those paired datasets that failed the test of normality (e.g., comparing data from site PM12 to data from site PM13).
- Analysis of Variance (ANOVA)
  - One-way, repeated measures: assessed effects related to sulfate status; low sulfate, PM12, PM20; elevated sulfate, PM11, PM19. The repeated measures ANOVA of the low sulfate/elevated sulfate sites relied on normality as assessed for the pair-wise analyses, though this method is fairly robust to mild violations of this assumption.
  - Two-way, with one repeated measure: assessed effects from mining status (low sulfate, elevated sulfate) and rain storm event (storm, non-storm). The repeated measures ANOVA relied on normality as assessed for the pair-wise analyses, and as stated above this method is robust to mild violations of this assumption.

Note: because the individual stream datasets are relatively small ( $n = 8$ ), statistical analysis of paired data was conducted using both t-tests and ANOVA to provide additional investigative power to identify significant differences between background sites and sites with elevated sulfate.

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**Table 2. Summary of statistical analyses conducted on the additional baseline monitoring data collected from July to early November, 2009 for the NorthMet Project. (background sites, low sulfate, PM12, PM20; sites with elevated sulfate, PM11, PM19)**

Comparison	Null hypothesis	Difference test [1]	p-value	95% CI (ng/L) (power [2])	90% CI (ng/L) (power [2])	Interpretation [3]
<b>Assessing MeHg</b>						
MeHg within high sulfate sites – PM11 versus PM19	Mean difference between MeHg concentrations at PM11 and PM19 is zero	Paired t-test	0.08	-0.32 to 0.02 (68%)	-0.29 to -0.01 (82%)	Marginally significant difference; PM 19 higher
MeHg within low sulfate sites – PM12 versus PM20	Mean difference between MeHg concentrations at PM12 and PM20 is zero	Paired t-test	0.16	-0.22 to 1.07 (68%)	-0.09 to 0.94 (82%)	No significant difference
	Median difference between MeHg concentrations at PM12 and PM20 is zero	Wilcoxon signed-rank	0.03	N/A	N/A	Significant difference; PM12 higher
MeHg between PM11 and PM12	Mean difference between MeHg concentrations at PM11 and PM12 is zero	Paired t-test	0.09	-1.14 to 0.10 (68%)	-1.02 to -0.02 (82%)	Marginally significant difference; PM12 higher
	Median difference between MeHg concentrations at PM11 and PM12 is zero	Wilcoxon signed-rank	0.02	N/A	N/A	Significant difference; PM12 higher
MeHg between PM11 and PM20	Mean difference between MeHg concentrations at PM11 and PM20 is zero	Paired t-test	0.17	-0.24 to 0.05 (68%)	-0.21 to 0.02 (82%)	No significant difference
	Median difference between MeHg concentrations at PM11 and PM20 is zero	Wilcoxon signed-rank	0.27	N/A	N/A	No significant difference
MeHg between PM19 and PM12	Mean difference between MeHg concentrations at PM19 and PM12 is zero	Paired t-test	0.17	-0.94 to 0.20 (68%)	-0.82 to 0.08 (82%)	No significant difference
	Median difference between MeHg concentrations at PM19 and PM12 is zero	Wilcoxon signed-rank	0.02	N/A	N/A	Significant difference; PM12 higher
MeHg between PM19 and PM20	Mean difference between MeHg concentrations at PM19 and PM20 is zero	Paired t-test	0.24	-0.05 to 0.16 (68%)	-0.03 to 0.14 (82%)	No significant difference
MeHg by location (PM12, upstream / PM13, downstream) [4]	Mean difference between MeHg concentrations at sites upstream and downstream of mine is zero	Paired t-test	0.24	-0.88 to 0.26 (68%)	-0.77 to 0.15 (82%)	No significant difference
	Median difference between MeHg concentrations at sites upstream and downstream of mine is zero	Wilcoxon sign-rank	0.25	N/A	N/A	No significant difference
MeHg by location during non-storm conditions (PM12, upstream / PM13, downstream)	Mean difference between MeHg concentrations at sites upstream and downstream of mine features is zero during non-storm conditions	Paired t-test	0.76	-0.15 to 0.19 (40%)	-0.11 to 0.15 (58%)	No significant difference

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Comparison	Null hypothesis	Difference test [1]	p-value	95% CI (ng/L) (power [2])	90% CI (ng/L) (power [2])	Interpretation [3]
MeHg by location during rain (storm) events  (PM12, upstream / PM13, downstream)	Mean difference between MeHg concentrations at sites upstream and downstream of mine features is zero during storm events	Paired t-test	0.25	-3.19 to 1.48 (18%)	-2.44 to 0.73 (32%)	No significant difference
<b>Assessing “% that is MeHg”</b>						
Percent that is MeHg within high sulfate sites – PM11 versus PM19	Mean difference between percent that is methyl at PM11 and PM19 is zero	Paired t-test	0.16	-15.9 to 3.2 (68%)	-14.0 to 1.3 (82%)	No significant difference
Percent that is MeHg within low sulfate sites – PM12 versus PM20	Mean difference between percent that is methyl at PM12 and PM20 is zero	Paired t-test	0.38	-9.5 to 22.2 (68%)	-6.4 to 19.1 (82%)	No significant difference
	Median difference between percent that is methyl at PM12 and PM20 is zero	Wilcoxon signed-rank	0.20	N/A	N/A	No significant difference
Percent that is MeHg between PM11 and PM12	Mean difference between percent that is methyl at PM11 and PM12 is zero	Paired t-test	0.30	-16.9 to 6.0 (68%)	-14.6 to 3.8 (82%)	No significant difference
	Median difference between percent that is methyl at PM11 and PM12 is zero	Wilcoxon signed-rank	0.64	N/A	N/A	No significant difference
Percent that is MeHg between PM11 and PM20	Mean difference between percent that is methyl at PM11 and PM20 is zero	Paired t-test	0.81	-8.1 to 9.9 (68%)	-6.3 to 8.1 (82%)	No significant difference
Percent that is MeHg between PM19 and PM12	Mean difference between percent that is methyl at PM19 and PM12 is zero	Paired t-test	0.84	-9.7 to 11.6 (68%)	-7.6 to 9.5 (82%)	No significant difference
Percent that is MeHg between PM19 and PM20	Mean difference between percent that is methyl at PM19 and PM20 is zero	Paired t-test	0.06	-0.3 to 14.9 (68%)	1.2 to 13.4 (82%)	Marginally significant difference; PM19 higher
Percent that is MeHg by location (PM12, upstream/ PM13, downstream) [4]	Mean difference between percent that is methyl at sites upstream and downstream of the mine is zero	Paired t-test	0.34	-20.1 to 7.9 (68%)	-17.3 to 5.1 (82%)	No significant difference
	Median difference between percent that is methyl at sites upstream and downstream of the mine is zero	Wilcoxon signed-rank	0.46	N/A	N/A	No significant difference
Percent that is MeHg by location during non-storm conditions	Mean difference between percent that is methyl at sites upstream and downstream of the mine is zero during non-storm conditions	Paired t-test	0.23	-2.7 to 8.2 (40%)	-1.4 to 6.9 (58%)	No significant difference
Percent that is MeHg by location during rain (storm) events	Mean difference between percent that is methyl at sites upstream and downstream of the mine is zero during storm events	Paired t-test	0.22	-71.7 to 29.9 (18%)	-55.3 to 13.6 (32%)	No significant difference

MeHg = methylmercury

Percent that is methyl = “% that is MeHg”

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Footnotes to Table 2

- [1] Paired differences were tested for normality using the Shapiro-Wilk test. Those which generated p-values below 0.05 using this test were analyzed using the non-parametric Wilcoxon signed-rank test along with the paired t-test.
- [2] Power values represent the percent of times a true difference of one standard deviation would be identified given significance levels of 0.05 and 0.1 for the 95% CI and 90% CI, respectively.
- [3] For the paired t-test: If both the 95% CI and 90% CI encompass zero, an interpretation of “no significant difference” is reported; If only the 95% CI encompasses zero, an interpretation of “marginally significant difference” is reported; If neither CI encompasses zero, an interpretation of “significant difference” is reported. For the Wilcoxon signed-rank test: the identical respective reporting categories are  $p\text{-value} > 0.1$ ,  $0.1 \geq p\text{-value} > 0.05$ , and  $0.05 \geq p\text{-value}$ .
- [4] PM12 represents the upstream site, upstream of the former LTVSMC Tailings Basin; PM13 represents the downstream site, site is downstream of the expected influence of the Tailings Basin seeps.

The summary results of comparing the individual sites (elevated sulfate (PM11, PM19) to background sites (PM20, PM12)) are as follows:

- MeHg concentrations
  - Sites PM11 and PM19, respectively, are significantly lower than site PM12 (background).
  - Sites PM11 and PM19, respectively, are not significantly different than site PM20 (background).
- “% that is MeHg”
  - Site PM11 is not significantly different than background sites (PM12, PM20, respectively).
  - Site PM19 is not significantly different than site PM12.
  - Site PM19 is marginally significantly higher than site PM20 (paired t-test; p-value = 0.06).

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### **Rain Storm versus Non Storm Events**

To evaluate whether rain storm events have a significant effect on MeHg concentration, the stream data were separated into storm events (three storm events) and non-storm events (five non-storm events) (Table 3). The data in Table 3 suggest that the mean MeHg concentration and mean “% that is MeHg” for site PM19 (elevated sulfate) and PM12 (background) for storm events are higher than the respective mean for the non-storm event data. However, for sites PM11 (elevated sulfate), PM20 (background) and PM13 (downstream of mining features) the mean MeHg concentration and “% that is MeHg” for storm events is similar to non-storm events (Table 3). Overall, the sites with elevated sulfate (PM11, PM19) tend to have MeHg concentrations and “% that is MeHg” similar to the background sites (PM12, PM20) for storm and non-storm events, respectively.

Figure 6 provides a comparison of the average values of “% that is MeHg” for background sites and the sites having elevated sulfate for both storm and non-storm sampling events and indicates there is no consistent pattern that higher “% that is MeHg” is associated with sites having elevated sulfate concentration. Figure 7 provides a comparison of the “% that is MeHg” values for individual storm events and Figure 8 provides a comparison of “% that is MeHg” for individual non-storm events. For both storm events (Figure 7) and non-storm events (Figure 8), there is an inconsistent pattern of “% that is MeHg”. being elevated for the sites with elevated sulfate concentration (PM11, PM19). Overall, there appears to be more similarity than differences between background sites and sites with elevated sulfate.

If elevated sulfate concentration was having a significant effect on mercury methylation, the sites with elevated sulfate (PM11, PM19) should be notably higher in MeHg concentration and “% that is MeHg” than the background sites (PM12, PM20). However, as shown in Figure 7 and Figure 8, that does not seem to be the case. For example, sites PM11 and PM19 have the highest sulfate concentrations (PM11, average for storm events = 142 mg/L; PM19, average for storm events = 13.7 mg/L; Table 3). But Figure 7 indicates that “% that is MeHg” values for site PM11 are typically lower than for the streams draining background wetlands and that site PM19 is similar to background site PM12 (average sulfate = 0.38 mg/L, storms). Based on the data presented in Table 3 and plotted in Figure 7 for storm events, elevated sulfate concentration does not seem to have a notable effect on MeHg concentration or methylation efficiency (as indicated by “% that is MeHg”).

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**Table 3. Methylmercury and sulfate concentrations for storm and non-storm events for each stream sampling site included in the additional baseline monitoring conducted for the NorthMet Project in 2009 (July – November).**

Sample Date	Site PM11 [1]			Site PM19			Site PM12			Site PM20			Site PM13		
	Unnamed Creek (Elevated sulfate)			Trimble Creek (Elevated sulfate)			Embarrass River, (Background site)			Bear Creek (Background site)			Embarrass River; (downstream of mining features)		
	MeHg	Percent MeHg	Sulfate	MeHg	Percent MeHg	Sulfate	MeHg	Percent MeHg	Sulfate	MeHg	Percent MeHg	Sulfate	MeHg	Percent MeHg	Sulfate
	ng/L	%	mg/L	ng/L	%	mg/L	ng/L	%	mg/L	ng/L	%	mg/L	ng/L	%	mg/L
<b>Storm Event [2]</b>															
7/21/2009	0.08	5.0	151	0.35	25	18.4	0.54	21	0.5*	0.19	13	1.27	0.27	9	48.3
7/28/2009	0.15	10	150	0.55	26	15.9	0.65	15	1.05	0.51	15	0.5*	0.29	9	37.3
8/26/2009	0.4	28	124	0.67	37	6.91	2.7	63	0.5*	0.4	13	1.07	0.76	19	31.4
<i>Average</i>	0.21	14	142	0.52	29	13.7	1.30	33	0.68	0.37	14	0.95	0.44	12	39.0
<i>Standard Deviation</i>	0.17		15.3	0.16		6.04	1.22		0.32	0.16		0.40	0.28		8.58
<b>Non-Storm Event</b>															
7/9/2009	0.21	15	147	0.60	33	10.1	0.57	17	0.5*	0.57	34	1.11	0.37	13	47.2
8/20/2009	0.31	16	141	0.36	20	7.82	0.63	13	1.73	0.23	9	1.82	0.62	20	25.9
9/10/2009	0.16	11	155	0.15	11	7.69	0.32	10	1.18	0.16	8	1.35	0.46	14	27.4
10/13/2009	0.13	18	188	0.05*	8.3	33.6	0.21	14	1.4	0.14	11	1.39	0.27	18	44.2
11/3/2009	0.16	9.4	160	0.05*	2.6	40.6	0.12	3.2	3.61	0.13	3.3	2.05	0.23	6.6	45.8
<i>Average</i>	0.19	14	158	0.24	15	20.0	0.37	11	1.68	0.25	13	1.54	0.39	14	38.1
<i>Standard Deviation</i>	0.071		18.2	0.24		15.9	0.22		1.17	0.19		0.38	0.16		10.5
<b>All Samples</b>															
<i>Average</i>	0.20	14	152.0	0.35	20	17.6	0.72	20	1.1	0.29	13	1.3	0.41	14	38.4
<i>Standard Deviation</i>	0.11		18.1	0.25		12.8	0.83		1.20	0.18		0.60	0.19		9.19

MeHg = methylmercury    Percent MeHg = methylmercury as a percent of total mercury    ng/L = nanogram per liter    mg/L = milligram per liter

\* denotes a concentration that is one-half the reporting limit

[1] For Site PM11, duplicate sample concentrations for MeHg and sulfate are available and used to develop an “average” concentration for each parameter for each sampling event (average of the concentration in the original sample and in the duplicate sample).

[2] Rainfall amounts for storm events:

7/21/2009 sample collection:            1 inch of rain on 7/14  
 7/28/2009 sample collection            0.87 inch of rain on 7/21  
 8/26/2009 sample collection            1.5 inches of rain beginning on 8/19

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Analysis of variance (ANOVA) was used to assess the effect of mining status (low sulfate, background; elevated sulfate) and storm status (storm event; non-storm event) on MeHg concentrations and “% that is MeHg”. The ANOVA was conducted using one-way repeated measures and two-way with one repeated measure model structures.

- One-way repeated measures.
  - MeHg concentration from sites with elevated sulfate (PM11, PM19) compared to the low sulfate (background). The results indicate that elevated sulfate concentration has a marginally significant inverse relationship with mean MeHg concentration ( $\Pr(>F) = 0.08$ ) (see Attachment D); as sulfate concentration increases, MeHg concentration decreases.
- Two-way ANOVA with one repeated measures factor. Rain storm status is another factor considered in addition to mining-related sulfate that could affect MeHg concentrations and “% that is MeHg”. The effect from rain storm events (and mining) was assessed using a two-way ANOVA with one repeated measure. Results are summarized below (output from the statistical package “R” provided in Attachment D):
  - MeHg concentration
    - Sulfate status is a marginally significant inverse predictor of MeHg concentration for these sites (i.e., elevated sulfate sites have a marginally significant reduction in MeHg).
    - Flushing (i.e., storm event) is not a significant predictor of MeHg concentration.
    - Interaction: Mining status (elevated sulfate) interacting with flushing status does not have a significant effect on the mean MeHg concentration, but results indicate that storm events may flush more MeHg from background sites than from sites with elevated sulfate (Table 4).
  - “% that is MeHg”
    - Sulfate status and storm status do not have a significant effect on “% that is MeHg”.
    - Interaction: Mining status interacting with storm status does not have a significant effect on “% that is MeHg”.

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Table 4 provides partial output from the two-way ANOVA and indicates that both MeHg concentration and “% that is MeHg” increase for rain events, but there is an increase for both background sites (PM12, PM20) and the sites with elevated sulfate (PM11, PM19). Flushing has a near marginally significant ( $Pr(>F) = 0.12$ ) interactive effect on the relationship between MeHg concentration and sulfate status (i.e., flushing may create a bigger MeHg concentration differential between high- and low-sulfate sites) and the interaction statistics suggest that more MeHg may be flushed from background wetlands (Table 4; value of 0.83 ng/L for background sites PM12/PM20 compared to a value of 0.37 ng/L for sites with elevated sulfate) (see Attachment D for additional ANOVA output).

Overall, ANOVA results indicate that elevated sulfate concentration in seepage water from the tailings basin is not a significant factor with regard to flushing of MeHg from the PM11 or PM12 watersheds during storm events and elevated sulfate is not a significant factor with regard to MeHg concentration (or “% that is MeHg”) for non-storm events.

**Table 4. Partial Analysis of Variance (ANOVA) results assessing the significance of mining status and storm event status on methylmercury concentration and methylmercury as a percent of total mercury (“% that is MeHg”) for sites included in the additional baseline monitoring conducted for the NorthMet Project in 2009 (July – November). (two-way repeated measures analysis of variance)**

ANOVA model output		Factor = Storm Event Status	
		0 (no) (non-storm event)	1 (yes) (rain storm event)
MeHg concentration			
Factor = Mining status	0 (no) [background; Sites PM12, PM20]	0.31 ng/L	0.83 ng/L
	1 (yes) [elevated sulfate; Sites PM11, PM19]	0.22 ng/L	0.37 ng/L
“% that is MeHg”			
Factor = Mining status	0 (no) [background; Sites PM12, PM20]	12 %	23 %
	1 (yes) [elevated sulfate; Sites PM11, PM19]	14 %	22 %



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## **B) Sabin and Wynne Lakes**

Sabin and Wynne lakes are part of the Embarrass River chain of lakes and are downstream of the tailings basin. Concerns were expressed by state agency staff that elevated sulfate from the tailings basin that enters the chain of lakes could be causing increased methylation of mercury and elevated fish mercury concentrations.

Hypothesis: Water-column MeHg concentrations in Wynne and Sabin Lakes are primarily from upstream watershed contributions and not from in-lake processes.

### **Assessment of Trends**

#### ***Vertical Profile of Methylmercury in the Water Column***

Research findings indicate that MeHg production in a lake can occur at the metalimnion, just below the well-oxygenated epilimnetic zone (Watras et al., 1995; Regnell et al., 1997), and in the sediment, coming from either diffusion (dissolved in porewater) or advection (possibly as groundwater pushes MeHg out of the porewater). The lake sampling was intended to collect data for these two specific locations within the water column of each lake.

The approximate depth and thickness of the metalimnion was expected to vary for each sampling event. Temperature and dissolved oxygen concentration data were collected during each sampling event to identify the stratification of the water column and to determine specific sampling depths for the metalimnion (oxygenated side and anoxic side) and hypolimnion. The collected data indicates that moderate development of the hypolimnions in Sabin and Wynne Lakes was occurring in late June, and was fairly well developed by late July and through September (Figure 9, Sabin Lake; Figures 10, Wynne Lake).

The sample collection depth is also included in the respective plots of temperature and dissolved oxygen concentration (identified with X's), allowing visualization of where water samples were collected in relation to the metalimnion and hypolimnion. Samples of the hypolimnion were collected from approximately one meter above the lake bottom, with special care being taken to avoid contamination with sediment.



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Hg = mercury    MeHg = methylmercury    % MeHg = methylmercury as a percent of total mercury    ng/L = nanogram per liter    mg/L = milligram per liter

\*Includes the average concentration of the original sample and duplicate sample for specific sampling dates.

Blank cells indicate no data were collected for that sampling event and/or no values (e.g., % that is MeHg) were calculated.

Footnotes to Table 5 (continued)

[1] Sample depth

Surface = within one meter of the water surface (0 to ~0.1 meters)

mid-1 = This sample was meant to approximate the upper portion of the metalimnion; approximate depth of 5 to 6 meters below the water surface. The specific depth varied with sampling date (See Attachment D).

mid-2 = This sample was meant to approximate the bottom edge of the metalimnion (top of the hypolimnion); approximate depth of 7 to 9 meters below the water surface.

The specific depth varied with sampling date (See Attachment D).

bottom = sample collected approximately one meter above the lake bottom.

In Sabin Lake, the bottom sample was collected at a depth of 9.5 to 11 meters below the lake surface.

In Wynne Lake, the bottom sample was collected at a depth of 11 to 13 meters below the lake surface.

The specific depth varied with sampling date (See Attachment D).

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Vertical profiles of MeHg concentrations by sampling date are shown in Figures 11 through 15. The MeHg concentration for both Sabin Lake (blue dotted line) and Wynne Lake (black dotted line) are shown, along with the MeHg concentration at the inlet to Sabin Lake (site PM23, Embarrass River; red open circle). Overall, the vertical profiles do not suggest a trend of elevated MeHg concentration at the metalimnion or near the bottom of the lake (1m above the bottom) (Figures 11 – 15). In addition, the concentration of MeHg in both Sabin Lake and Wynne Lake is similar to the MeHg concentrations in the Embarrass River (site PM23) entering the lakes.

Figures 11 – 15 also indicate there is no apparent decline in MeHg in the surface water from photodegradation, a known loss mechanism of MeHg. Depletion of MeHg in surface waters has rarely been observed as a function of photodegradation in tea-colored waters where the photic zone is relatively thin compared to clear-water systems. Color values for both Sabin and Wynne Lakes are greater than 100 platinum-cobalt units and indicates that both lakes can be classified as dark-water (i.e., tea-colored systems) (color data provided in Attachment C).

Statistical analysis of the MeHg concentrations with depth and with sulfate concentration was conducted using ANOVA and linear regression, respectively.

- The Shapiro-Wilk test was applied to the vertical profile data from each lake and found no violation of normality for either dataset (p-values ranged from 0.19 to 1.00 for Sabin Lake, PM21; 0.3 to 0.98 for Wynne Lake, PM22).
- ANOVA (one-way repeated measures) results for each lake, excluding the 7/9/2009 sampling event because it did not include data for all sampling depths (Table 5), indicates that lake depth is not a significant predictor of the variance in MeHg concentration within either site (i.e., there is no trend of increasing MeHg concentration with depth in the water column). Additional results from the ANOVA run are provided in Attachment D.
  - Sabin Lake, PM21:  $F(1,2,3,7) = 2.4$ ,  $\Pr(>F) = 0.21$  [corrected for non-sphericity using Greenhouse-Geisser epsilon]
  - Wynne Lake, PM22:  $F(3,9) = 0.9$ ,  $\Pr(>F) = 0.49$ .
- Regression analysis (simple linear) was used to assess whether MeHg concentration was associated with sulfate concentration. Simple linear regressions of MeHg concentration versus sulfate concentration were run for Sabin Lake (PM21) and Wynne Lake (PM22), respectively.

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- For Sabin Lake it was found that there was a significant inverse relationship between sulfate concentration and MeHg concentration (slope =  $-0.0102 \pm 0.0025$ ). As sulfate concentration increases, MeHg concentration decreases.
- For Wynne Lake, an inverse relationship also exists between sulfate and MeHg concentration (as sulfate concentration increases, MeHg concentration decreases), but it is not significant (slope =  $-0.0033 \pm 0.0018$ ).

Overall, the regression results for both Sabin Lake and Wynne Lake indicate that in these lakes, elevated sulfate concentration does not result in elevated MeHg concentration. These results further indicate that the probability of a positive relationship between sulfate concentration and MeHg concentration (i.e., as sulfate increases, MeHg increases) in either of the two lakes is low.

#### ***Horizontal Distribution of Methylmercury (lake-to-lake comparison)***

There was interest in assessing whether Sabin Lake was acting as a source of elevated MeHg to Wynne Lake. The horizontal distribution of MeHg concentration was assessed in the lakes using data from three sites: Embarrass R. inlet to Sabin L. (PM23), Sabin Lake (PM21), and Wynne Lake (PM22). Only the surface water samples (0 meters) from Sabin and Wynne Lakes are used in this analysis and compared to the MeHg concentrations in the Embarrass River (site PM23, inlet to Sabin Lake) (Figure 16). Because there is no significant increase with depth in either lake as found in the assessment of MeHg concentration with depth, the surface water concentration can be considered to represent each individual lake. In addition, as flow-through lakes, mixing of water between the epilimnion and the hypolimnion is low and the Embarrass River effectively flows through only the epilimnion.

As shown in Figure 16, the Wynne Lake MeHg concentration is consistently less than the MeHg concentration in Sabin Lake on each sampling date. There is no net increase in MeHg concentration from Sabin Lake to Wynne Lake. Therefore, the elevated sulfate input to Sabin Lake does not appear to result in elevated MeHg concentrations being transported downstream to Wynne Lake.

Figure 17 compares the “% that is MeHg” for the inlet to Sabin Lake and for the surface water samples from Sabin Lake and Wynne Lake. The “% that is MeHg” in Wynne Lake tends to reflect

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that of Sabin Lake. This data indicates that the elevated sulfate input to Sabin Lake does not result in a higher proportion of MeHg to total mercury being passed to the downstream lake.

To determine if a trend in MeHg concentration was evident between the lakes (i.e., increasing MeHg concentration in downstream waters), a one-way repeated-measures ANOVA was run on the time series ( $n_{\text{sampling}} = 5$ ) of surface MeHg concentration data from sites PM23 (Sabin Lake inlet), PM21 (body of Sabin Lake), and PM22 (body of Wynne Lake). The Shapiro-Wilk test was applied to the MeHg concentration data from each sampling date and found no violation of the assumption of normality (p-values ranged from 0.22 to 0.98). The ANOVA results indicate that the order of station locations (upstream to downstream) was not a significant predictor of the variance in MeHg concentration:  $F(2,8) = 0.8$ ,  $\text{Pr}(>F) = 0.45$ . This indicates that there is no trend in MeHg concentration across surface samples at these locations.

The same ANOVA (one way repeated measures) was run on the “% that is MeHg” for the surface samples (PM23, PM21, PM22), after testing for violations from normality using the Shapiro-Wilk test (p-values ranged from 0.07 to 0.67). Summary statistics from this ANOVA also indicate that the order of station locations was not a significant predictor of variance in the “% that is MeHg”:  $F(2,8) = 1.6$ ,  $\text{Pr}(>F) = 0.26$ . As is the case with the MeHg concentration, the ANOVA results for “% that is MeHg” indicates that there is no trend across surface samples at these locations.

Care should be taken in the interpretation of the test of trend for both MeHg concentration and “% that is MeHg” as there is the possibility that there is a lagged correlation between data at the three sampling sites (PM23, PM21, PM22). In other words, a value upstream on an earlier date may be correlated to values downstream on a later sampling date(s). This is potentially important because the endpoint of interest is identifying whether MeHg concentration or “% that is MeHg” is elevated compared to the upstream site(s) and further identifying whether higher values downstream are due to within-lake effects and not simply mass transfer from upstream to downstream. The repeated-measures model structure should correct for some of the temporal error variance (i.e., variance in trend over different dates) but it cannot account for any lagged correlation unless specified within the model. Presently for the monitoring sites, not enough is known about the temporal correlation of site-specific effects and not enough data are available to explore various lagged correlation model structures.

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### **Preliminary Methylmercury Mass Balance in Sabin and Wynne Lakes**

A preliminary mass balance of MeHg was constructed for Sabin Lake and Wynne Lake using the following equation:

$$\text{MeHg mass (mg/mo)} = \text{Inputs} - \text{Outputs} \pm \text{Gains and Losses}$$

Where:

MeHg mass (mg/mo) = the mass burden of MeHg in the lake, milligrams per month

Inputs = MeHg concentration x water flow

(includes Embarrass River inflow to Sabin Lake; precipitation)

Outputs = MeHg concentration x water flow

Gains (+) and Losses (-) = e.g., gains, increased methylation; e.g., losses burial in sediments and transformations such as photodegradation

Because site specific losses (e.g., transformations) of MeHg are unknown for the lakes, the equation was set up using the “losses” as the unknown, and the preliminary results were considered within the context of “can these inputs and outputs reasonably explain MeHg concentration in the lakes?” This preliminary mass balance assumes a steady state condition for MeHg. Because lake volume fluctuated by about one foot during the study period, which represents about 3% of the total lake volume, and MeHg concentrations were fairly stable lake-wide, a net steady state assumption is reasonable for the initial mass balance calculations.

Data on in-lake MeHg transformations and processes are available from other studies in similar boreal landscapes (e.g. Marcell Experimental Forest near Grand Rapids, MN; Experimental Lakes Area, Ontario, Canada) at similar latitude, providing a context in which to assess the hypothesis that elevated MeHg concentrations are occurring within either Sabin or Wynne Lake. An important consideration in the mass balance is whether the assumed burial rate of MeHg is physically possible.

MeHg concentration in Sabin Lake, Wynne Lake and the tributary streams were estimated from the approximately monthly samples collected from July – November 2009. Stream flow measurements were taken for the tributary streams during each sampling event; approximately monthly. MeHg concentration in the inlet to Sabin Lake (PM23) is fairly stable; average =  $0.31 \pm 0.19$  (s.d.) ng/L. The Embarrass River flow at PM23 is more variable (average =  $55 \pm 36$  (s.d.) cubic feet per second (cfs), and when coupled with the average concentration, the average mass input to Sabin Lake is approximately  $1.5 \pm 4.0$  (s.d.) grams per month (g/mo – average flow x average mass) (Table 6). For

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perspective, the lake-wide average MeHg mass is approximately 1.0 g in Sabin Lake and 1.8 g in Wynne Lake based on the July – November 2009 data. It is noted that the inflow to Wynne Lake at site PM25, southeast shoreline, was intermittent and considered an insignificant input to the lake

Wet deposition (rain) of MeHg (g/mo) was estimated from 1) precipitation records (weather station COOP 212576 at Embarrass, MN) and 2) the average MeHg concentration from five monitoring sites around the Great Lakes (1997-2003 data) that are not immediately near any point sources: avg. MeHg = 0.14 ng/L  $\pm$  0.051 (s.d.) min.= 0.02, max.= 0.23) (Hall et al., 2005). (Lake Superior sites: Brule River, WI; Eagle Harbor, MI; Isle Royale National Park; Tahquamenon Falls, MI; Other regional site: Devil's Lake, WI.) Table 6 indicates that wet deposition of MeHg is estimated to be a minor input to the respective lakes.

Table 6 shows the estimated MeHg mass loading as it progresses from the Embarrass River (site PM23) to Sabin (site PM21) and then to Wynne Lake (site PM22), respectively. The estimated monthly mass load via the Embarrass River decreases sequentially by about 50% from the inlet to Sabin Lake (1.5 g/mo at PM23) to the outlet of Wynne Lake (0.73 g/mo). This decrease in MeHg concentration indicates the lakes function as net sinks for MeHg, meaning overall loss of MeHg from the Embarrass River as it flows through the chain of lakes. The preliminary estimates indicate that the Embarrass River supplies roughly the lake-wide mass of MeHg each month and that the Embarrass River is the largest source of MeHg to the lakes.

It is currently assumed that the difference between the inputs and outputs presented in Table 6 are accounted for mostly by burial of MeHg to sediments. The larger loss for Sabin Lake (0.74 g/mo) relative to Wynne Lake (0.20 g/mo) could be due to Sabin Lake acting like a primary settling basin, allowing the Embarrass River sediment load and associated MeHg to fall out primarily in Sabin Lake. Supporting the idea that Sabin Lake acts as a primary settling basin is the fact that chlorophyll-a (surface samples, 0 m) and total suspended solids (all depths) are generally higher in Sabin Lake than in Wynne Lake.



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**Table 6. Preliminary average monthly<sup>[1]</sup> methylmercury mass balance for Sabin Lake and Wynne Lake based on depth averaged concentrations for the lakes and estimated monthly stream flow for tributary streams, averaged over all sampling dates (July – November, 2009).**

	Embarrass River [2]	Wet Deposition [3]	Lake Mass	Embarrass River [4]	Unnamed Stream [5]	“Loss” Input – Output [6]	Flushing Rate
	Input	Input	(steady-state)	Output	Input	(steady-state)	July - Nov.
	(g/mo)	(g/mo)	(g)	(g/mo)	(g/mo)	(g/mo)	(times/month)
Sabin Lake	1.5	0.011	1.0	0.80	NA	0.74	1.8
Wynne Lake	0.80	0.010	1.8	0.73	0.12	0.20	1.3

g = grams      g/mo = grams per month      MeHg = methylmercury      NA = not applicable

[1] Lake sampling and stream flow measurements approximately monthly and is used to estimate a monthly mass balance.

Flow measurements for major streams tributary to Sabin and Wynne Lakes, and the outflow from Wynne Lake.

Date	Inlet to Sabin, PM23	Inlet to Wynne*, PM24	Outlet from Wynne
	m3/s	m3/s	m3/s
6/25/2009	6.21	--	7.29
7/9/2009	--	0.03	0.90
7/29/2009	1.08	0.05	1.53
8/21/2009	2.34	0.16	1.13
9/22/2009	0.34	0.02	1.35
11/4/2009	2.40	--	2.32

m3/s = cubic meters per second; measured with Marsh-McBirney flow meter.

\* Inflow to Wynne Lake at site PM25, southeast shoreline, was intermittent and considered an insignificant input to the lake.

[2] The Embarrass River flows into the northern part of Sabin Lake (site PM23), and leaves at the southern end of the lake and connects Sabin Lake to Wynne Lake. Approximately monthly flow data and chemistry data are available from site PM23.

[3] Wet deposition of methylmercury estimated based on precipitation depth recorded at Embarrass, MN (weather station COOP site 212576) for the study period and MeHg concentration data from Hall et al. (2005) for the Great Lakes.

[4] Discussions with the MPCA and MDNR staff indicates that surface concentrations of MeHg at the mid-lake sampling location could be used as a surrogate for the outflow from Sabin Lake into Wynne Lake.

[5] The Unnamed Stream enters Wynne Lake on its northern shoreline, on the west side of the narrows that connects Sabin Lake to Wynne Lake (site PM24). Approximately monthly flow data and chemistry data are available from site PM23.

[6] Loss assumed to be the difference between inputs and outputs; “Loss” of MeHg within the lake assumed to be primarily due to burial in the sediments. Burial rates were calculated for each lake, dividing the loss in g/mo by the surface area to derive an areal estimate (assumes area of the lake bottom = the surface area, conservative assumption): Sabin L: 0.0073 µg/m<sup>2</sup>/yr; Wynne L: 0.0022 µg/m<sup>2</sup>/yr, loss assumed to be burial.

The estimated MeHg burial rates for Sabin and Wynne Lakes are not higher than the detailed burial rate of 0.32 µg/m<sup>2</sup>/yr estimated for Spring Lake in the Marcell Experimental Forest near Grand Rapids, MN (Hines and Brezonik, 2007).

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The respective loss rate of MeHg to sediment (burial) estimated for each lake on a gram/month basis was converted to an areal basis by dividing the loss rate by the lake surface area (and assuming the area of the lake bottom is the same as the surface area): Sabin L =  $0.0073 \mu\text{g}/\text{m}^2/\text{yr}$ ; Wynne L =  $0.0022 \mu\text{g}/\text{m}^2/\text{yr}$ . These estimated burial rates for Sabin and Wynne Lakes are lower than the detailed MeHg sediment accumulation rate of  $0.32 \mu\text{g}/\text{m}^2/\text{yr}$  measured at Spring Lake in the Marcell Experimental Forest (near Grand Rapids, MN) (Hines and Brezonik, 2007).

It is noted that several components are absent from the preliminary mass balance (Table 6), including photodegradation (sink; loss), upland runoff (source), dry deposition (source), and the net sediment contribution (either sink or source). The first three are likely minor and would not be expected to be associated with sulfate from mining features. The net sediment contribution, however, could be a source of MeHg to the respective lakes. However, if there were a significant input of MeHg to the lake from the sediment, then higher MeHg concentrations should be found in the bottom sample (approximately one meter off the bottom of the respective lake, which was not observed). It is also noted that if these other inputs would be accounted for in the mass balance, it is likely that the estimated loss of MeHg to sediment would also increase and become more similar with the loss rate estimated for Spring Lake (Hines and Brezonik, 2007).

In summary, the preliminary mass balance calculations indicate that the Embarrass River (site PM23) is the primary source of MeHg to the lakes, and that overall the lakes are net sinks of MeHg. The elevated sulfate concentrations in the respective lakes do not appear to be causing elevated levels of MeHg to be transported out of either Sabin Lake or Wynne Lake to downstream waters. As previously stated, the vertical profile of MeHg in each lake does not show a significant increase with depth in the water column, indicating that elevated sulfate concentrations are not resulting in elevated MeHg concentrations within the two study lakes.

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### **C) Transect Analysis of Methylmercury Concentrations in the Embarrass River**

An initial analysis of upstream/downstream concentrations in the Embarrass River was conducted for stream sites PM12 (upstream) and PM13 (downstream). Figure 4 indicates that the average MeHg concentration at site PM13 is slightly lower than at site PM12. In addition, Figure 5 indicates that the average “% that is MeHg” at site PM13 is similar to site PM12. A statistical comparison of sites PM12 and PM13, using the Wilcoxon signed-rank test to account for non-normality between the datasets, indicates there is no significant difference in MeHg concentration or “% that is MeHg” between the two sites (Table 2). The data for sites PM12 and PM13 were separated into storm and non-storm events (Table 3). Paired t-tests were conducted for the storm event data and the non-storm data due to the inability of the Wilcoxon signed-rank test to detect differences with paired sample sizes of fewer than six. No significant differences in MeHg or “% that is MeHg” were identified for either storm event data or non-storm data (Table 2).

As previously discussed for the lakes, a short transect analysis was conducted for sites PM23 (Embarrass River, inlet to Sabin Lake), PM21 (Sabin Lake) and PM22 (Wynne Lake) for data collected approximately monthly. That analysis showed no trend of MeHg concentration or “% that is MeHg” increasing with downstream monitoring location.

Even though the two segmented transect analyses showed no significant differences in MeHg concentration or “% that is MeHg” between upstream and downstream sites, a transect analysis combining stream sites PM12 and PM13 with lake sites PM23, PM21, and PM22 was conducted to further assess MeHg transport in the Embarrass River. As in the other two segmented comparisons, this transect analysis evaluated whether MeHg concentration and “% that is MeHg” increases from upstream to downstream. Data for this larger transect analysis are shown in Table 7 and include only those events where stream and lake sampling occurred together; stream data from sampling on 7/21, 8/26 and 10/13 were excluded from this analysis. Data for sites PM12 and PM13 are from filtered samples; data from sites PM23, PM21, and PM22 are from unfiltered samples and as such bias the downstream concentrations higher. The transect data are plotted in Figure 18 (MeHg concentration) and Figure 19 (“% that is MeHg”). Even with data from unfiltered samples for sites PM23, PM21 and PM22 there is an overall decrease in MeHg concentration and “% that is MeHg” from site PM12 (upstream of mining features) through PM22 (Wynne Lake).

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**Table 7. Transect of mercury, methylmercury and sulfate concentration in the Embarrass River (upstream to downstream) for five sites included in the additional baseline monitoring conducted for the NorthMet Project in 2009 (July – November).**

		PM12, Embarrass River (upstream)				PM13, Embarrass River				PM23, Embarrass River, Inlet to Sabin				PM21		Sabin Lake		PM22		Wynne Lake		
Date [1]	Depth [2]	Total Hg ng/L	MeHg ng/L	% MeHg %	Sulfate mg/L	Total Hg ng/L	MeHg ng/L	% MeHg %	Sulfate mg/L	Total Hg* ng/L	MeHg* ng/L	% MeHg %	Sulfate* mg/L	Total Hg* ng/L	MeHg* ng/L	% MeHg %	Sulfate* mg/L	Total Hg ng/L	MeHg ng/L	% MeHg %	Sulfate mg/L	
7/9/2009	surface	3.3	0.57	17%	0.5	2.9	0.37	13%	47.2	2.7	0.32	12%	34.7	4.8	0.38	8.0%	23.15	5.0	0.30	6.0%	18.2	
7/29/2009	surface	4.3	0.65	15%	1.05	3.3	0.29	8.8%	37.3	3.1	0.24	7.7%	32.9	3.2	0.34	11%	24	3.6	0.25	6.9%	19.5	
8/21/2009	surface	5	0.63	13%	1.73	3.1	0.62	20%	25.9	3.5	0.63	18%	26.9	2.1	0.18	8.6%	27	2.2	0.22	10%	22.3	
9/22/2009	surface	3.2	0.32	10%	1.18	3.4	0.46	14%	27.4	1.9	0.12	6.3%	14.4	2.3	0.125	5.4%	25.7	2.8	0.17	6.1%	24.8	
11/4/2009	surface	3.7	0.12	3.2%	3.61	3.5	0.23	6.6%	45.8	4.8	0.23	4.8%	39.5	3.3	0.16	4.8%	33.5	2.0	0.11	5.5%	29	
<b>Statistics</b>																						
Mean	Surface	3.90	0.46	12%	1.61	3.24	0.39	12%	36.72	3.19	0.31	9.8%	29.68	3.09	0.23	7.5%	24.96	3.12	0.21	6.9%	22.76	
St. Dev.		0.75	0.23		1.20	0.24	0.15		9.96	1.07	0.19		9.66	1.21	0.12		1.72	1.22	0.07		4.32	

\* Includes the average concentration of the original sample and duplicate sample for specific sampling dates.

[1] Sample dates:

Stream sampling dates on 7/21, 8/26 and 10/13/2009 for sites PM12 and PM13 are excluded from this data set because there is no corresponding sampling date for lakes (PM23, PM21, PM22).

It is assumed that the stream sampling on 9/10/2009 for sites PM12 and PM13 can be matched with the lake sampling conducted on 9/16/2009 for sites PM23, PM21, and PM22.

[2] Surface = within one meter of the water surface (0 to 1 meters)

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The Shapiro-Wilk test was applied to the MeHg concentration data for the 5 sites (Table 7) and no violations in the assumption of normality were found (p-values ranged from 0.22 to 0.98). An ANOVA (one-way repeated measures) was run on the time series ( $n_{\text{sampling}} = 5$ ) of surface MeHg concentration data from the five monitoring sites. The repeated measures analysis found that the means across the sites were different and followed a decreasing trend and it was also found that the order of monitoring site locations from upstream to downstream was a significant predictor of variance in MeHg concentration:  $F(4,16) = 3.3$ ,  $\text{Pr}( > F ) = 0.04$ . The mean MeHg concentration decreases by more than half from site PM12 (0.46 ng/L; upstream of mining features) to site PM22 (0.21 ng/L; Wynne Lake).

An ANOVA (one-way repeated measures) was also run for the 5 sites and sampling dates (Table 7) on the time series ( $n_{\text{sampling}} = 5$ ) of the “% that is MeHg”. Prior to conducting the ANOVA run, application of the Shapiro-Wilk test found no violation in the assumption of normality (p-values ranged from 0.07 to 0.77). The repeated measures analysis found that the means across sites were marginally significant and the order of station location was only a marginally significant predictor of the variance for “% that is MeHg”:  $F(4,16) = 3.0$ ,  $\text{Pr}( > F ) = 0.052$ . The data in Table 7 indicate a mild decline in the average “% that is MeHg”, from 12 percent at PM12 to 6.9 percent at PM22, with a small peak at PM13 (12.3%). Figure 19 identifies the small peak in “% that is MeHg” for site PM13 that occurred during 3 of the 5 sampling events (8/20/2009, 9/16/2009; 11/3/2009).

Overall, the ANOVA results indicate there is a net decrease in MeHg concentration as one moves downstream and based on the lake-to-lake comparison, the largest loss likely occurs with sediment burial in Sabin Lake. The “% that is MeHg” shows a similar decline, although the trend is considered only marginally significant. These results provide a further indication that elevated sulfate from the tailings basin is not a significant factor in MeHg concentration or “% that is MeHg” in downstream waters of the Embarrass River.

As discussed earlier with regard to the analysis of the trend across Sabin and Wynne Lakes, care should be taken in the interpretation of the results from this transect analysis as well, as the same issue of potential lagged correlation among sites is not explicitly accounted for in the present analysis.

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## Uncertainty Discussion

### Designation of Sampling Events as “Non-storm Events”

The Work Plan for the collection of additional baseline monitoring data in 2009 included sampling of a maximum of three storm events. A storm event was considered to be a 24-hour rainfall that equaled or exceeded 0.75 inches. Under this definition of a storm event the first two samplings occurred on 7/21/2009 and 7/28/2009. In a July 31, 2009 conference call, MPCA and MDNR staff expressed interest in having the third storm event sampling occur after a larger rainfall event; a 24-hour rainfall of 1.5 inches or greater. The third storm event sampling occurred on 8/26/2009 following a 1.5 inch rainfall on 8/20/2009.

Previous work from Berndt and Bavin (2009) indicates that sulfate concentration in the St. Louis River and its tributaries varies depending on stream flow. Higher sulfate concentrations were observed during lower stream flow and lower sulfate concentrations were observed during high stream flow or flushing events.

Data presented in Table 2 indicates that some of the lowest sulfate concentrations for the respective sites were measured for the samples collected on 7/9/2009 (4 sites), 8/20/2009 (3 sites), and 9/10/2009 (2 sites). However, precipitation data available from the Hoyt Lakes area does not indicate that a large storm event (24-hour rainfall greater than 0.75 inches) occurred within 7 days prior to the sampling that occurred on 7/29/2009 and 9/10/2009. It is known that a large storm event began on 8/20 and carried into 8/21/2009, and it is possible that the sampling for site PM11 and PM19 that occurred on 8/20/2009 reflects flushing related to the storm event. However, the low sulfate concentrations are not consistently observed at all sites for the 8/20/2009 sampling.

The lower sulfate concentrations during some non-storm sampling events suggest that some flushing of the respective watersheds may have been occurring. However, there is insufficient information to reclassify those sampling events as being storm-related, but it does suggest some uncertainty in the designation of some sampling events as being non-storm events.

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## **Methylmercury Concentrations at Site PM12**

The highest MeHg concentration measured in the 2009 additional baseline monitoring was at site PM12 (upstream of the tailings basin influence) during storm-related sampling on 8/26/2009 (2.7 ng/L). Percent that is MeHg (“% that is MeHg”) was also high in the 8/26/2009 sample; 63% as MeHg. This 8/26/2009 data point is noticeably different from the other concentrations measured at site PM12, and is higher than the MeHg concentrations at the other stream sites. However, data QA/QC, including review of field sampling duplicates, method blanks and laboratory blanks indicate there was no contamination of the samples collected on 8/26/2009. Therefore, the MeHg concentration from the 8/26/2009 sampling event is considered to be a valid concentration.

As shown in Table 2 and Figure 7, MeHg concentrations measured for the 8/26/2009 sampling event were the highest measured for the study period for four of the five stream sites. Only site PM20 did not show a higher MeHg concentration for the 8/26/2009 sampling event. The lack of response in MeHg concentration at site PM20 to the 8/20/2009 storm event compared to the other streams is curious and likely demonstrates the individuality of watershed response to what was considered a relatively large storm system that was thought to affect all study sites similarly. The response of site PM12 to the 8/20/2009 storm event (sampled on 8/26/2009) seems to be generally consistent with the response of the other stream sites to that event. Furthermore, because there is no indication that the data from the 8/26/2009 sampling event is due to contamination or laboratory or sampling error, the MeHg concentration on 8/26/2009 from site PM12 is considered to be a valid data point for use in statistical analyses.

## **Analysis of Variance – Uncertainty in the Use of Repeated-Measures**

The use of repeated-measures ANOVA as a tool for determining factor-specific differences in the dependent variables (concentration of MeHg, “percent that is methyl”) invokes a number of sources of uncertainty. Some of these sources can be identified and quantified, some can be corrected for use in quantitative estimates, and some remain unquantifiable. A major potential source of uncertainty is that ANOVA requires near-normality within and between groups, depending on the structure of the analysis, and can be sensitive to extreme violations of normality within the data. Another important potential source of uncertainty is the heterogeneity of and correlation among levels of variance within different model strata. A final potential source of uncertainty is representativeness of the sample dataset, especially with regard to the associated factors that have been analyzed.

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### **Normality**

Though repeated measures ANOVA is robust to mild violations of normality in the between-subject dependent variable (in this case, MeHg concentration or “% that is methyl” by sampling location), it can be highly sensitive to large violations. As such, it was necessary to check normality in sampling site data. There was one violation of normality in MeHg concentration at the  $p=0.05$  level (PM12) within the four-station (i.e., 4 monitoring site) repeated measures ANOVA analysis of sulfate and rain storm event status (Attachment D). This was due to a single high MeHg concentration measurement during a rain storm event. The result of this is that there is an increased likelihood that the marginally significant finding of an inverse relationship between sulfate level and MeHg concentration is spurious. There were two violations of normality in “% that is methyl” at the  $p=0.05$  level (PM12 and PM20) within the four-station (i.e., 4 monitoring site) repeated measures ANOVA analysis of sulfate and rain storm event status. The result of this is that there may be an increased likelihood that the finding of no significant difference between high-sulfate and low-sulfate sites is an incorrect rejection of the alternative hypothesis (type II error). Weighing against this increased risk of type II error is the fact that paired analyses of these sites, which used non-parametric tests in the presence of deviations from normality, found no significant differences among the four. There were no violations of normality at the  $p=0.05$  level for any of the transect analyses. Thus, the uncertainty resulting from this assumption in the transect analysis should be minimal. Despite this, the small sample size in both sets of analyses makes the determination of distributional characteristics difficult and confers a degree of uncertainty on the results.

### **Homogeneity of variance**

If the variance at different factor levels (e.g., location along the river-lakes transect) is not homogenous and this heterogeneity is correlated, then the data are said to violate sphericity. If this is the case, the repeated measures ANOVA has a number of corrections to degrees of freedom (and, hence, the metric of effect significance— $\text{Pr}(>F)$ ) available that make the result more robust. The test for sphericity (Mauchly’s test) and corrections for non-sphericity (the Huynh-Feldt and Greenhouse-Geisser epsilons) are built into the analyses, thereby minimizing the likelihood of bias in the ANOVA results. Although these corrections are useful tools, the degree of precision they confer can be limited, especially on tests with small sample sizes. All results to which either correction has been applied have been labeled as such.



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## Extrapolation of Results to Other Areas

Because this study seeks to answer questions about the relationship between sulfate concentrations, rain storm events, MeHg concentrations, and the percent that is methylmercury in one river-lake system in northern Minnesota, the representativeness of the sampling sites greatly influences the ability to generalize results to other areas. The metric of “representativeness” is difficult to define, especially in systems as complex as those under study. The small sample size acts to compound this uncertainty. As such, there is a degree of uncertainty associated with the ability to extrapolate the results from this analysis to other boreal forest areas.

## Summary

The additional baseline monitoring data collected in 2009 from five stream monitoring locations on the Embarrass River and selected tributary streams, and the two lakes and their inlet streams, indicates the following:

- Stream sites: For streams with elevated sulfate concentration (PM11, PM19), MeHg concentration and “% that is MeHg” were not elevated compared to background sites (PM12, PM20). In some cases the background sites had higher MeHg concentration and “% that is MeHg”.
  - Storm events were not a significant factor with regard to MeHg concentration or “% that is MeHg”.
  - Storm events did not result in flushing more MeHg or have more “% that is MeHg” for the sites with elevated sulfate as compared to background sites.
- Lakes: MeHg concentration in both lakes did not show a significant trend with depth in the lake; essentially MeHg concentration in both lakes was similar at all depths.
  - Sulfate concentration in the lakes does not result in elevated MeHg concentration or elevated “% that is MeHg” over the dates sampled. There is an inverse relationship between sulfate and MeHg in both lakes; as sulfate concentration increases, MeHg concentration decreases. The inverse relationship is significant in Sabin Lake but not in Wynne Lake.
  - In the initial mass balance calculations, the Embarrass River (inlet to Sabin Lake, site PM23) is estimated to be the major input of MeHg to the lakes.

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- Transect Analysis (upstream/downstream): Overall, there is a net decrease in MeHg concentration from upstream to downstream monitoring sites (site PM12 upstream of the tailings basin to site PM22, Wynne Lake).
  - The lakes appear to be net sinks of MeHg; sulfate from the tailings basin does not appear to be resulting in elevated MeHg concentration or “% that is MeHg” being exported to these downstream waters.

In summary, while the tailings basin may be contributing sulfate to what is considered by the MPCA/MDNR to be a high risk environment (i.e., wetlands to the north/northwest of the basin that contribute their water to the Embarrass River and the downstream chain of lakes), the 2009 additional baseline monitoring data does not indicate that the elevated sulfate concentrations are resulting in elevated MeHg concentrations or in elevated “% that is MeHg” compared to background conditions. Based on these findings, and noting that the tailings basin has been a watershed feature for some 40+ years, it is unlikely that continued operation of the tailings basin by PolyMet will have an effect on the sulfate and MeHg dynamics in the Embarrass River watershed.

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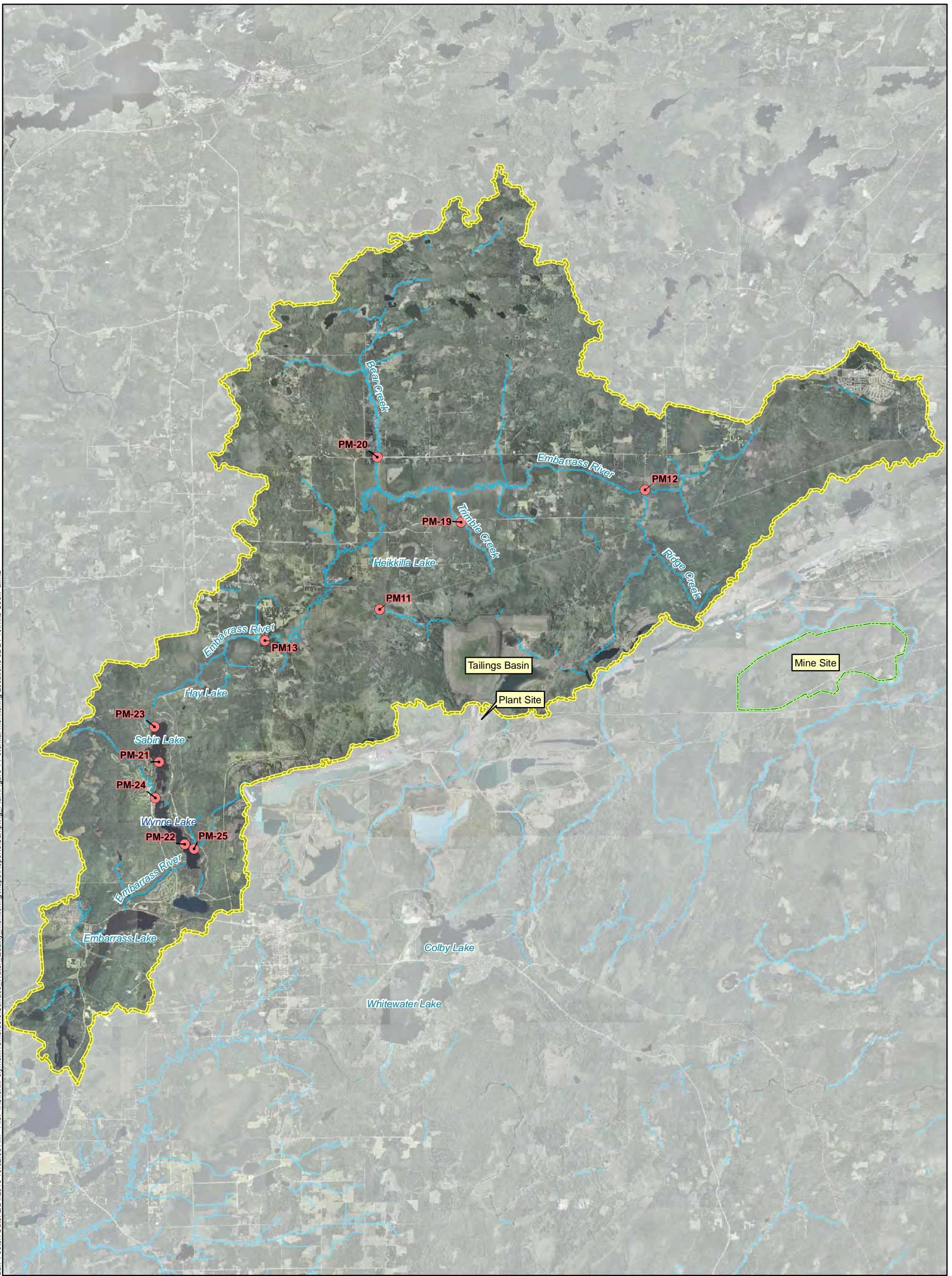
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## FIGURES



- Surface Water Monitoring Locations
- ~ Rivers and Streams
- ⬡ Watershed Boundaries

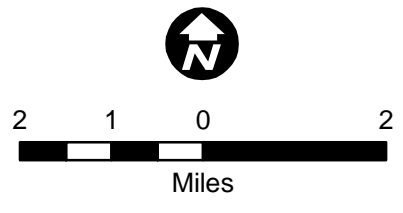
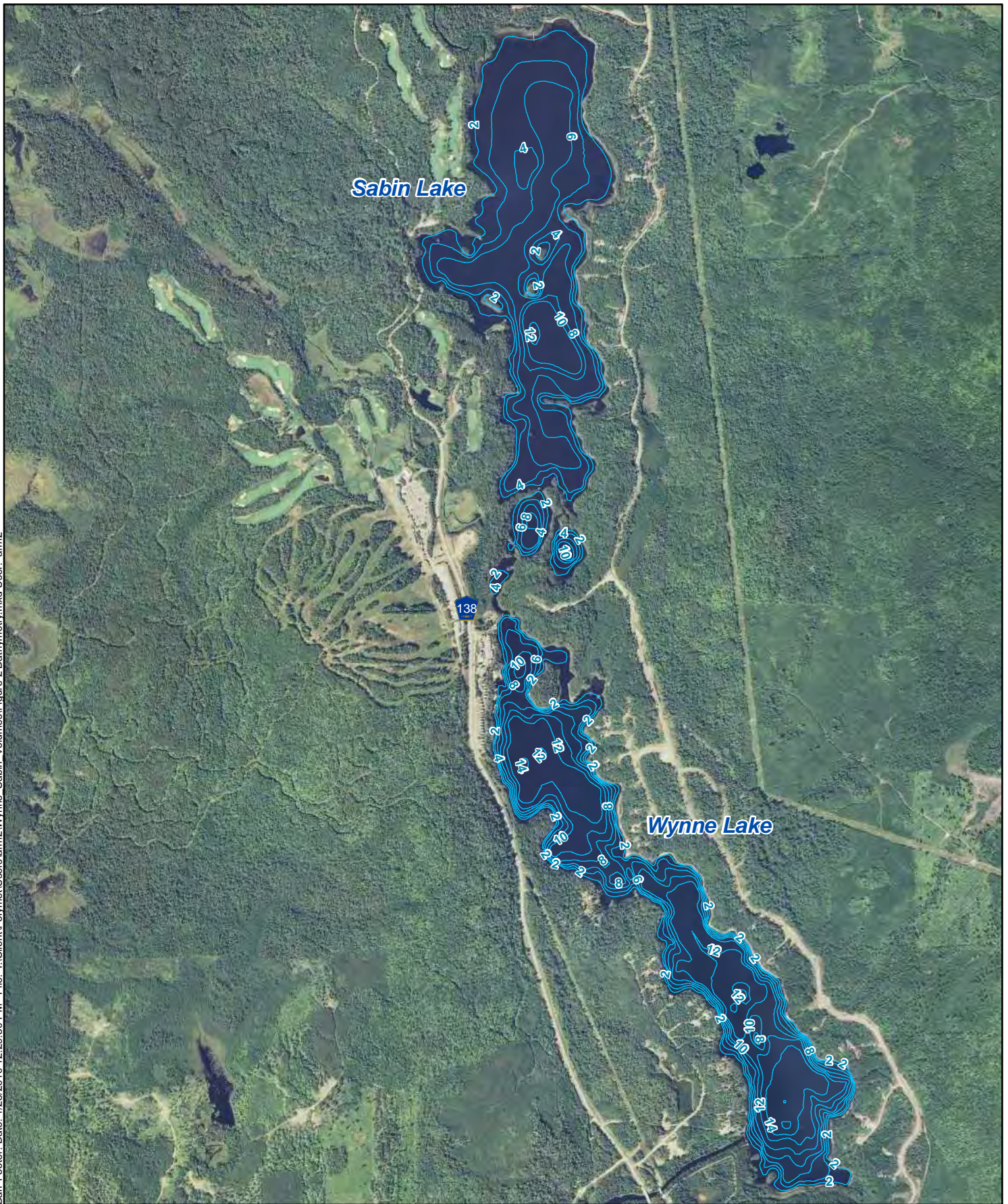


Figure 1  
PolyMet Mining, NorthMet Project  
Monitoring Locations for the Additional  
Baseline Monitoring Conducted in  
2009 (July - November)



— 2 Meter Depth Contour

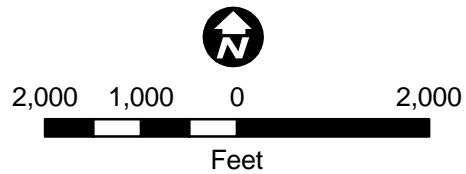


Figure 2  
SABIN LAKE AND WYNNE LAKE  
BATHYMETRY  
PolyMet Mining Inc.  
Hoyt Lakes, Minnesota

Figure 3. PolyMet Additional Baseline Monitoring, Sabin and Wynne Lakes, Surface Water Fluctuations

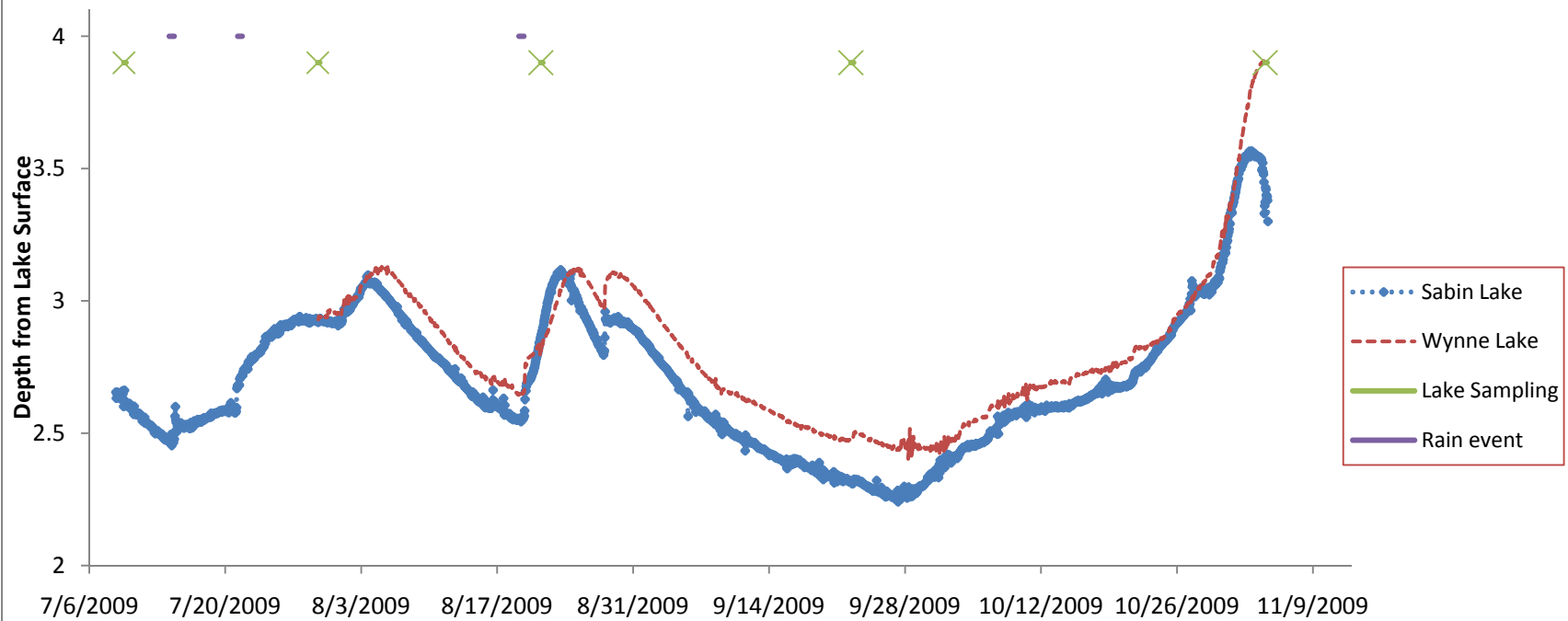
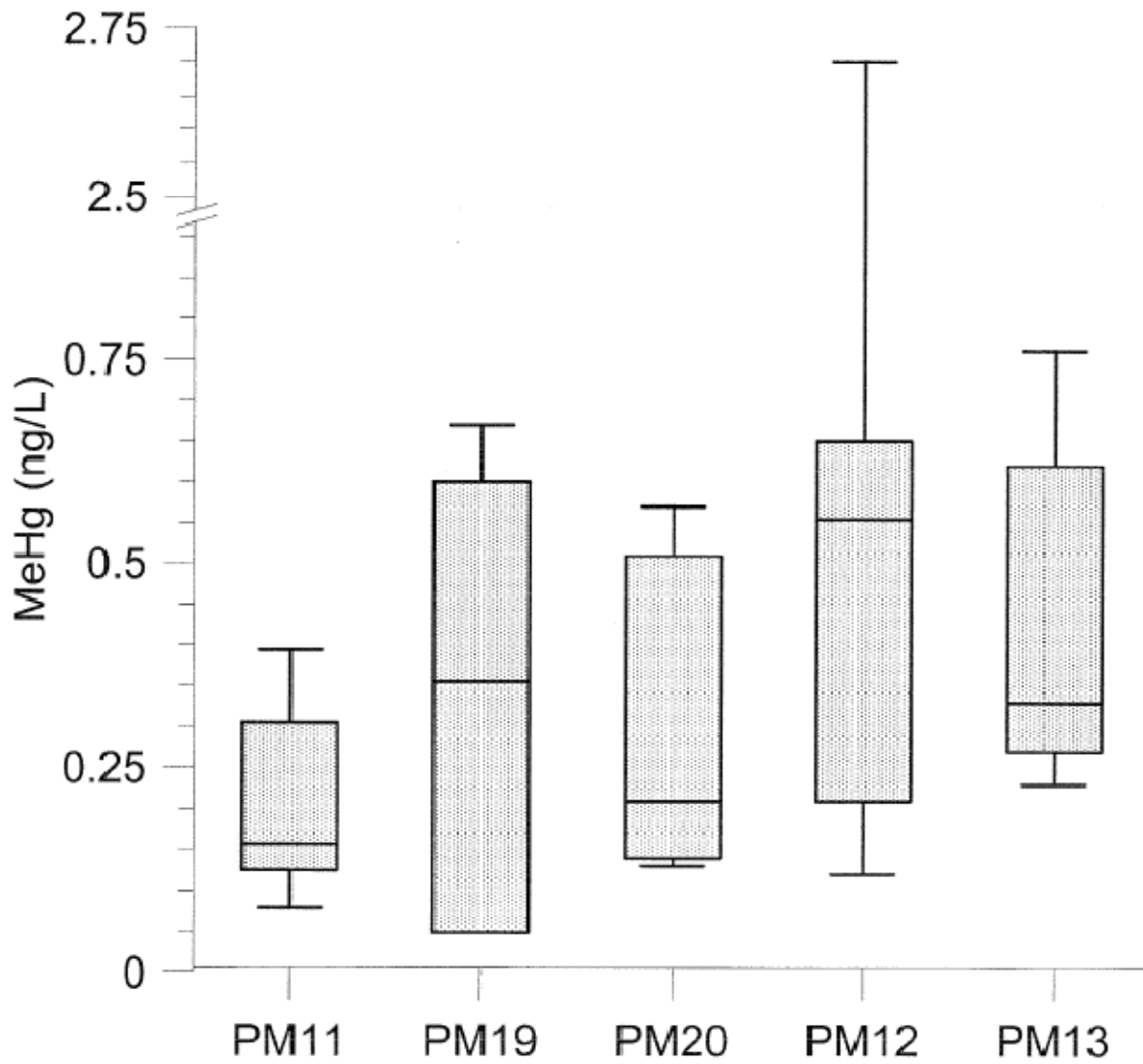




Figure 4. Baseline Monitoring Data for PolyMet Mining. Methylmercury Concentrations in Streams, July to November, 2009.



Key :

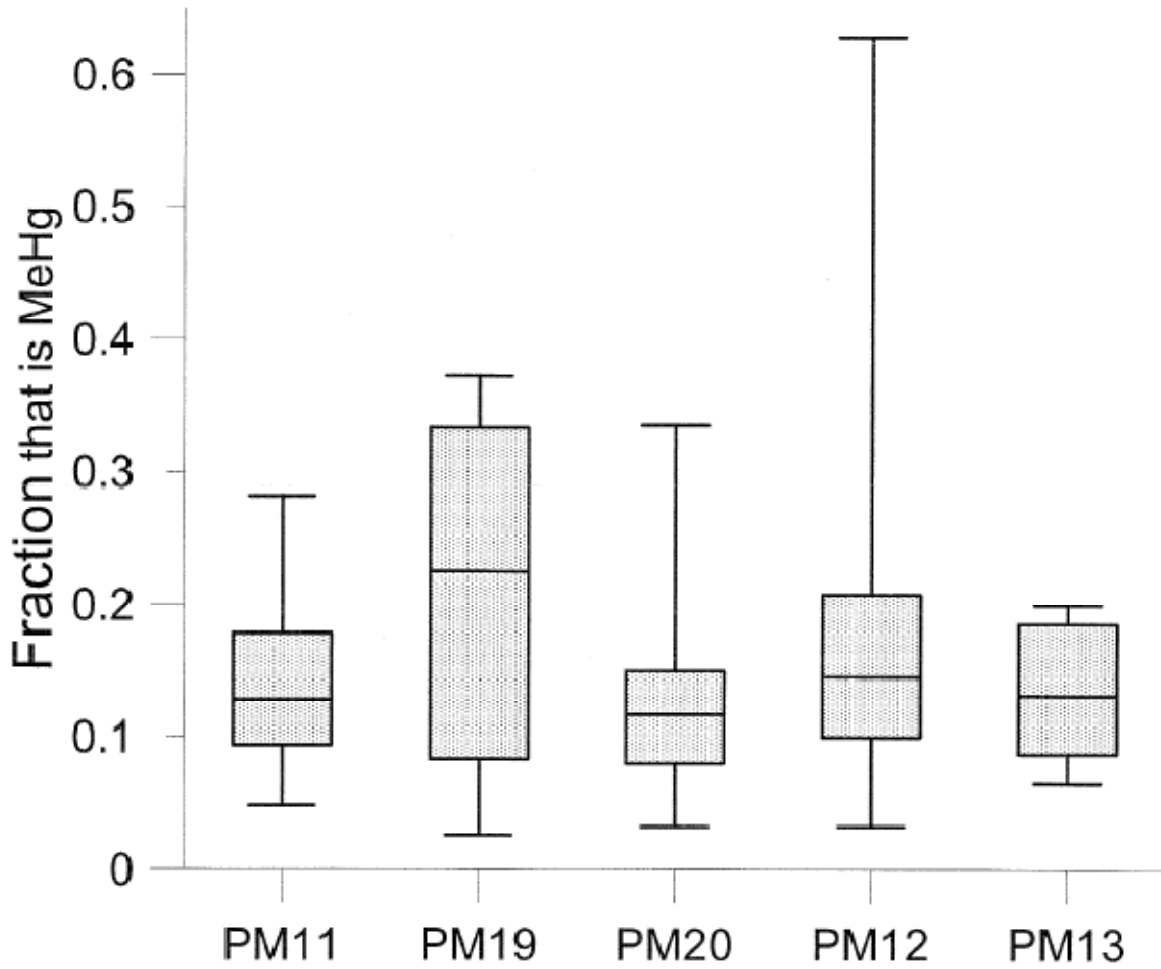
Error Bar = Max., Min.

Box = 75th (upper), 25th (lower) percentile

Line = Median

Figure 5. Baseline Monitoring Data for PolyMet Mining.

Fraction that is Methylmercury  
in Streams, July to November, 2009.



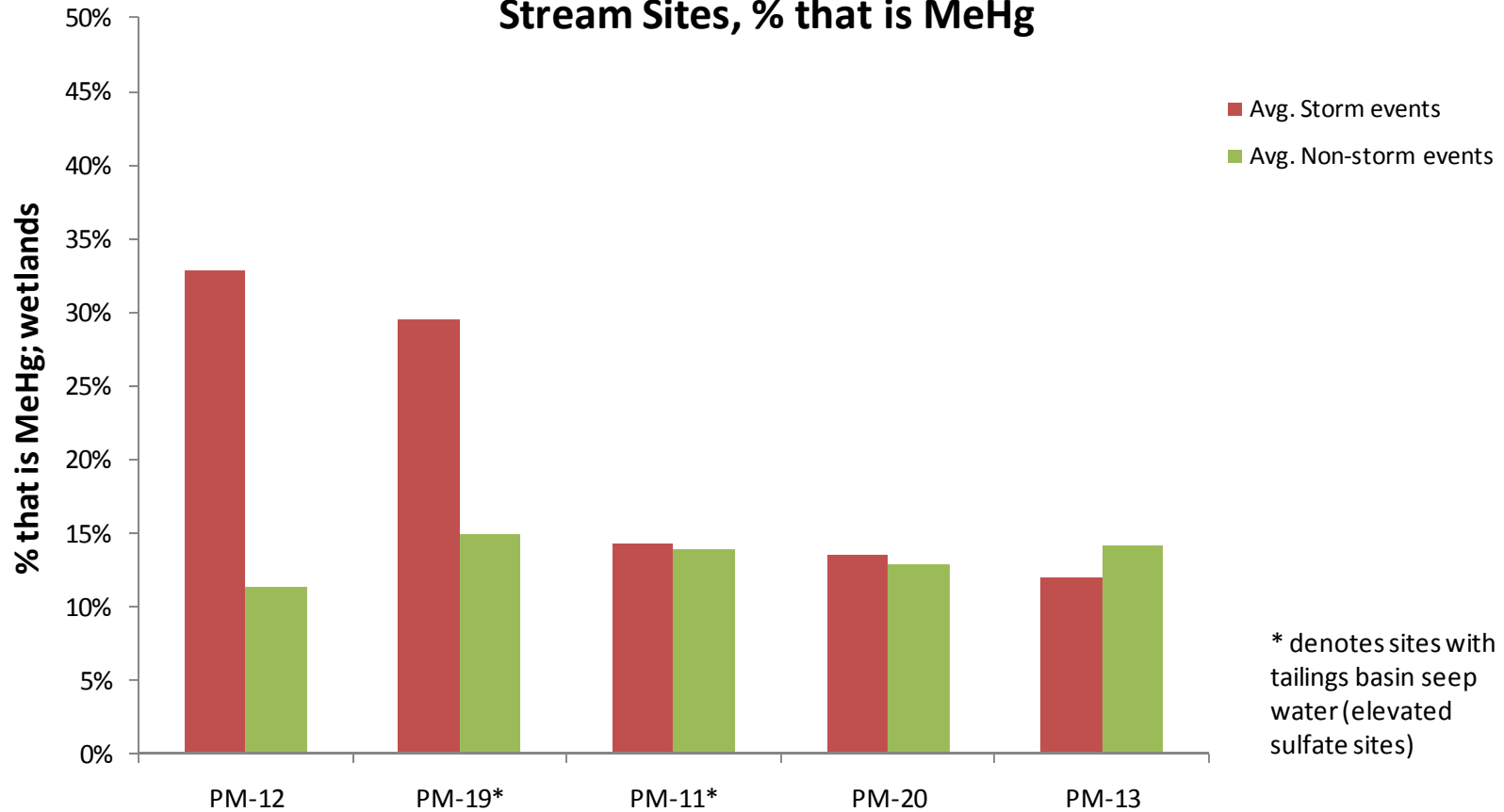
Key :

Error Bar = Max., Min.

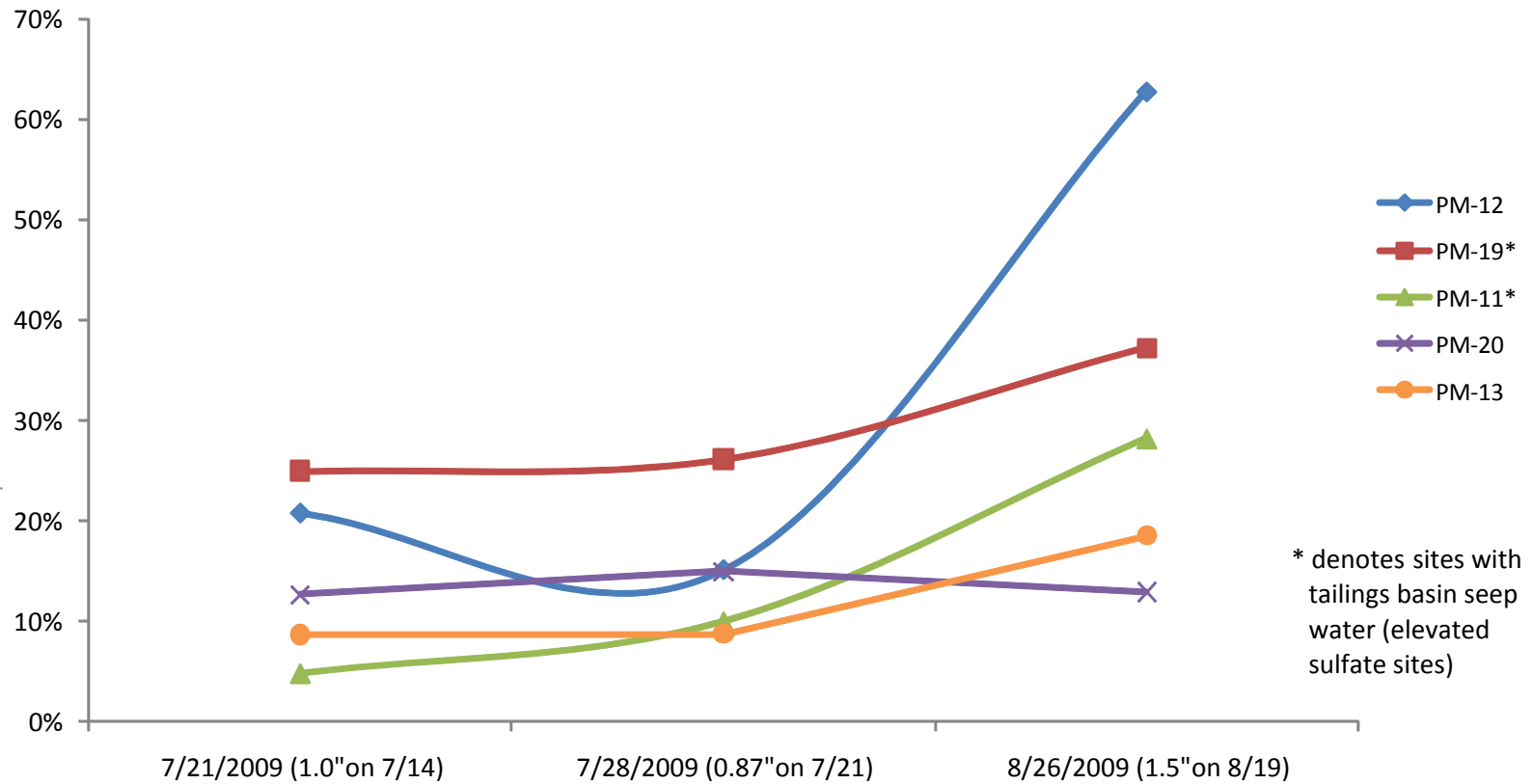
Box = 75th (upper), 25th (lower) percentile

Line = Median

**Figure 6. Additional Baseline Monitoring for PolyMet Mining,  
Stream Sites, % that is MeHg**

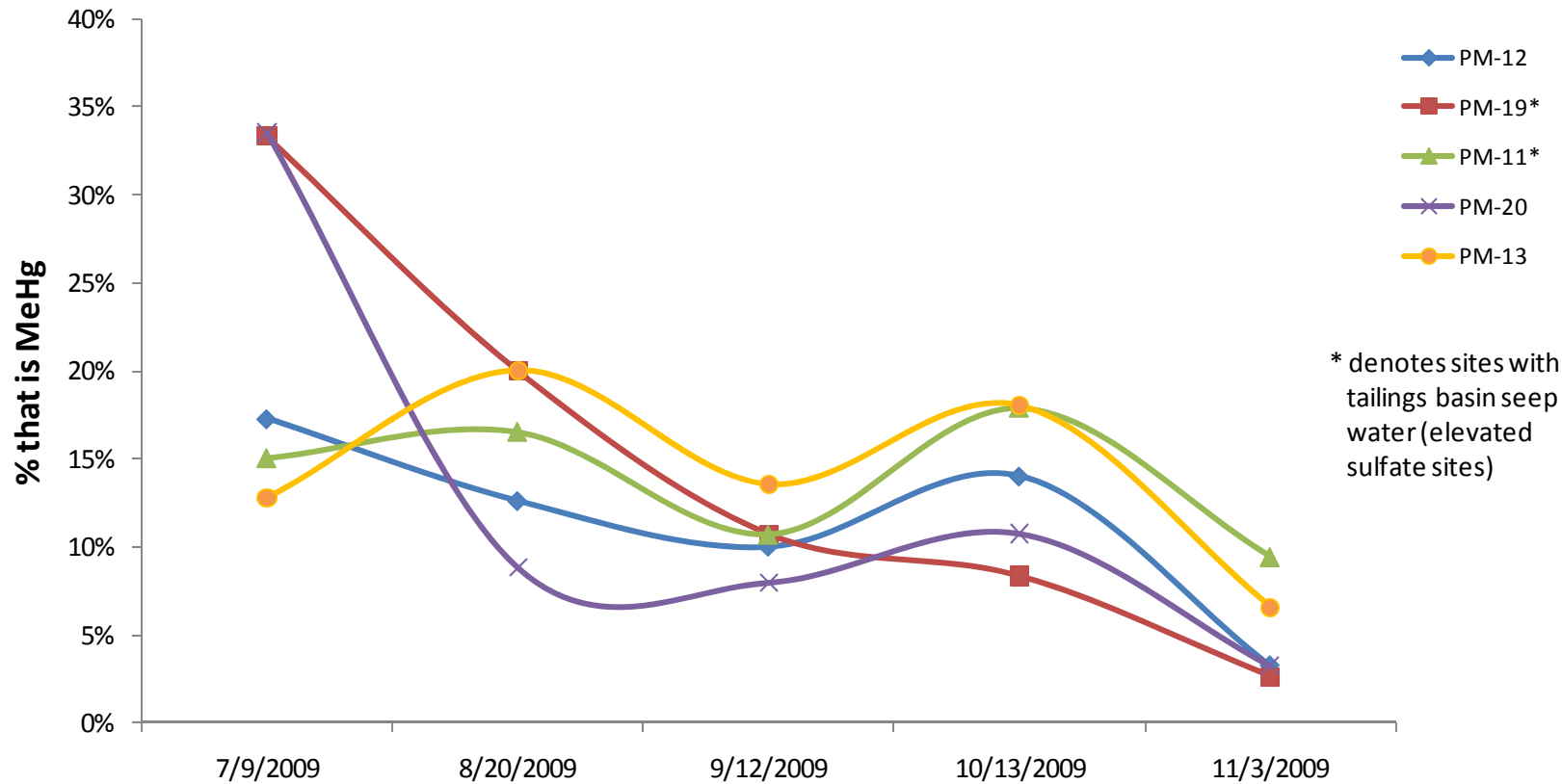


**Figure 7. Additional Baseline Monitoring for PolyMet Mining  
Embarrass River, Stream Sites, Storm Events**

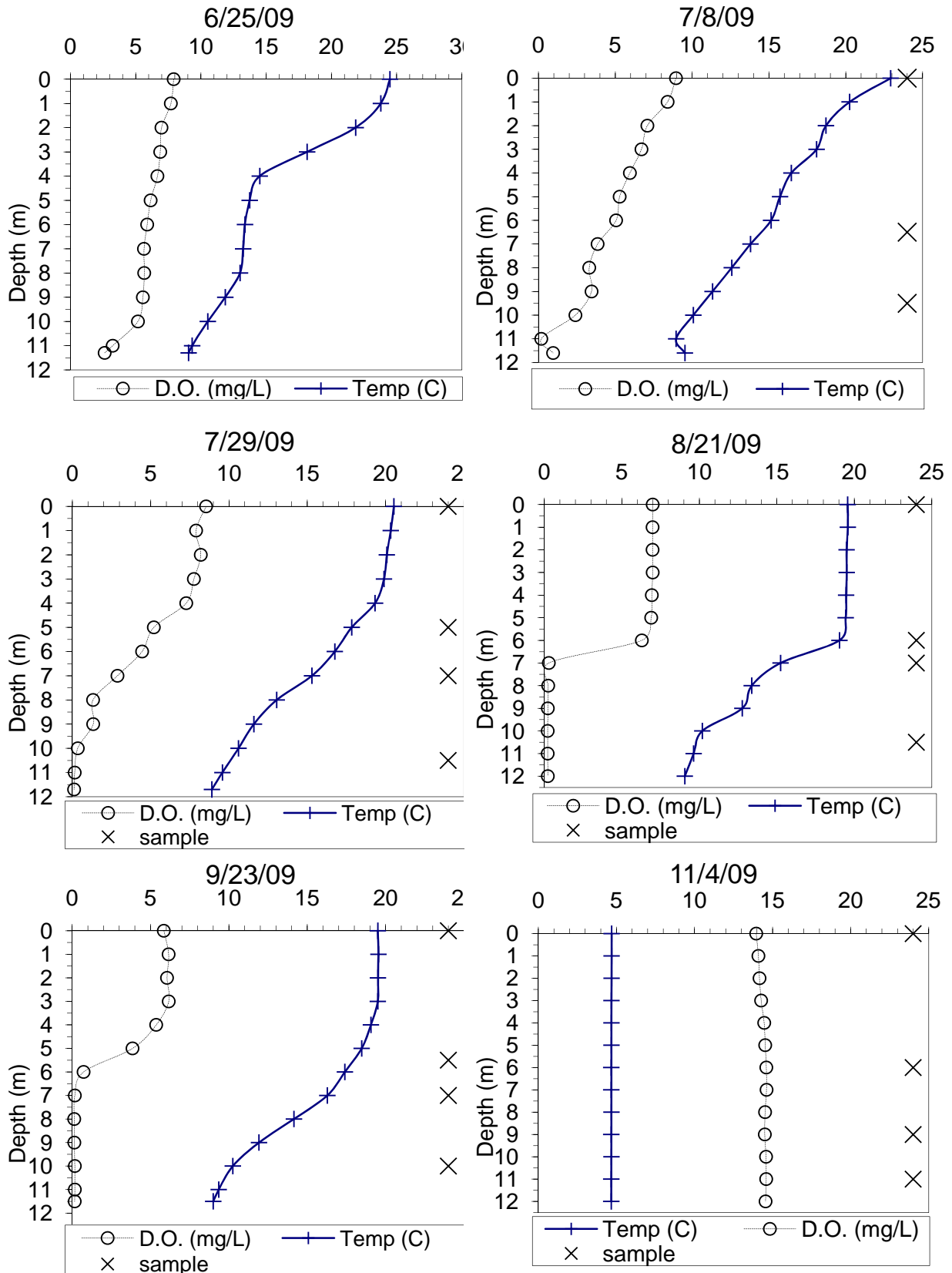


\* denotes sites with tailings basin seep water (elevated sulfate sites)

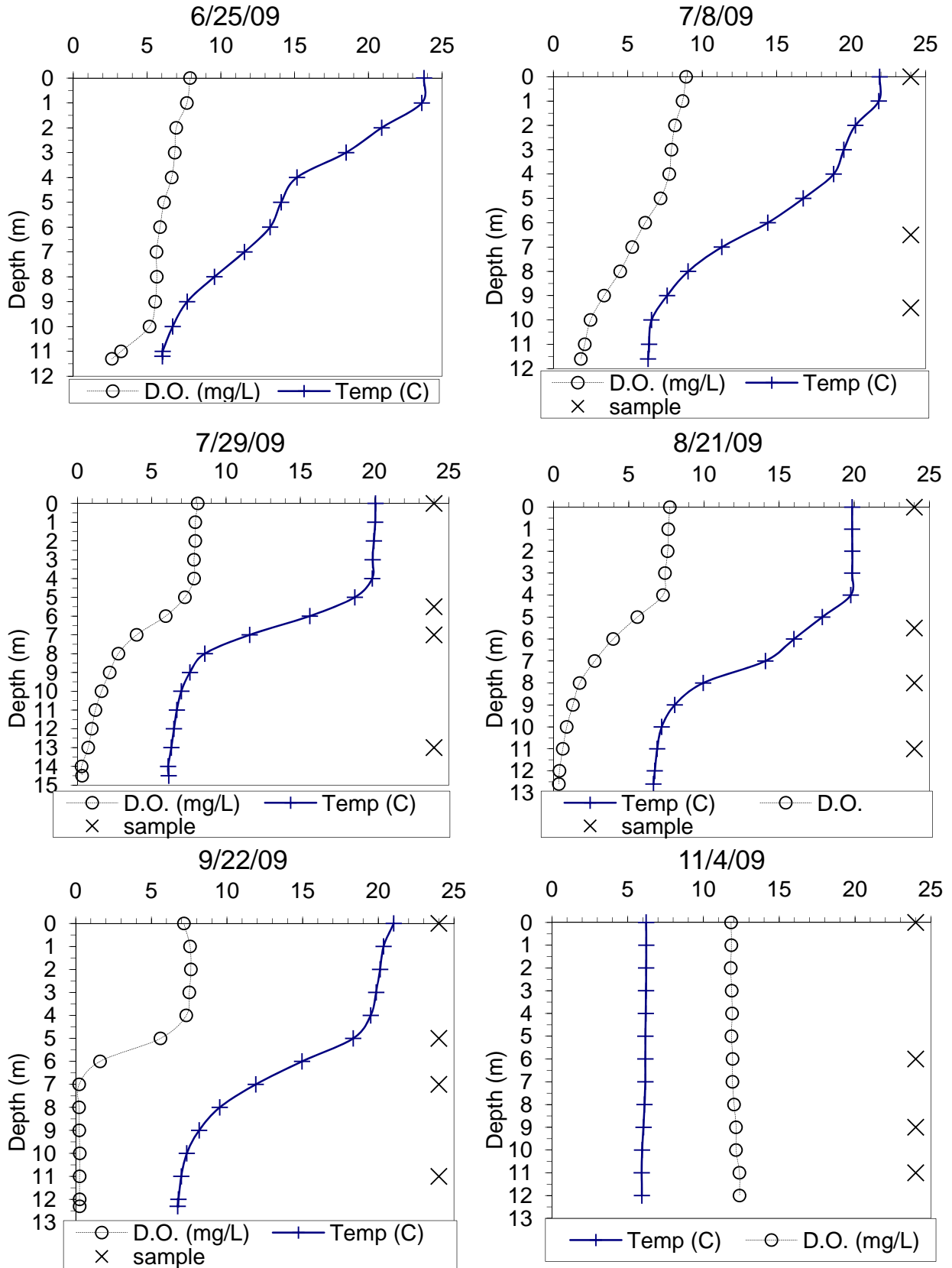
**Figure 8. Additional Baseline Monitoring for PolyMet Mining  
Embarrass River, Stream Sites, Non-Storm Events**



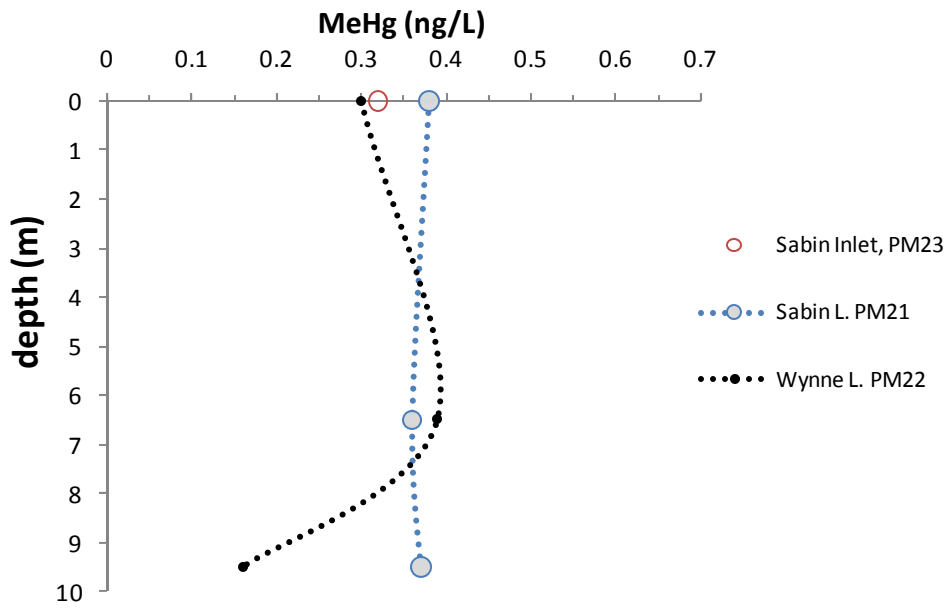
**Figure 9. Additional Baseline Monitoring for PolyMet Mining, Sabin Lake Depth Profiles, Temp (C) and D.O. (mg/L)**



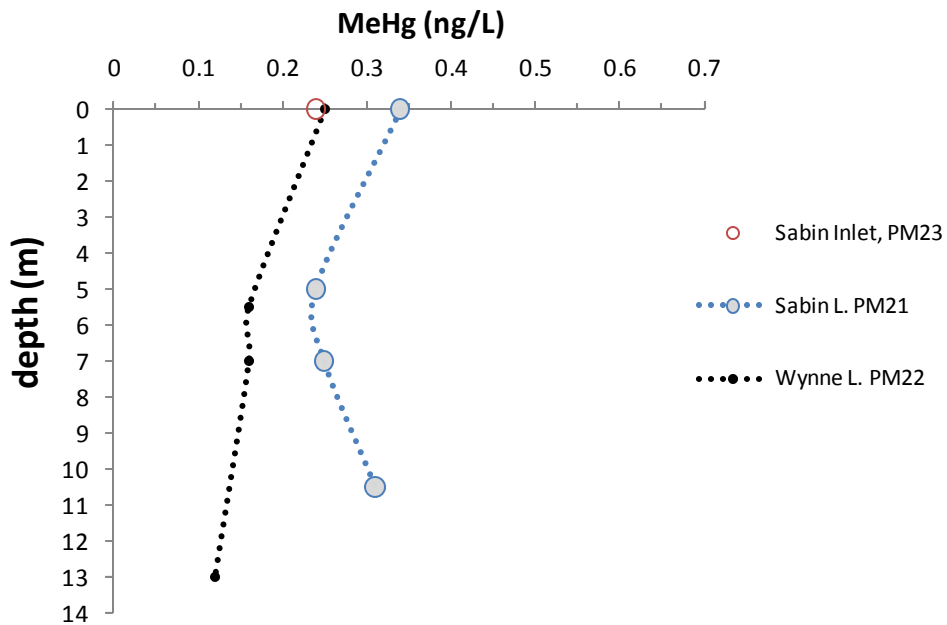
**Figure 10. Additional Baseline Monitoring for PolyMet Mining, Wynne Lake Depth Profiles, Temp (C) and D.O. (mg/L)**



**Figure 11. Additional Baseline Monitoring for PolyMet Mining, Sabin-Wynne, 7/9/09**

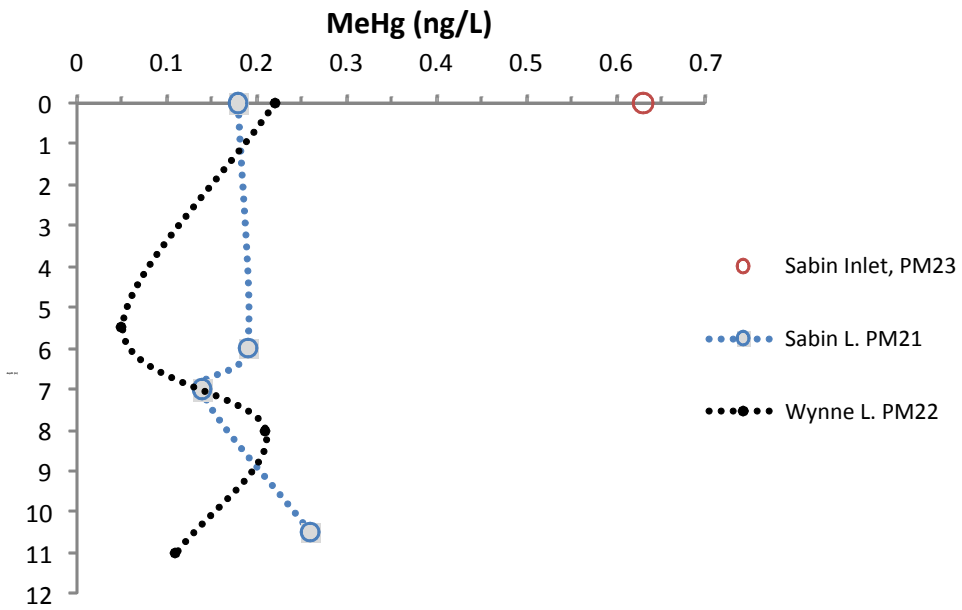


**Figure 12. Additional Baseline Monitoring for PolyMet Mining, Sabin-Wynne, 7/29/09**

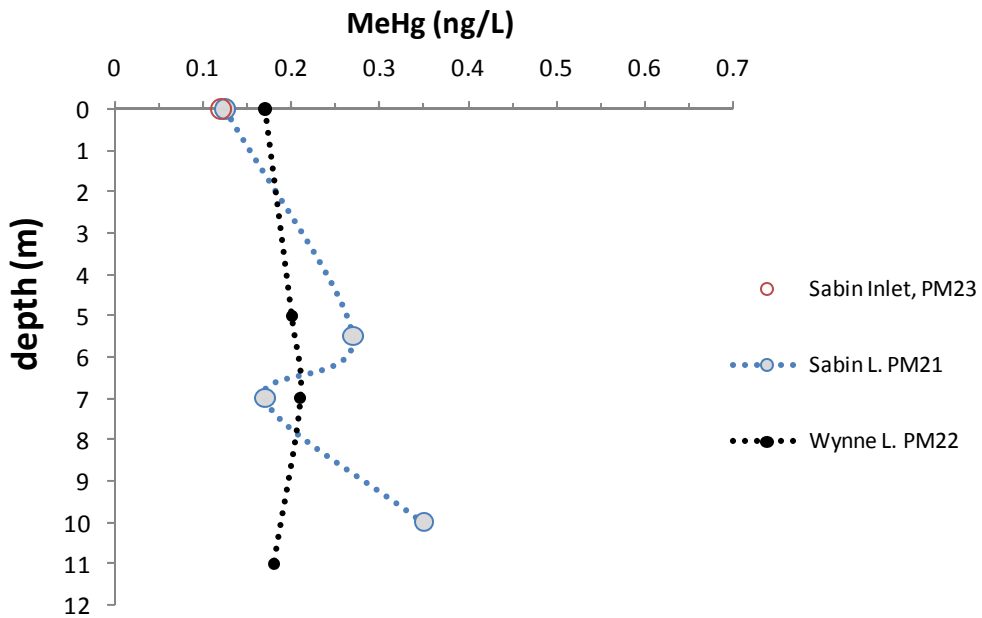




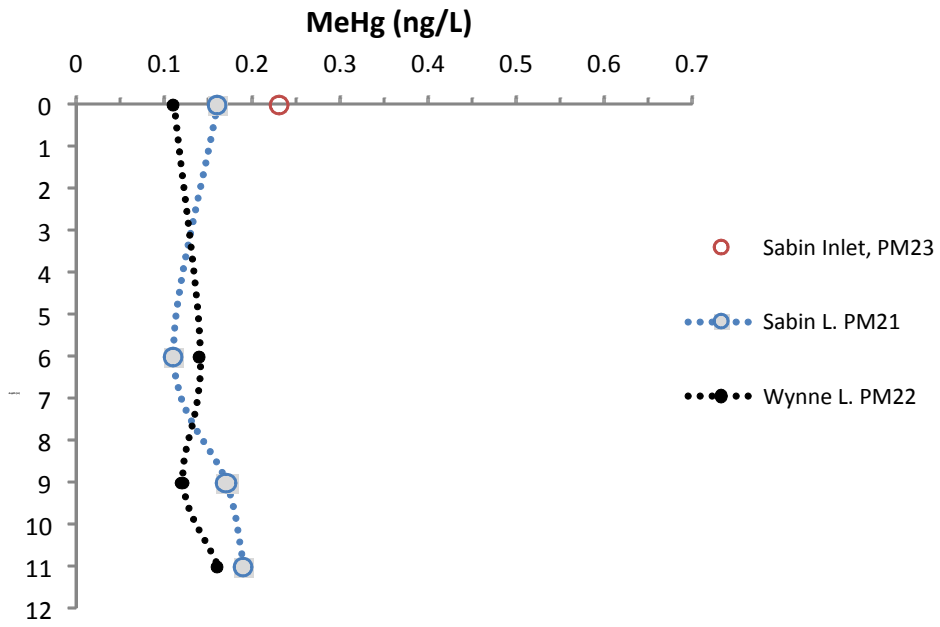
**Figure 13. Additional Baseline Monitoring for PolyMet Mining, Sabin-Wynne, 8/21/09**



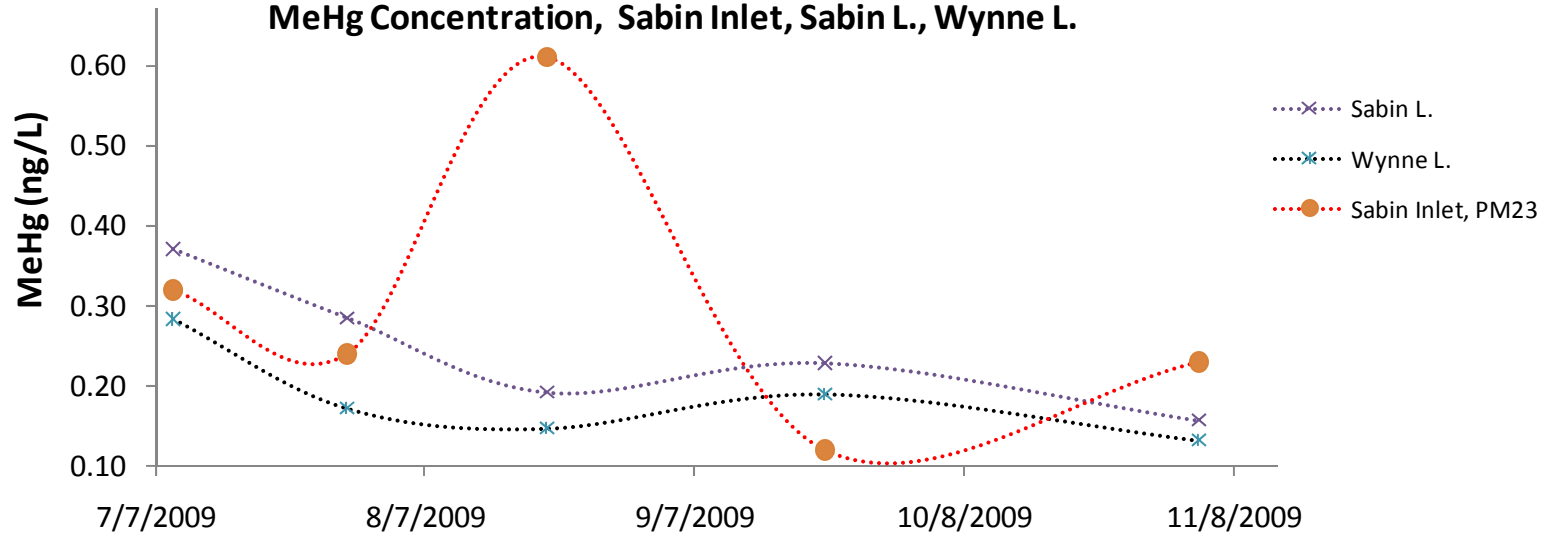
**Figure 14. Additional Baseline Monitoring for PolyMet Mining, Sabin-Wynne, 9/22/09**



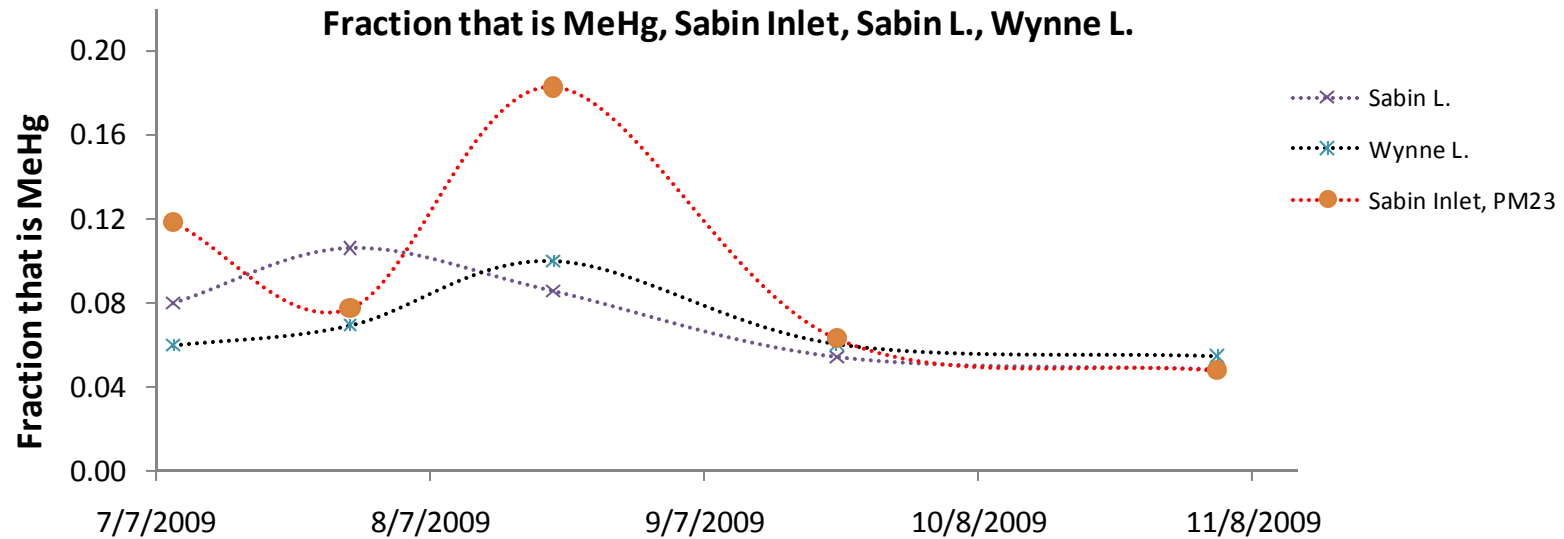
**Figure 15. Additional Baseline Monitoring for PolyMet Mining, Sabin-Wynne, 11/4/09**



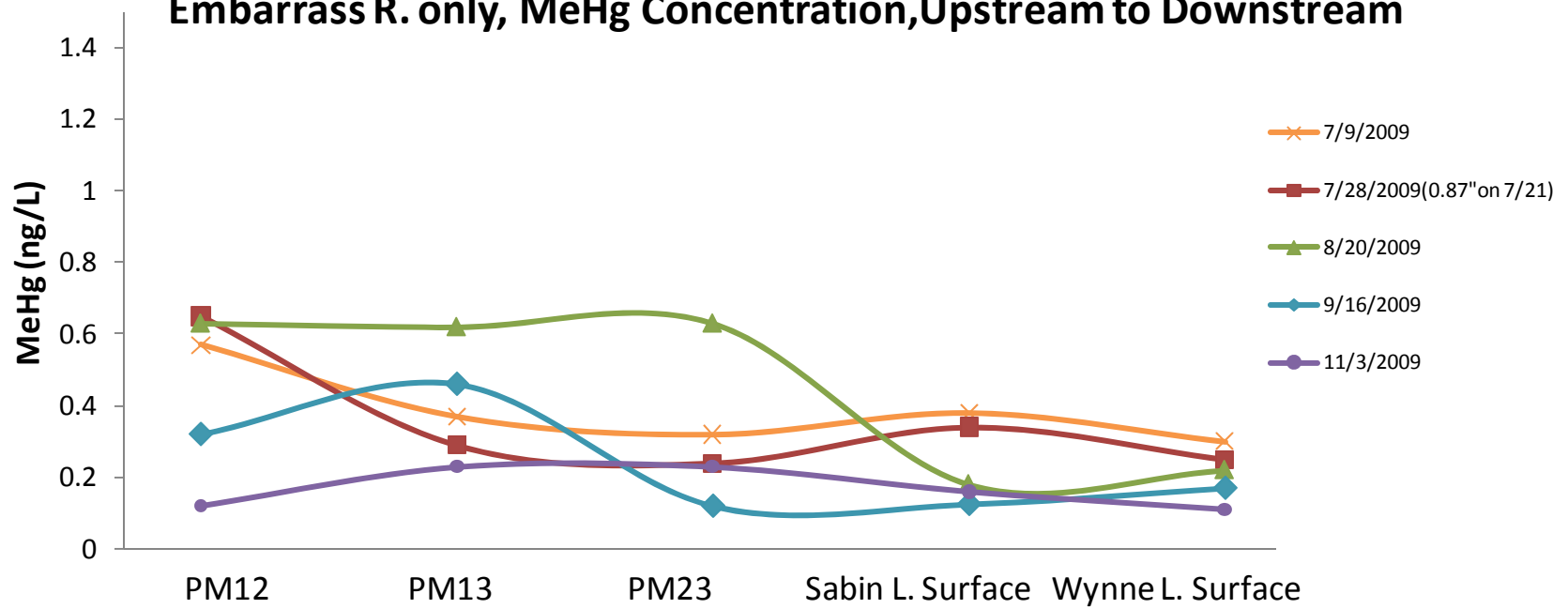
**Figure 16. Additional Baseline Monitoring for PolyMet Mining  
MeHg Concentration, Sabin Inlet, Sabin L., Wynne L.**



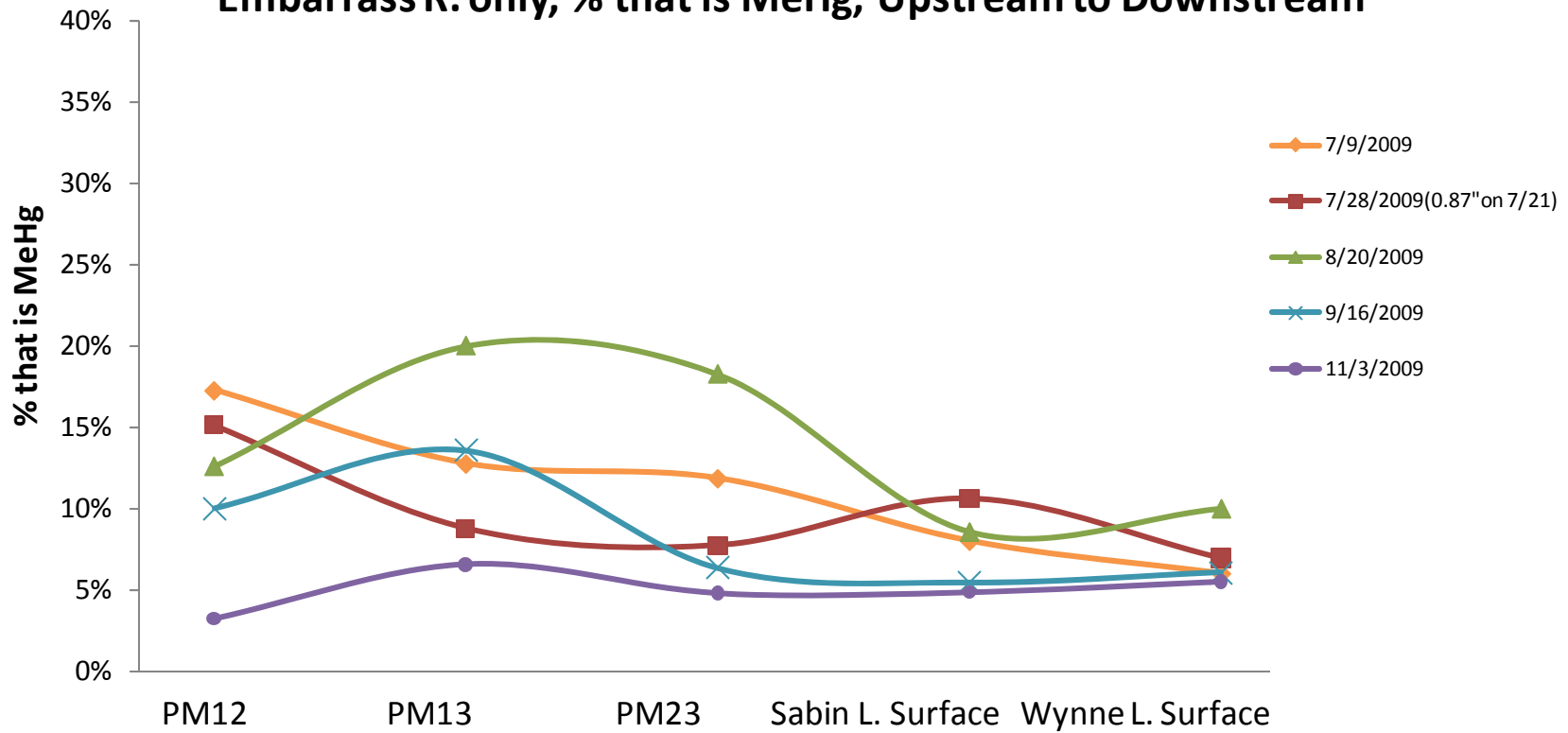
**Figure 17. Additional Baseline Monitoring for PolyMet Mining  
Fraction that is MeHg, Sabin Inlet, Sabin L., Wynne L.**



**Figure 18. Additional Baseline Monitoring for PolyMet Mining  
Embarrass R. only, MeHg Concentration, Upstream to Downstream**



**Figure 19. Additional Baseline Monitoring for PolyMet Mining Embarrass R. only, % that is MeHg, Upstream to Downstream**



## **ATTACHMENT A**

### **Work Plan for Additional Baseline Monitoring for Sulfate and Methylmercury in the Embarrass River Watershed, Revised (Updated October 2009)**

As requested by the Minnesota Pollution Control Agency (MPCA) and Department of Natural Resources (MDNR), a draft outline of a monitoring plan for collecting additional baseline surface water quality data for 2009 has been developed. The main goal of the monitoring plan is to further characterize background conditions with regard to sulfate loading from the existing LTV Steel Mining Company (LTVSMC) tailings basin and its effect on methyl mercury generation within two aquatic environments. The first consists of the large wetland complexes that lie north and west of the LTVSMC tailings basin. The second consists of the chain of lakes located in the lower Embarrass River.

Note: This sampling plan outline represents the extent of the background surface water data collection to be conducted for the NorthMet Project in 2009. At this time, this additional sampling focuses on the Embarrass River watershed. Discussions to date with the cooperating agencies indicate that sampling in the Partridge River watershed is not necessary in 2009.

The outline of the monitoring plan and associated support information were developed based on the comments made by the participants of a conference call/meeting originating from the MDNR offices on May 21, 2009. The revised outline presented in this memorandum incorporates the suggestions from ERM, MPCA and MDNR staff during a follow-up conference call/meeting originating from the MPCA offices on June 11, 2009. The update on 10/14/09 is provided to communicate minor revisions made during field sampling for filtered versus unfiltered samples for the parameters of chloride, sulfate, and organic carbon.

Ten monitoring sites are proposed (Figure A-1).

- Five monitoring sites are located on streams that receive drainage from wetlands (PM-11 is a small stream within the wetland near the LTVSMC tailings basin; PM-12 and PM13 are in the Embarrass River; two new creek monitoring sites, Trimble Creek = PM-19 and Bear Creek = PM-20).
- Five monitoring sites are associated with lake sampling. Two monitoring locations are lake sites (PM-21, PM-22; proposed sampling over the deepest part of each lake) with associated sampling locations for inlet streams (PM-23, Embarrass River entering Sabin Lake; PM-24, an unnamed creek entering the northern tip of Wynne Lake; PM-25, an unnamed creek entering the east/southeast shoreline of Wynne Lake).

Different sampling frequencies are proposed for the streams draining wetlands and the lakes. In addition to sampling frequency, the outline of the monitoring plan also identifies the physical and chemical parameters that will be monitored, and other specifics such as the depth of sample collection for each site. Table A-1 provides a rationale for each monitoring site. Table A-2 provides a listing of samples for each location and the parameters to be analyzed.

Please contact Cliff Twaroski (952-832-2642) or Neal Hines (952-832-2708) to discuss additional details of this sampling plan.

### **Sampling Plan for Additional Data on Sulfate and Methylmercury, Outline:**

#### **A. Streams That Drain Wetlands**

Emphasis: comparisons on a watershed basis; stream flow and chemistry from watersheds receiving LTVSMC tailings basin sulfate compared to stream flow and chemistry from background watersheds.

Hypothesis: methylmercury concentrations in drainage water and the flux of methylmercury (grams methylmercury per square meter of watershed area) from wetlands receiving sulfate from the LTVSMC tailings basin is not different from concentrations or flux from background wetlands.

##### 1. Sampling Sites

- a. High Sulfate Sites (reflect contributions from wetlands near the LTVSMC tailings basin):
  - i. Site PM-11, Unnamed Creek, west/northwest of the tailings basin
  - ii. Site PM-19, Trimble Creek
- b. Background; Low Sulfate Sites (reflect contributions from natural wetlands):

- i. Site PM-20 (Bear Creek, a tributary on the north side of the Embarrass River)
  - ii. Site PM-12 (Embarrass River, upstream of the LTVSMC tailings basin; upstream of Spring Mine Creek that discharges sulfate from Area 5)
- c. Additional Site: PM-13 (Embarrass River, downstream of LTVSMC tailings basin influence)
  - i. Data collected at this location provides a measure of LTVSMC tailings basin influence on sulfate and methylmercury concentrations and loading in the river.

## 2. Sampling Frequency

- a. Events = total of 6 events (all sites; some time between early July and end of August, 2009), with preference for storm events
  - i. Storm Events = (at least) 3. Sampling triggered by approximately a 0.75 inch daily rainfall. Rainfall amounts will be determined from a gauge located at the City of Biwabik wastewater treatment plant (gauge read daily; rainfall amounts to be reported to Barr staff).
    - A 0.75 inch rain during summer months should result in a response from the wetlands based on analysis of precipitation and flow data for the Embarrass River and the Partridge River (1971-2001 time period). Sampling will target the falling limb of the hydrograph, which is anticipated to capture the flush of methylmercury from the wetlands. Sampling is expected to occur approximately 7 days after a storm event but may occur sooner depending upon the actual stream response to storm events. Continuous flow monitoring data will be collected from all stream monitoring locations. Stream flow data will be telemetered to Barr's Hibbing office and will provide an early indicator when the storm flow is subsiding and provide the data to be used in determining the specific day for sampling.
    - For the third storm event, a rainfall of 1.5 inches or greater was to be sampled, per discussion with Agencies and Tribes on July 31, 2009.
  - ii. Non-storm Sampling, July - August = (no more than) 3
    - Provides comparison to "storm event" data
- b. Routine = 3 (all sites) (monthly; September, October, November 2009)



### 3. Monitoring Parameters

#### a. Field

- i. Continuous: flow and specific conductance (all sites; PM-12, PM-13, PM-11, PM-19, PM-20).
- ii. At time of sample collection (all sites): pH, temperature, dissolved oxygen, conductivity, reduction/oxidation potential (redox);
- iii. Sample Collection: one raw water sample (unfiltered) for core parameters; one raw water sample for sulfur isotopes; filtered samples for analysis of dissolved constituents.
  - After the filtering of samples in the field, samples will be acidified with 0.8% low mercury HCl (follows MDNR procedures used for the 2007-2008 St. Louis River study).
  - Sample collection will include Field blanks and the collection of Duplicate samples for quality assurance/quality control purposes.

#### b. Laboratory

- i. Core stream parameters (all sites):
  - Filtered water samples; dissolved phase: Total Hg, methyl Hg; organic carbon (DOC), total phosphorus, total iron
  - Unfiltered, raw water samples: total suspended solids (TSS), chloride, sulfate, color, ortho phosphorus, acid volatile sulfide (AVS),  $^{34}\text{S}$  – sulfate.
    - data may be helpful in assessing loading to downstream lakes
  - Sulfur isotope ( $^{34}\text{S}$ ) (provides an indicator of biological activity versus weathering of sulfide minerals from mining features such as stockpiles)
- ii. Blanks and duplicates: the current recommendation is one duplicate sample per 10 field samples; at least one field blank for low level Hg per sampling event (per discussions with Northeast Technical Services, NTS; Virginia, MN).

## B. Lakes

Emphasis: develop methylmercury budgets for two study lakes receiving sulfate loading from mining features and determine the predominant source of methylmercury in the lakes: upstream watershed production versus in-lake production.

Hypothesis: methylmercury concentrations in Wynne and Sabin lakes are primarily from upstream watershed contributions and not from in-lake processes.

1) Sampling Sites

- a. Two lakes from the Embarrass chain-of-lakes: Sabin (PM-21), Wynne (PM-22)

Rationale: these two lakes had the highest walleye Hg concentrations (normalized to 40 cm; Barr, 2008) in the Embarrass chain-of-lakes.

- b. Inlet streams to the study lakes (provide additional support data for the mass balance):

- i. Embarrass River entering Sabin Lake (PM-23).
- ii. Unnamed creek entering the northern tip of Wynne Lake at the west side of the narrows (PM-24).
- iii. Unnamed creek entering the east/southeast shoreline of Wynne Lake (PM-25).

2) Sampling Frequency: approximately monthly (early July, mid-late July, August, September, October).

Rationale: Although wetland sampling frequency will be storm event driven, methylmercury in lakes is less responsive to storm events but more sensitive to time of year and redox status (in addition to non-controllable variables of landscape, parent bedrock, microbial ecology, bioavailability, and food chain structure). To track methylmercury concentrations over time, lakes will be monitored during the summer and fall (to capture lake turnover).

3) Sampling and Parameters

- a. Field measurements pH, temperature, conductivity, dissolved oxygen, redox, used to define intervals for water sampling to capture the oxidized and reduced sides of the oxycline.

- b. Field measurements, other:

- i. Secchi disc (transparency) readings will be taken at the mid-lake site.
- ii. Inlet/outlet streams: Water inflow and outflow to/from each lake will be estimated using a portable flow meter at the time of sample collection (a portable flow meter to be used to estimate velocity for the respective inlet/outlet stream cross-section). The data from Site PM-23 (Embarrass River entering Sabin Lake) will be compared to the continuous stream flow

data from Site PM-13 and used in adjusting mass balance calculations if deemed to be appropriate.

- iii. Lake stage: a continuous recorder for lake stage will be placed in each lake. The relationship between lake stage and inflow/outflow estimates will be used in mass balance calculations.

c. Sample collection

- i. Mid-lake sample collection: water sampling will be conducted based on the profile: surface (0m), oxycline (just above and just below), and 1m off the bottom (without disturbing the sediment). Raw water samples for analysis of “total” concentrations. All lakes samples are unfiltered water.
- ii. Inlet stream sample collection: raw water (unfiltered) samples for analysis of “total” concentrations.

d. Laboratory analysis:

i. Lakes

- Surface samples only: chlorophyll a; adsorption(254)
- All unfiltered (raw water) samples: methyl Hg, total Hg, TOC, sulfate; total iron; total phosphorus and ortho phosphorus; total suspended solids (TSS); total chloride, color (platinum cobalt units), <sup>34</sup>S – sulfate.

Note: for the October lake sampling, TOC vs. DOC samples will be analyzed per telephone discussion between Ed Swain (MPCA) and Neal Hines on 10/5/09.

ii. Inlet Streams

- Unfiltered (raw water) sample): methyl Hg and total Hg; sulfate; total iron; total organic carbon (TOC); total phosphorus and ortho phosphorus; total suspended solids (TSS); total chloride; <sup>34</sup>S – sulfate.

### **C. Data Analysis & Interpretation**

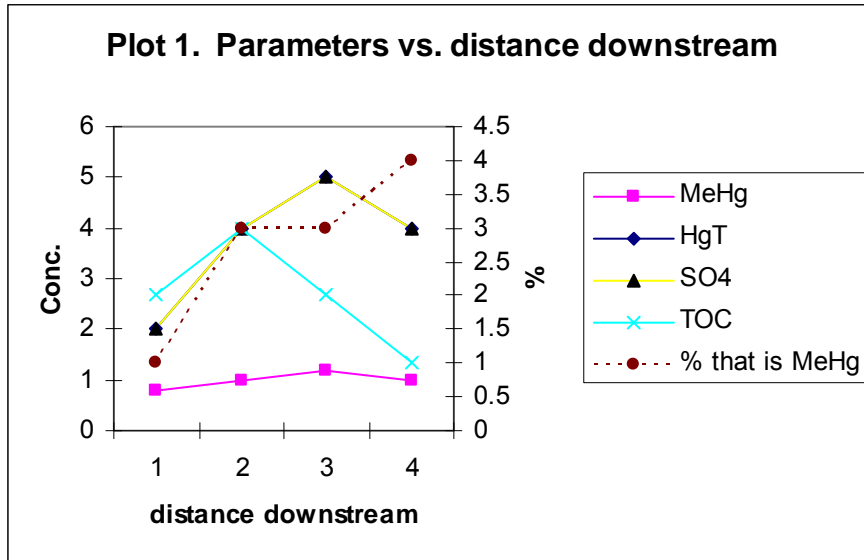
Several types of analyses will be conducted to determine if the high sulfate sampling sites (streams or lakes) are different from control sites. Examples of the data analyses that are expected are provided below.

The current expectation is that PolyMet / Barr Engineering would provide a draft report to the Agencies for review and comment. This report would emphasize the comparisons between

watershed (high sulfate to background) and whether there were, or were not, significant differences identified and whether methylmercury was elevated in the streams draining watershed receiving sulfate from the tailings basin. One meeting could be held with Agency staff to discuss the report and findings, with submittal of a final report to the Agencies based on their verbal and written comments. The data would then be available for use in the final EIS.

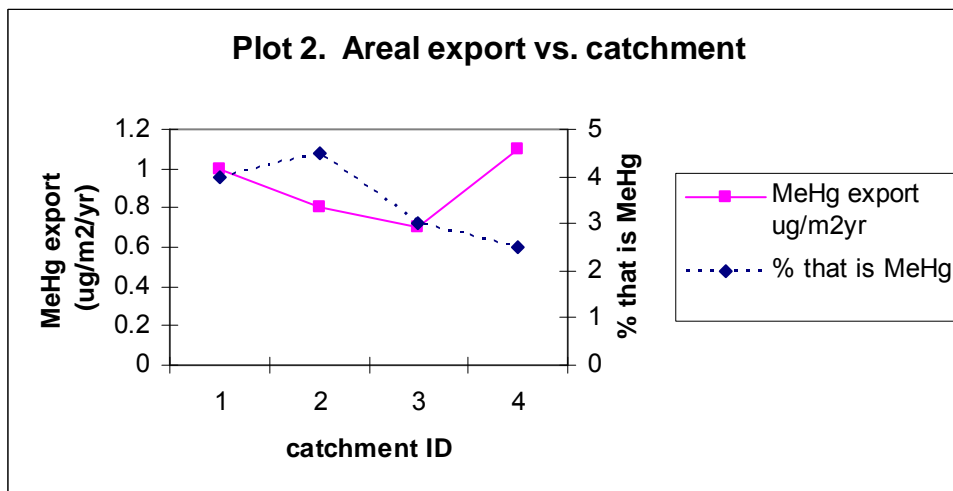
### Example 1

This plot identifies the methylmercury profile with respect to discharge, or a chemograph.



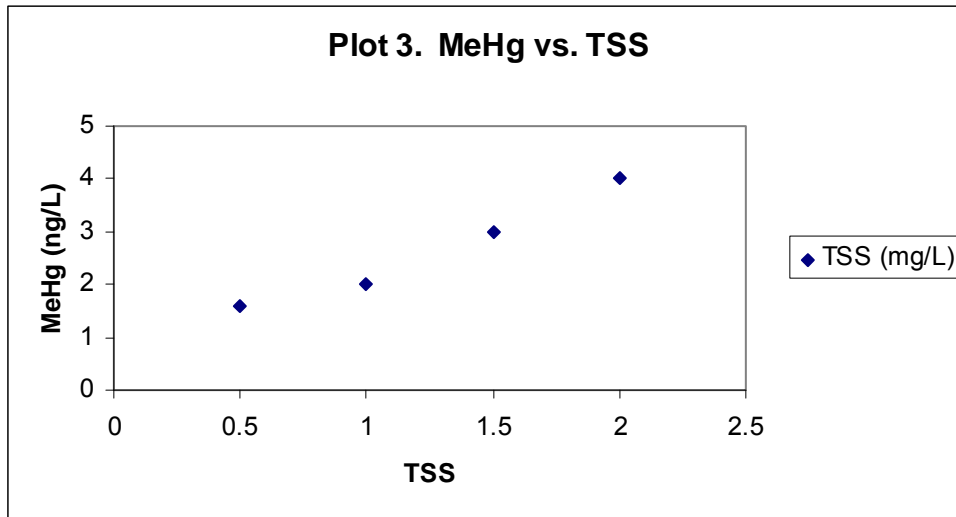
### Example 2

This plot portrays the areal export of MeHg from catchments draining sulfate impacted waters and non-sulfate impacted waters.



### Example 3

This example follows the work of Balogh et al. (2008) and may identify similarities or differences between high sulfate and low sulfate sites.



## Other Information and Data Comparisons

1) Streams:

a. GIS related data:

- i. Watershed area contributing to a stream sampling location (approximate)
- ii. Wetlands in a watershed (acreage; % of watershed area)
- iii. Types of wetlands and acreage (e.g., black spruce/sphagnum, 85 acres)

b. Data Comparisons (examples)

<b>Ratios Between Parameters</b>	<b>Background / Control Streams/Watersheds (PM-12 and PM-20)</b>	<b>Sulfate Affected Streams/Watersheds (PM-11 and PM-19)</b>
MeHg/THg versus Sulfate		
MeHg/THg versus DOC		
MeHg/THg versus Iron		
Others?		

MeHg = methylmercury

THg = total mercury

DOC = dissolved organic carbon

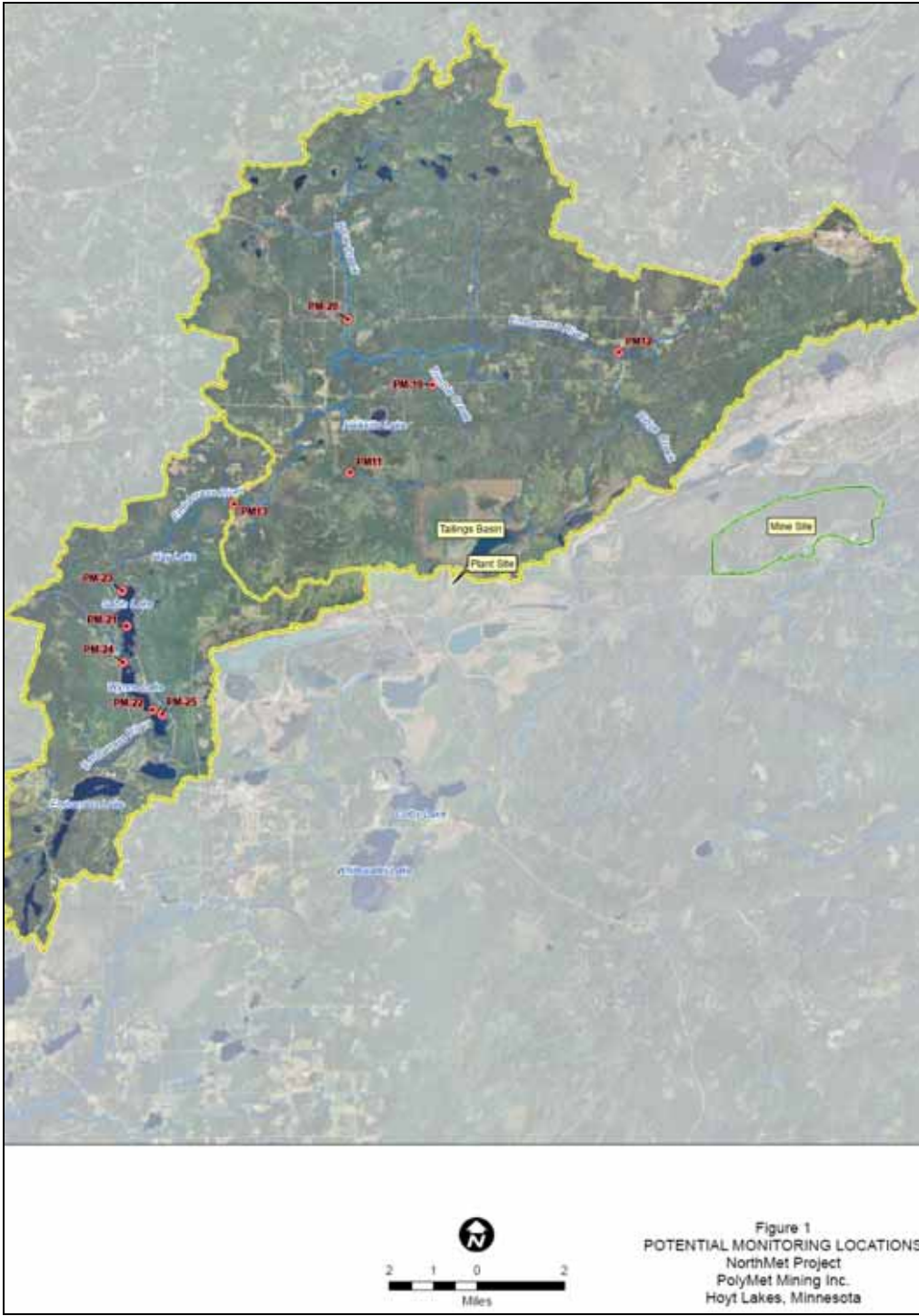


Figure A-1. Proposed monitoring locations for additional baseline monitoring in 2009.



**Table A-1. Reasoning behind monitoring site selection for 2009 baseline data collection.**

<b>Site</b>	<b>Basis of Need for Monitoring Location</b>
<b><i>Streams that drain wetlands</i></b>	
PM-11	Existing Stream Site. Location to assess the methylmercury generation potential because it is downstream of wetlands receiving sulfate from the tailings basin.
PM-12	Existing Stream Site. Embarrass River; Upstream of tailings basin influence. Can be used as a "control location" (not affected by mining).
PM-13	Existing Stream Site. Embarrass River; Downstream of tailings basin influence. Integrates watershed influences (mining, non-mining) and provides an indicator of the significance of tailings basin contributions to overall chemical concentrations in the Embarrass River.
PM-19	New Stream Site, Trimble Creek. Considered a good location to assess the methylmercury generation potential because it is downstream of wetlands receiving sulfate from the tailings basin.
PM-20	New Stream Site, Bear Creek. Control location. Creek is downstream of several wetlands. Creek should have low sulfate. Can use data from the site to determine seasonal changes in methylmercury for wetlands that are not affected by mining activity.
<b><i>Lakes (and associated inlet streams)</i></b>	
PM-21	New Site, Sabin Lake. Lake monitoring site downstream of the PolyMet tailings basin. To characterize the physical and chemical condition of the lake as it relates to the potential for methylmercury generation in the lake.
PM-22	New Site, Wynne Lake. Lake monitoring site downstream of the PolyMet tailings basin. To characterize the physical and chemical condition of the lake as it relates to the potential for methylmercury generation in the lake.
PM-23	New Site, Sabin Lake. Embarrass River enters the lake. To characterize the chemistry of the major inflow to Sabin Lake at its point-of-entry. Raw water (unfiltered) samples to be collected and analyzed for total mercury, total methylmercury, sulfate and other parameters for use in mass balance calculations for the lake. TOC to also be analyzed.
PM-24	New Site, Wynne Lake. An unnamed creek enters the lake near its northern tip. To characterize one of two small streams that enter the lake. Raw water (unfiltered) samples to be collected and analyzed for total mercury, total methylmercury, sulfate and other parameters for use in mass balance calculations for the lake. TOC to also be analyzed.
PM-25	New Site, Wynne Lake. An unnamed creek enters the lake near its northern tip. To characterize one of two small streams that enter the lake. Raw water (unfiltered) samples to be collected and analyzed for total mercury, total methylmercury, sulfate and other parameters for use in mass balance calculations for the lake. TOC to also be analyzed.

**Table A-2. Summary of lake and stream samples to be collected in 2009 baseline Monitoring.**

Site Name	Laboratory Analytical Parameters	Numbers of Samples for Analysis				Field Filter	Comment
		Per Sample Date	No. of Field Samples	Field Blk	Dup		
<b>Lake Group (5 dates) [1]</b>							
<b>Mid-Lake Samples (4 depths)</b>							Samples collected over the deepest part of each lake.
PM21 (Sabin)	Hg, MeHg, SO4, AVS, <sup>34</sup> S, Fe, Cl, TOC, color, Chl-a, TSS, TP, OP	one per each depth = 4	20				Only the surface sample analyzed for Chl-a; Filtering in the lab.
PM22 (Wynne)	Hg, MeHg, SO4, AVS, <sup>34</sup> S, Fe, Cl, TOC, color, Chl-a, TSS, TP, OP	one per each depth = 4	20				Only the surface sample analyzed for Chl-a; Filtering in the lab.
<b>Inlet Streams [2]</b>							
PM23, inlet 1, Embarrass R. enters Sabine Lake	Hg, MeHg, SO4, AVS, <sup>34</sup> S, Fe, Cl, TOC, TSS, TP, OP, Color	1	5				Flow measurements taken at time of sampling
PM24, inlet 2, Small stream that enters northwest tip of Wynne Lake (point flow measurement)	Hg, MeHg, SO4, AVS, <sup>34</sup> S, Fe, Cl, TOC, TSS, TP, OP, Color	1	5				Flow measurements taken at time of sampling
PM25, inlet 3, Small stream that enters Wynne Lake on the east/southeast shoreline (point flow measurement)	Hg, MeHg, SO4, AVS, <sup>34</sup> S, Fe, Cl, TOC, TSS, TP, OP, Color	1	5				Flow measurements taken at time of sampling
Duplicate (1 per sampling date)	Hg, MeHg, SO4, AVS, <sup>34</sup> S, Fe, Cl, TOC, TSS, TP, OP, Color	1				5	Duplicate samples randomly assigned to a lake sampling depth or an inlet stream.
Field Blank (1 per lake per date)	LL Hg	2			10		
<b>Sample total</b>					<b>70</b>		
<b>Stream Group (9 events) [3]</b>							
PM11, west/northwest of tailings basin;	Hg, MeHg, SO4, AVS, <sup>34</sup> S, Fe, Cl, DOC, TSS, TP, OP, Color	1	9			Hg, MeHg, DOC, Fe, TP	continuous flow measurement
PM12, Embarrass R. upstream of tailings basin	Hg, MeHg, SO4, AVS, <sup>34</sup> S, Fe, Cl, DOC, TSS, TP, OP, Color	1	9			Hg, MeHg, DOC, Fe, TP	continuous flow measurement
PM13, Embarrass R. below tailings basin	Hg, MeHg, SO4, AVS, <sup>34</sup> S, Fe, Cl, DOC, TSS, TP, OP, Color	1	9			Hg, MeHg, DOC, Fe, TP	continuous flow measurement
PM19, Trimble Creek, north of tailings basin	Hg, MeHg, SO4, AVS, <sup>34</sup> S, Fe, Cl, DOC, TSS, TP, OP, Color	1	9			Hg, MeHg, DOC, Fe, TP	continuous flow measurement
PM20, Bear Creek, north side of Embarrass R	Hg, MeHg, SO4, AVS, <sup>34</sup> S, Fe, Cl, DOC, TSS, TP, OP, Color	1	9			Hg, MeHg, DOC, Fe, TP	continuous flow measurement
Duplicate sample (1 per event)	Hg, MeHg, SO4, AVS, <sup>34</sup> S, Fe, Cl, DOC, TSS, TP, OP, Color	1				9	Duplicate samples are assigned so that one is collected at each stream over the course of the study.
Field blank (one per event)	LL Hg	1			9	LL Hg	A field blank will be randomly assigned to a stream for each event.
<b>Sample total</b>					<b>63</b>		
<b>Samples - grand total</b>					<b>133</b>		

<b>Parameters</b>	<b>Chl-a</b>	chlorophyll a	<b>OP</b>	ortho phosphorus
	<b>Cl</b>	chloride	<b>TSS</b>	total suspended solids
	<b>DOC</b>	dissolved organic carbon	<b>TP</b>	total phosphorus
	<b>Fe</b>	iron	<b>TOC</b>	total organic carbon
	<b>Hg</b>	Total mercury	<b>SO4</b>	Sulfate
	<b>MeHg</b>	methyl mercury	<b>AVS</b>	acid volatile sulfide
	<b>LL</b>	Low level (for Hg)	<b><sup>34</sup>S</b>	sulfur isotope, 34

**Footnotes**

- [1] Lake Group Approximately monthly sampling; 5 dates planned (early July, mid-late July; August, Sept., October)
- [2] Lake Group, Inlet Streams Raw water samples from Inlet streams to Sabin and Wynne lakes will be collected and analyzed for "total" concentrations. Data is NOT specifically for assessing sulfate and mercury relationships as is the case for other stream monitoring locations.
- [3] Stream Group 9 sampling events: 3 (minimum) storm events + 3 (maximum) non-storm samplings + 3 "routine" samplings (Sept., Oct., Nov.) = 9

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## **References**

Balogh et al. 2008. Characteristics of mercury speciation in Minnesota rivers and streams. *Environmental Pollution*, Vol. 154, 3-11.

Barr Engineering, 2008. NorthMet Project: Initial comparison of fish mercury concentrations from Hoyt Lakes area lakes with fish mercury concentrations from selected lakes in northeast Minnesota. Technical Memorandum. Prepared for PolyMet Mining, NorthMet Project. July 2008.

## **ATTACHMENT B**

### **Hydrologic Data Summary - Streams**



## Internal Memorandum

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**To:** Cliff Twaroski, Neal Hines, Miguel Wong  
**From:** Peter Hinck  
**Subject:** Sulfate and Methyl Mercury Investigation, 2009 — Hydrologic data summary (streams)  
**Date:** January 20, 2010  
**Project:** PolyMet Mining 23/69-0862.00-015-074

The purpose of this memorandum is to summarize the hydrologic data that has been collected from July 9 through November 15, 2009 for the methyl mercury study at the stream monitoring sites in the Embarrass River watershed. Data collected include stream level gauging, discrete stream flow measurements, site observations, daily precipitation observations and watershed and wetland data from the Minnesota DNR's GIS database. The discrete stream flow measurements were used to develop preliminary rating curves (stage vs. flow) for the majority of the stream monitoring locations included in this study.

### **Daily Precipitation**

Weather data, including precipitation, is collected daily at the NCDC Cooperative Weather Station (Coop #212576) in Embarrass, Minnesota. The weather station is located near the intersection of State Highway 21 and Waisanen Road, 500 feet from the Embarrass River and 2.9 miles northwest of the LTV Steel Mining Company (LTVSMC) Tailings Basin and approximately 18 miles downstream of the Embarrass River headwaters. The location of the weather station relative to the stream monitoring locations is shown in Figure 1. The stream monitoring locations range from 6.75 miles (PM-12) to 1.6 miles (PM-11) from this weather station.

The NCDC weather station at Embarrass has been in operation since October 1994. Based on data from 1995 to 2008 average annual precipitation at Embarrass is 28.3 inches and average total precipitation during the months of July through October is 14.6 inches. Daily and cumulative precipitation for this study period is presented in Figure 2. The total precipitation during the months of July through October was 12.1 inches (there was an additional one inch of precipitation from November 1-15). During this period there have been three precipitation events with total rainfall greater than one inch: July 15-18, July 22-24, and August 20-21. An additional 0.98 inches of

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precipitation fell from October 29-November 1, resulting in the highest flows measured during this study as discussed below. Note that precipitation data are collected at the station at 6:00 pm each day and represent precipitation for the previous 24 hours.

**PM-11**

PM-11 is a previously existing stream monitoring site on an unnamed stream 1.55 miles northwest of the LTVSMC Tailings Basin. The monitoring location is downstream of wetlands that receive seepage from the Tailings Basin, and has a contributing watershed area of approximately 2.91 square miles (excluding the LTVSMC Tailings Basin). Of this watershed area, 15% is delineated as wetland in the National Wetlands Inventory (NWI). See Table 1 for comparison with the watershed size and wetland percentage of the other stream monitoring locations.

Stream level (gauge) data have been collected at PM-11 since July 28, 2009, following the repair of beaver damage to the originally installed level sensor. The gauge data for PM-11 is shown in Figure 3. The stream stage at PM-11 tends to increase soon after precipitation events of as little as 0.3 inches, with levels varying by approximately 0.5 feet during the duration of this study.

The discrete flow measurements at PM-11 have not been sufficient to develop a detailed rating curve for this monitoring location, largely due to the ongoing influence of beaver activity on stream levels. Discrete flow measurements at PM-11 during the study period have ranged from 1.0 cfs to 4.6 cfs.

**PM-12**

PM-12 is a previously existing stream monitoring site on the Embarrass River 4.0 miles downstream of the Embarrass River headwaters near Babbitt, Minnesota. This monitoring location is upstream of the mining-related surface water impacts in the Embarrass River watershed, including the LTVSMC Tailings Basin and the outflow from the Area 5 pits. PM-12 has a contributing watershed area of approximately 18.9 square miles, of which 23% is delineated as wetland in the NWI.

Stream flow data was collected on the Embarrass River by the USGS (station #03153001) from 1943 through 1964 at a location near the NCDC weather station (approximately 18.1 miles downstream of the Embarrass River headwaters). Low, median, and high flows for the period of July through October from the USGS gauge data are presented in Table 2. Using the relative watershed areas of

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the USGS gauge location and PM-12, the historic median flow for July to October at PM-12 is estimated to be 4.93 cfs.

Stream level data have been collected at PM-12 since July 9, 2009 (see Figure 4). The stream stage at PM-12 is less consistent than at PM-11, possibly reflecting the daily cycles of discharge from the upstream Babbitt municipal waste water treatment facility (average discharge assumed to be 0.33 cfs in the surface water quality modeling, see RS74B pg. 42). Between July 9 and September 4, stream stage at PM-12 ranged approximately 0.5 feet, and discrete flow measurements ranged from 0.64 cfs to 1.4 cfs (i.e. near the 10<sup>th</sup> percentile of historic estimated flows).

After September 4, stream levels consistently increased at PM-12 as the flow was restricted by a downstream beaver dam. Discrete flow measurements between September 4 and October 31 showed little to no downstream flow. The downstream beaver dam appears to have been breached or removed during a period of high precipitation on October 29-31. Discrete flow measurements during the first two weeks of November ranged from 4.6 cfs to 10.1 cfs (i.e. above the median of historic estimated flows). Because of these changing hydraulic conditions, the discrete flow measurements at PM-12 have not been sufficient to develop a detailed rating curve.

**PM-13**

PM-13 is a previously existing stream monitoring site on the Embarrass River at the Highway 135 bridge crossing 24.2 miles downstream of the headwaters of the Embarrass River. This monitoring location is downstream of the LTVSMC Tailings Basin area of influence. PM-13 has a contributing watershed area of approximately 110 square miles (including the watersheds of the other monitoring locations discussed here and excluding the LTVSMC Tailings Basin), of which 37% is delineated as wetland in the NWI

Using the relative watershed areas of the USGS gauge location (station #03153001) and PM-13, the median July to October flow at PM-13 is estimated to be 30.0 cfs. Note that 1943-1964 gauge data represents conditions before construction of the LTVSMC Tailings Basin. According to Barr memo "Changes to the Tailings Basin Flows in the Embarrass River Watershed – PolyMet RS-74" (dated October 14, 2008) seepage from the existing LTVSMC Tailings Basin is approximately 4.0 cfs as determined by calibration to chloride concentrations. This seepage would represent additional inflow

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to the USGS gauging station and PM-13 that is not accounted for in the estimated historic flow values for PM-13.

Stream level data have been collected at PM-13 since July 9, 2009 (shown in Figure 5). As the most downstream monitoring location in the current study, PM-13 shows the greatest delay between precipitation events and the corresponding peak stream level response, although the delay appears to be less than one day. Stream levels have the greatest range at this location, with over 1.7 feet of variation in the study period. Discrete flow measurements during the study period ranged from 7.5 cfs to 101 cfs (i.e. from near the 10<sup>th</sup> percentile to well above the median of historic estimated flows).

The ten discrete flow measurements for PM-13 are sufficient to develop a rating curve for measured stream level and estimated flow (shown in Figure 6). This rating curve excludes one data point from July 28, 2009. The stream flow hydrograph developed from this rating curve and the continuous stream level data is shown in Figure 7. Because the data used to develop the rating curve does not include any measurements of flow greater than 101 cfs, the high flows shown in Figure 7 (i.e. above 100 cfs) should be treated as estimates of the true flow in the Embarrass River at PM-13.

**PM-19**

PM-19 is a new stream monitoring site on Trimble Creek, approximately 2.3 miles north of the LTVSMC Tailings Basin. The monitoring location is downstream of wetlands that receive seepage from the Tailings Basin, and has a contributing watershed area of approximately 6.2 square miles (excluding the LTVSMC Tailings Basin). In addition, most of the footprint of the existing LTVSMC Tailings Basin (approximately 4.2 square miles of the basin) drains towards PM-19. Of the non-Tailings Basin watershed area, 47% is delineated as wetland in the NWI.

Prior to October, stream gauging was not possible at PM-19 because of road and culvert construction that diverted flows at the monitoring site. Water quality samples were collected upstream of this disturbed area. The stream gauge was reestablished October 1 following the end of construction activities (see Figure 8). Discrete flow measurements in October and November ranged from 1.7 cfs to 3.8 cfs.

Although the data set of discrete flow measurements is limited (four data points) compared to that at PM-13 (ten data points), the data for PM-19 is sufficient to develop a rating curve for measured



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stream level and flow estimated flow (see Figure 9). The stream flow hydrograph developed from this rating curve and the stream level data from October 1 to November 15 is shown in Figure 10. Because the data used to develop the rating curve does not include any measurements of flow greater than 3.8 cfs, the high flows shown in Figure 10 (i.e. above 4.0 cfs) should be treated as estimates of the true flow in Trimble Creek at PM-19.

**PM-20**

PM-20 is a new stream monitoring site on Bear Creek on the north side of the Embarrass River watershed. Like PM-12, this site is upstream of all mining-related impacts to the Embarrass River; it is also downstream of several wetland complexes. PM-20 has a contributing watershed of approximately 29.6 square miles, of which 45% is identified as wetland in the NWI.

Stream level data have been collected at PM-20 since July 9, 2009 (shown in Figure 11). Despite its relatively large and undeveloped watershed, Bear Creek appears to be “flashy” and to increase stage quickly following precipitation events. Several rapid level increases in the study period are not tied to precipitation events at Embarrass, and may represent localized rainfall not captured at the Embarrass weather station or overflows from upstream lakes and wetlands. Stream levels have varied by approximately 2.4 feet at this location during the study period. Discrete flow measurements during the study period ranged from 2.4 cfs to 29.5 cfs.

The eight discrete flow measurements for PM-20 are sufficient to develop a rating curve for measured stream level and estimated flow (see in Figure 12). This rating curve excludes two data points due to flow measurement equipment malfunction. The stream flow hydrograph developed from this rating curve and the continuous stream level data is shown in Figure 13. Because the data used to develop the rating curve does not include any measurements of flow greater than 29.5 cfs, the high flows (i.e. above 30 cfs) shown in Figure 13 should be treated as estimates of the true flow in Bear Creek at PM-20.

**Summary and Conclusions**

Stream level data has been collected from July through mid-November 2009 in order to assist in the interpretation of water quality data collected as part of the methylmercury study in the Embarrass River watershed. Water level data has been collected on streams with watershed areas ranging from

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2.9 to 110 square miles and wetland surface area ranging from 15% to 47% of the total watershed area.

A total of 12.1 inches of precipitation has been measured at Embarrass from July through October compared with a 13-year median of 14.6 inches. For monitoring locations PM-12 and PM-13 on the Embarrass River, measured stream flows can be compared with the estimated historic flows for July through October based on the 1943-1964 USGS gauge record (station #03153001). At the upstream location (PM-12), flows in 2009 were generally low during the early part of the study, near the 10<sup>th</sup> percentile of the historic flow record. Late-season precipitation events led to measured flows above the median at PM-12 during the first half of November, including during the water quality sampling event on November 3.

At the downstream location on the Embarrass River (PM-13), estimated flows ranged from 6 to 140 cfs, with a median flow for the July through October period of 15.0 cfs (i.e. half of the historic median flow of 30 cfs). Flow at this location was above the historic median three times during the study period: from July 21 to August 8, from August 20 to 30, and from October 26 until the gauge was removed on November 11. Water quality samples were collected during relatively high flows on July 28, August 20, and November 3 (see Figure 7).

The hydrologic data collected for this study is sufficient to document the relationship between stream water quality sampling dates and the relative position on the hydrograph (rising limb, falling limb, constant stage, stagnant water, etc.). For several of the monitoring locations (PM-13, PM-19, and PM-20), the discrete flow measurements were sufficient to develop rating curves for measured stream level and estimated flow. For the other locations (PM-11 and PM-12), the observed flow measurements have not provided consistent stage vs. flow relationships. The utility of this dataset for developing precise relationships between measured water quality and stream flow is therefore variable and somewhat limited. However, the available data is sufficient to develop relationships between measured water quality and watershed area or wetland percentage.

**External Memorandum**

To: Cliff Twaroski, Neal Hines, Miguel Wong  
 From: Peter Hinck  
 Subject: Hydrologic data summary (streams)  
 Date: January 20, 2010  
 Page: 7

**Table 1: Stream Monitoring Location Watersheds and Wetlands Information**

	<b>PM-11</b>	<b>PM-12</b>	<b>PM-13</b>	<b>PM-19</b>	<b>PM-20</b>
Watershed (mi <sup>2</sup> )	2.91	18.9	110	6.2	29.6
% Wetlands	15%	23%	37%	47%	45%
<b>Wetlands by Type</b>					
Coniferous Swamp	19.1%	32.5%	51.7%	67.4%	55.4%
Hardwood Swamp	13.9%	25.3%	8.7%	10.4%	6.2%
Lake	--	2.6%	3.1%	--	6.3%
Open Bog	5.4%	--	1.0%	2.1%	0.8%
Shallow Marsh	10.3%	3.1%	3.8%	3.3%	1.3%
Shallow, Open Water	0.9%	0.6%	0.7%	0.5%	1.2%
Shrub-Carr	50.3%	35.9%	30.9%	16.3%	28.7%

Note: Watershed and wetland areas exclude the LTVSMC Tailings Basin, a total area of 4.7 mi<sup>2</sup>.

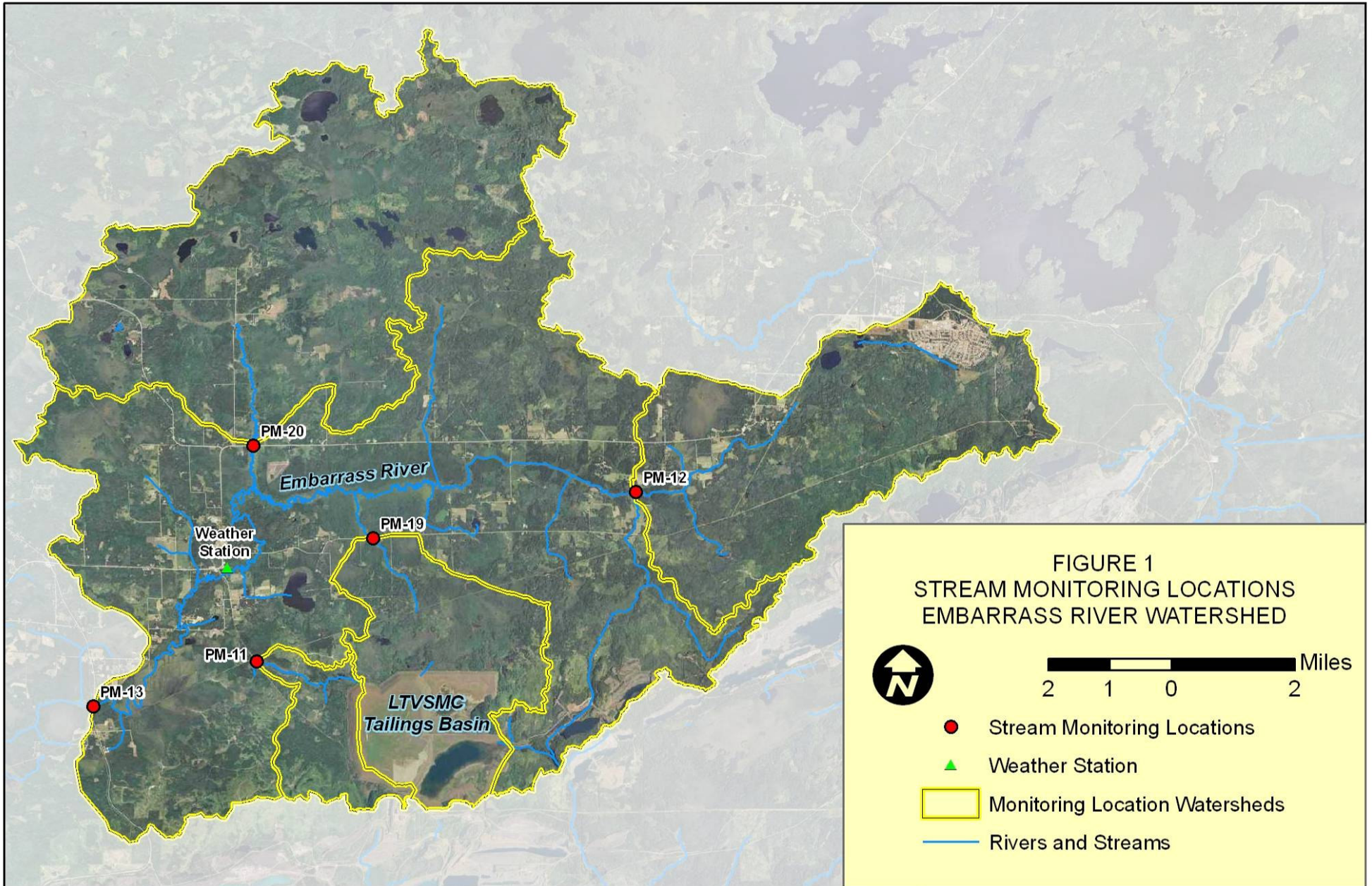
**Table 2: Recorded Range of July-October Flows in the Embarrass River (1943-1964)**

<b>Location</b>	<b>10<sup>th</sup> Percentile Flow (cfs)</b>	<b>50<sup>th</sup> Percentile Flow (cfs)</b>	<b>90<sup>th</sup> Percentile Flow (cfs)</b>
USGS Station 03153001 (actual data)*	5.30	23.0	119
USGS Station 03153001 (per mi <sup>2</sup> )*	0.059	0.260	1.34
PM-12 (based on 18.9 mi <sup>2</sup> )	1.12	4.93	25.4
PM-13 (based on 115 mi <sup>2</sup> )*	6.84	30.0	154

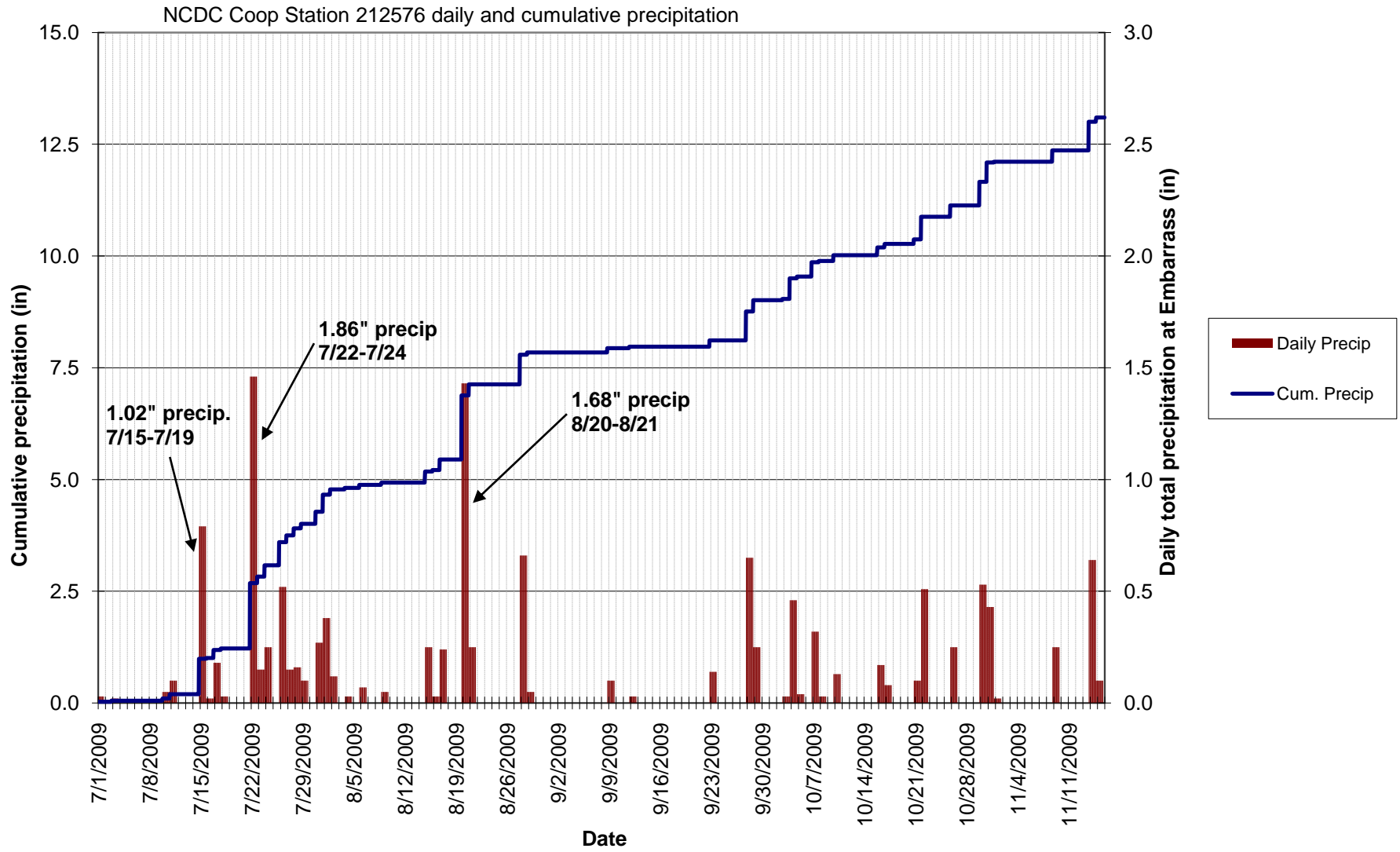
\* Note that 1943-1964 gauge data represents conditions before construction of the LTVSMC Tailings Basin. According to Barr memo "Changes to the Tailings Basin Flows in the Embarrass River Watershed – PolyMet RS-74" (dated October 14, 2008) seepage from the existing LTVSMC Tailings Basin is approximately 4.0 cfs as determined by calibration to chloride concentrations. This seepage would represent additional inflow to the USGS gauging station and PM-13 and is not accounted for in the above values.

**Internal Memorandum**

To: Cliff Twaroski, Neal Hines, Miguel Wong  
From: Peter Hinck  
Subject: Hydrologic data summary (streams)  
Date: November 2, 2009  
Page: 8



**Figure 2: Embarrass Precipitation Record**



**Figure 3: PM-11 Hydrograph (stage)**

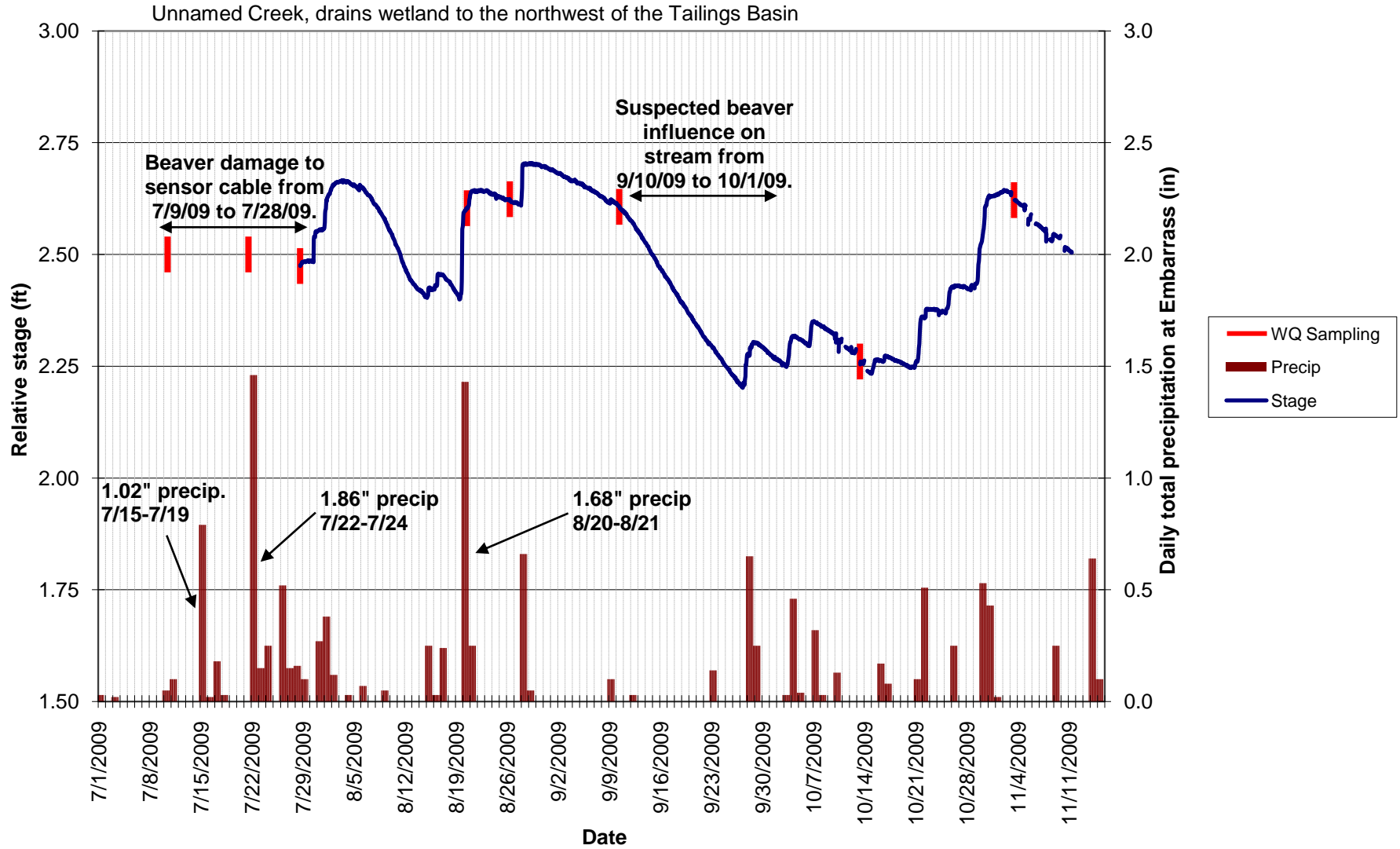


Figure 4: PM-12 Hydrograph (stage)

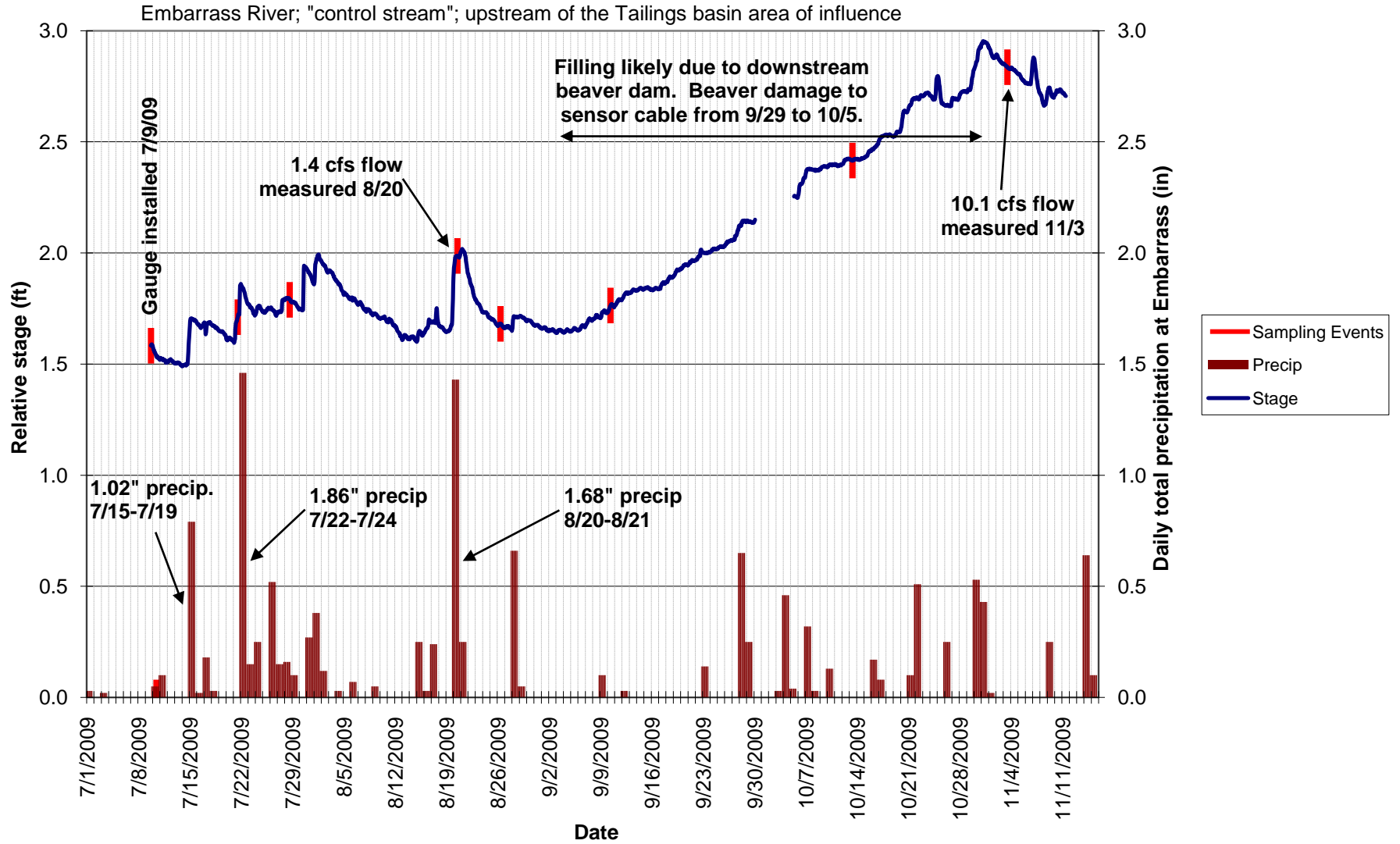


Figure 5: PM-13 Hydrograph (stage)

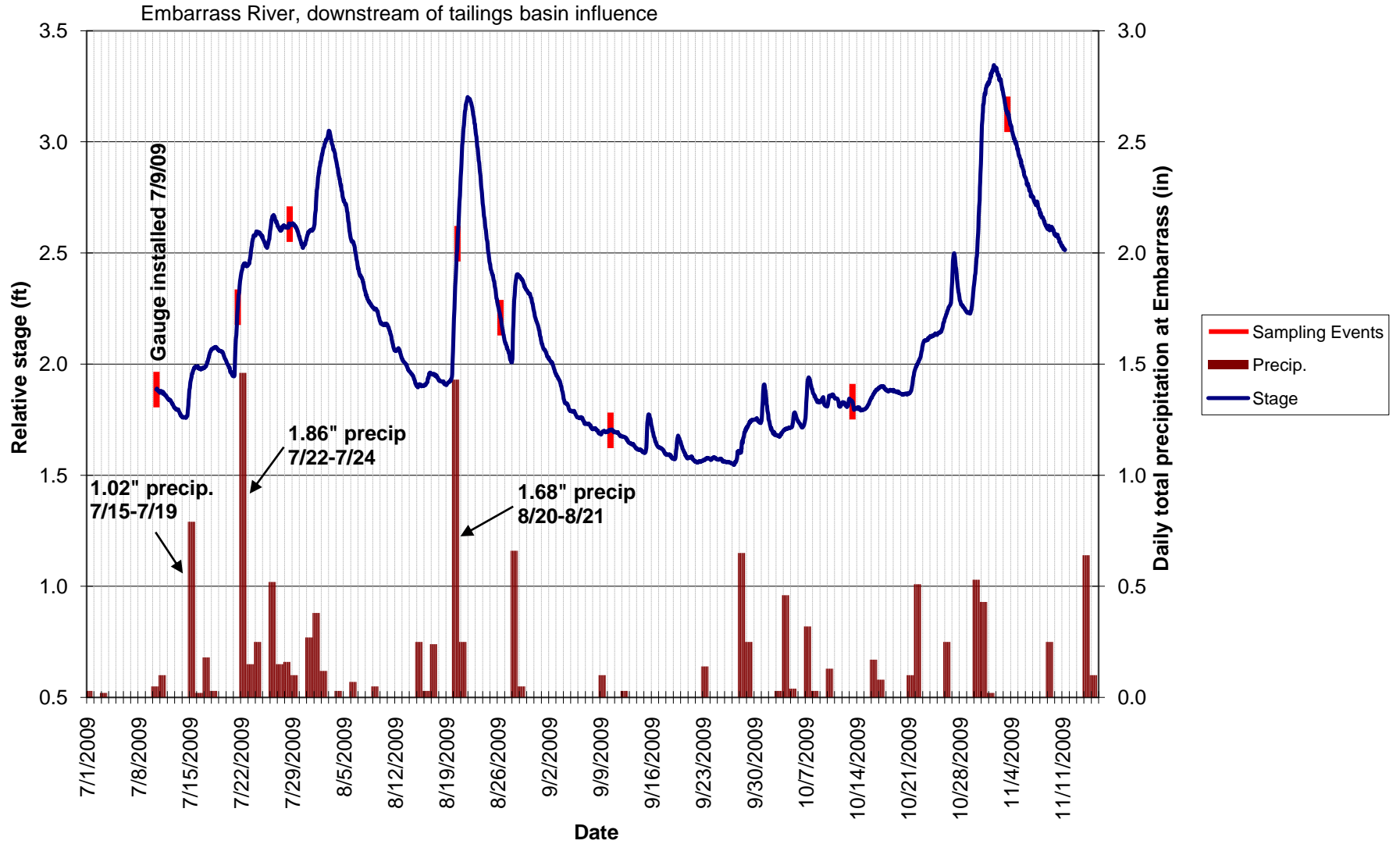




Figure 6: PM-13 Rating Curve

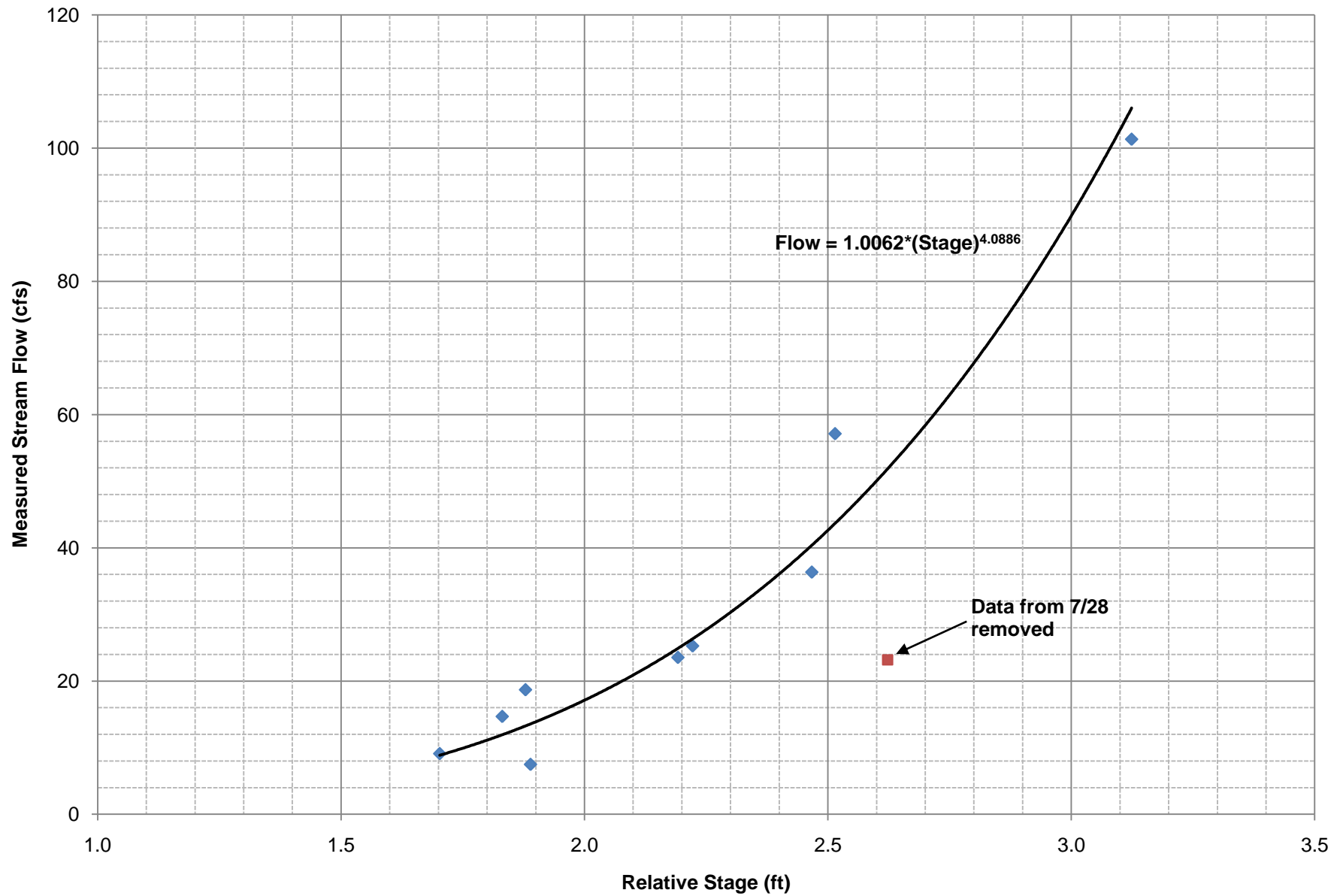
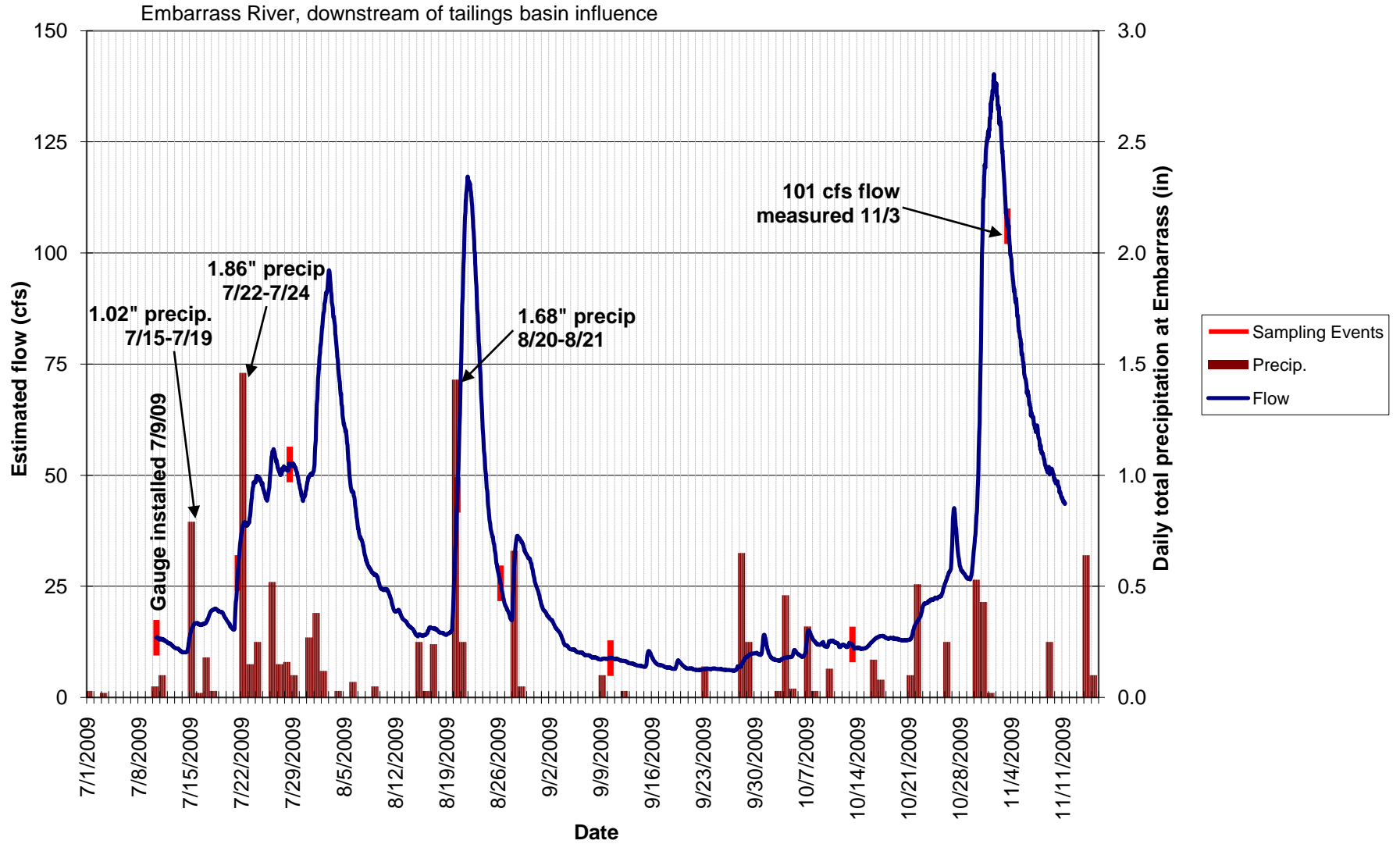


Figure 7: PM-13 Hydrograph (flow)



**Figure 8: PM-19 Hydrograph (stage)**

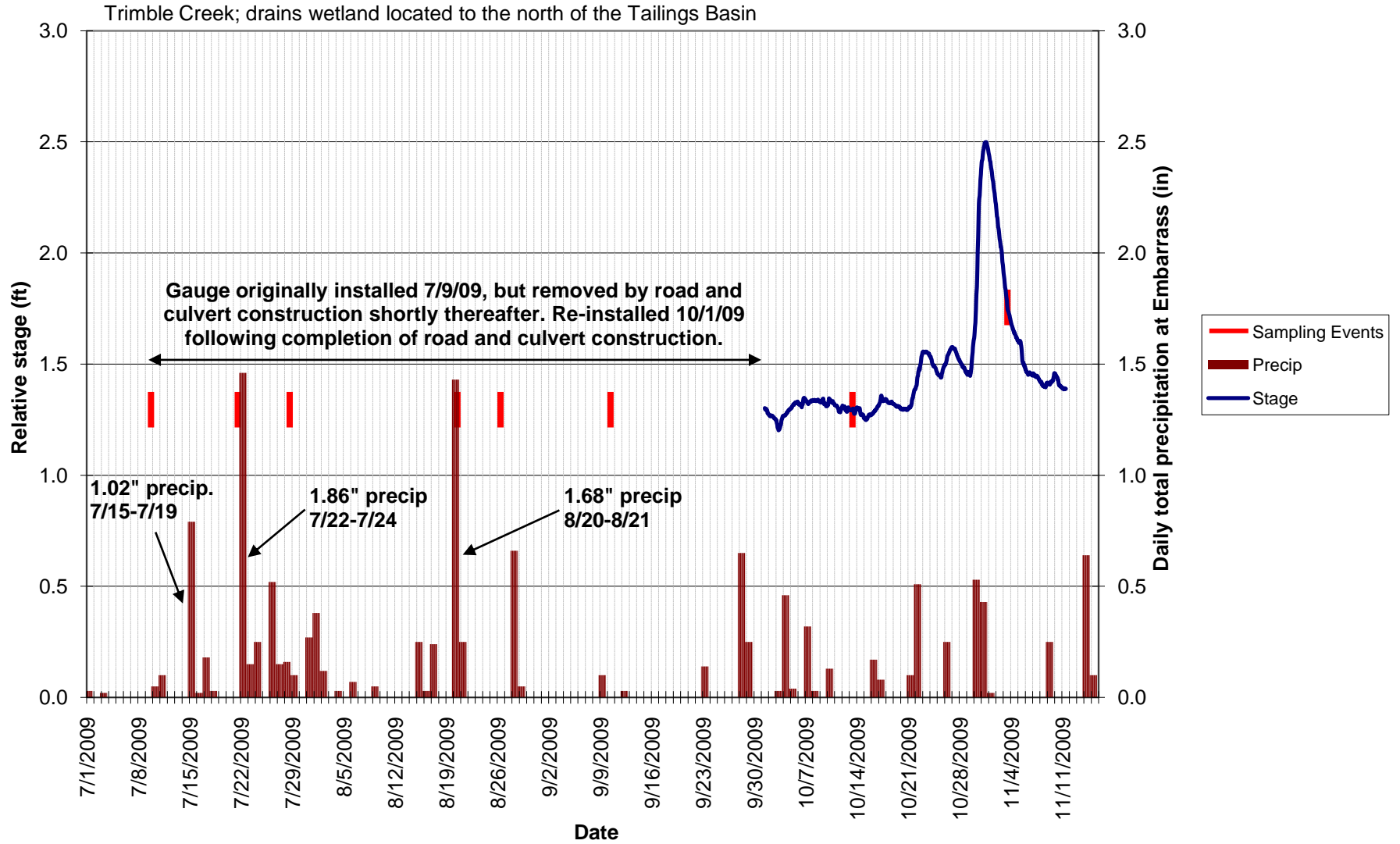
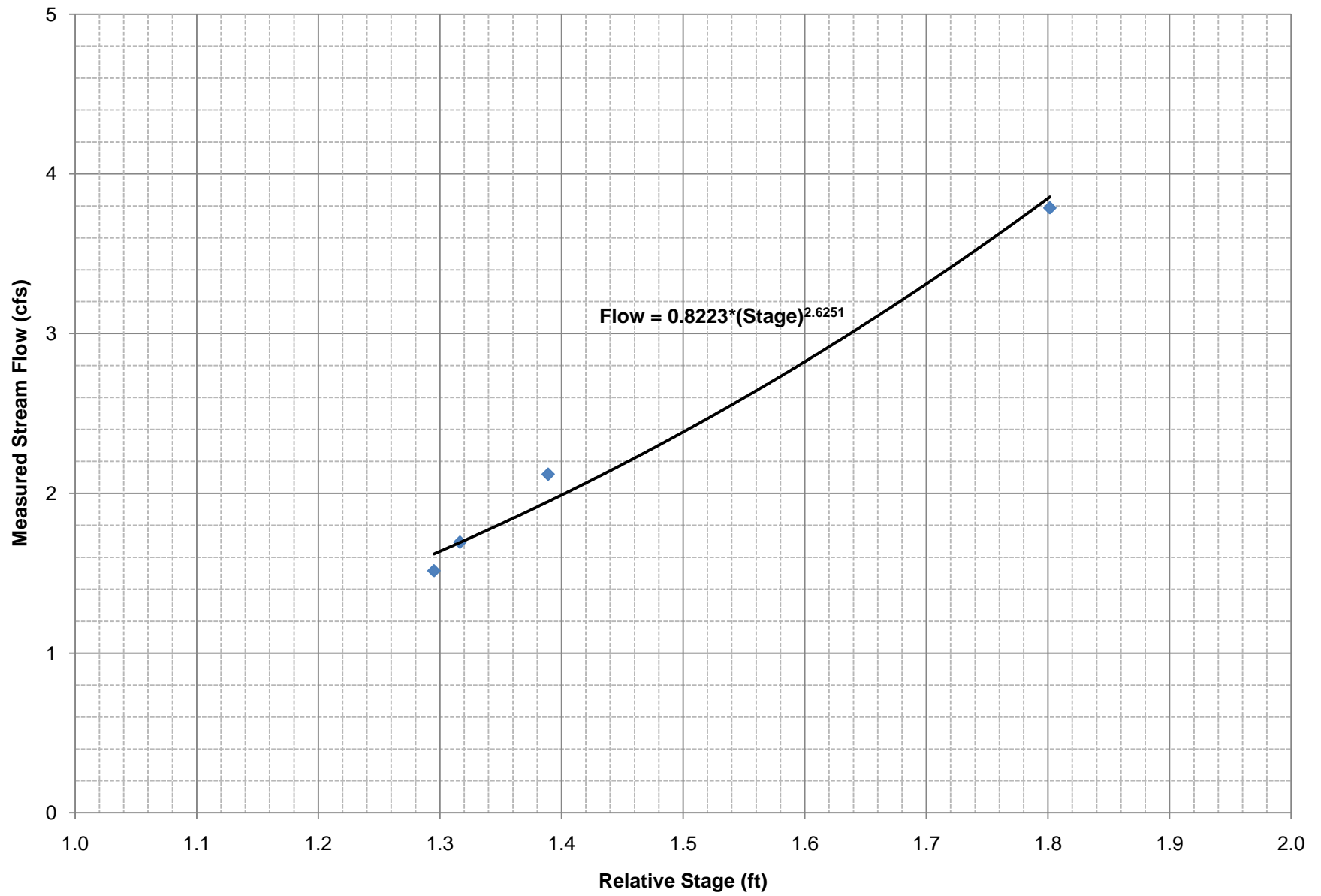


Figure 9: PM-19 Rating Curve



**Figure 10: PM-19 Hydrograph (flow)**

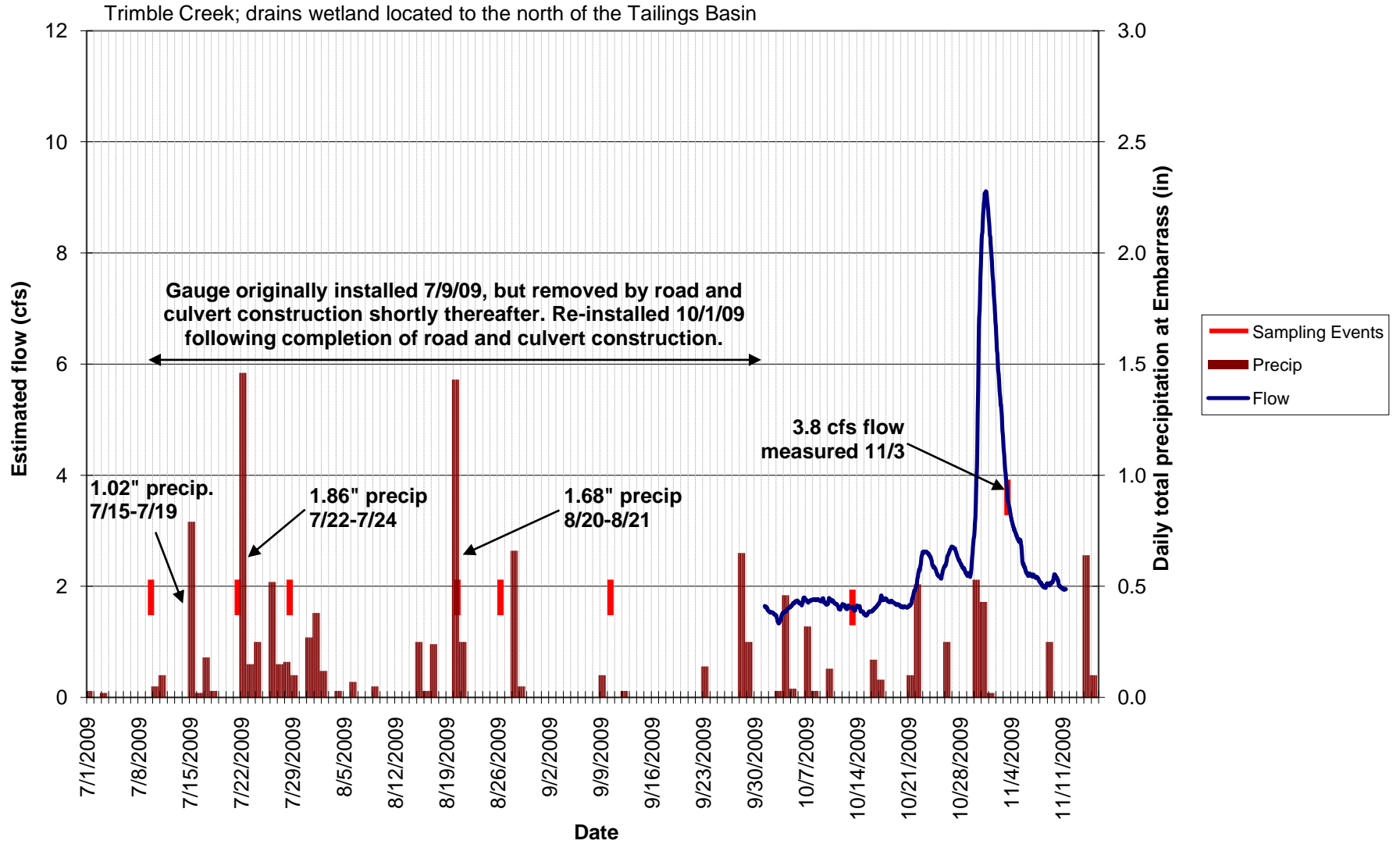


Figure 11: PM-20 Hydrograph (stage)

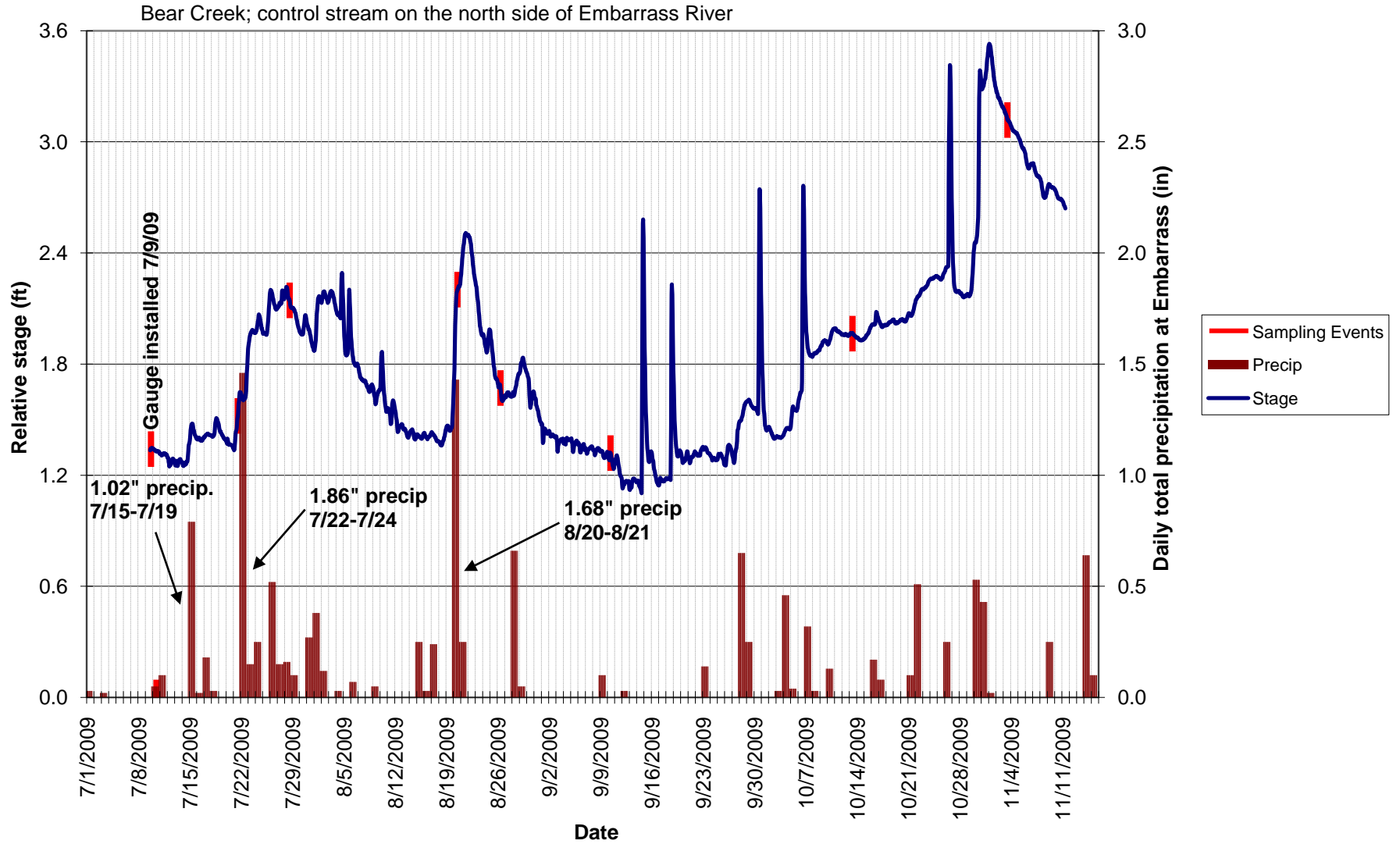


Figure 12: PM-20 Rating Curve

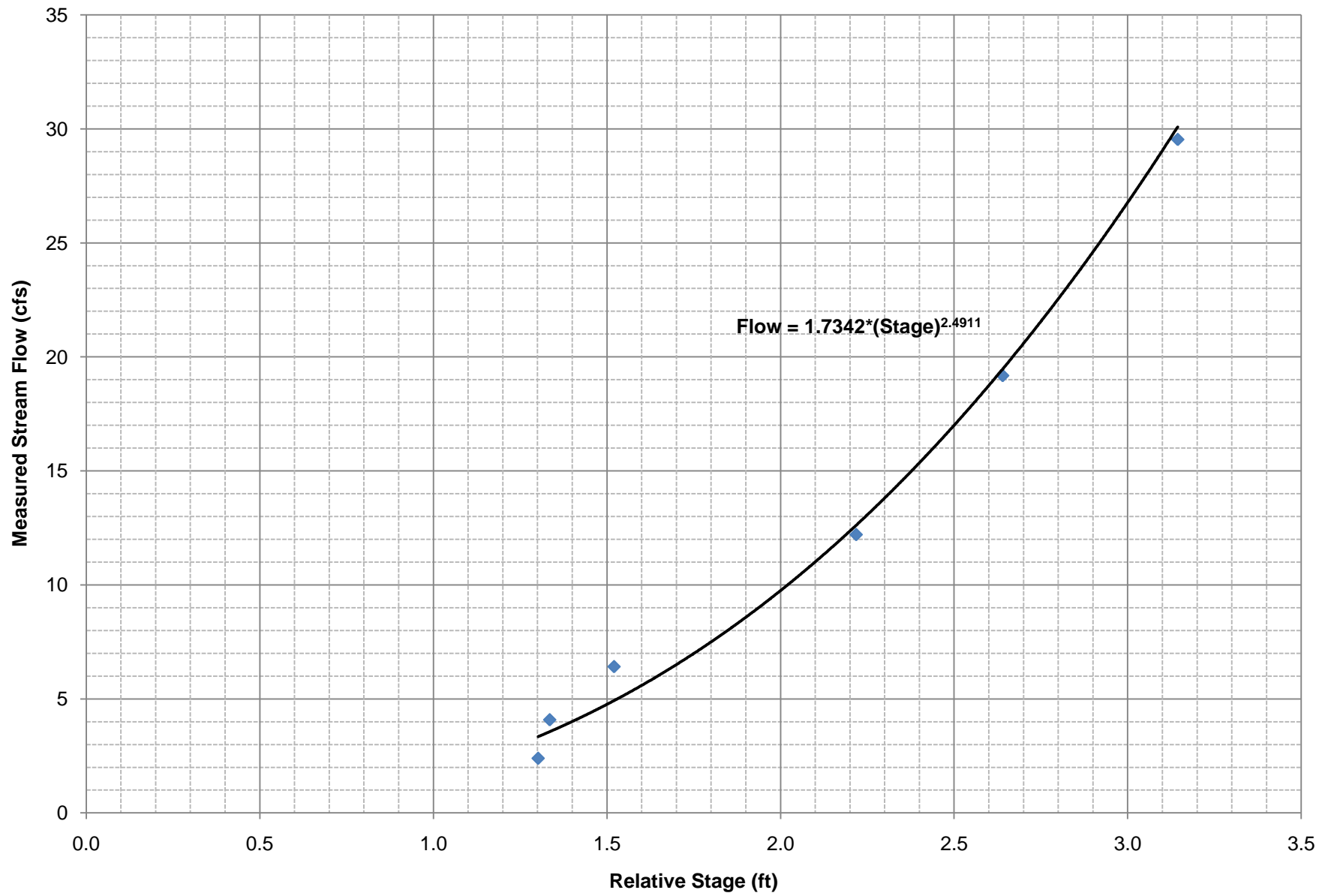
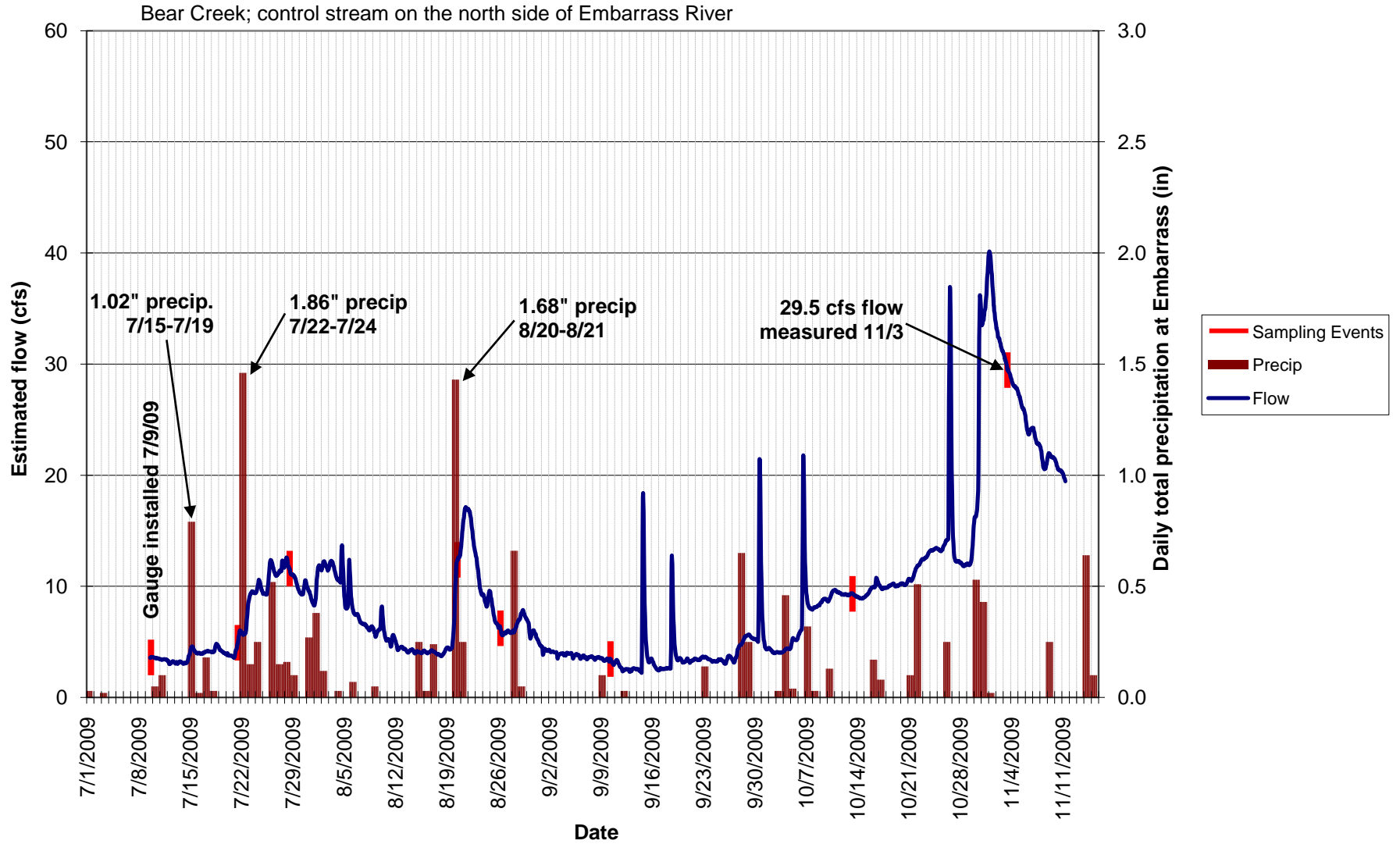


Figure 13: PM-20 Hydrograph (flow)





## Hydrologic Information for Sabin and Wynne Lakes

### Sabin Lake – Estimated Lake Volumes\*

Depth (m)	Approximate Elevation (m)	Surface Area (m <sup>2</sup> )	Incremental Volume (m <sup>3</sup> )	Cumulative Volume (bottom to surface) (m <sup>3</sup> )	Cumulative Volume (surface to bottom) (m <sup>3</sup> )
10	403	14,390	7,227	7,227	4,240,879
9	404	52,678	25,459	32,686	4,233,652
8	405	70,010	61,693	94,378	4,208,193
7	406	82,892	76,215	170,594	4,146,500
6	407	138,026	90,201	260,795	4,070,285
5	408	375,512	194,885	455,680	3,980,084
4	409	477,831	428,400	884,080	3,785,199
3	410	634,582	528,456	1,412,536	3,356,799
2	411	949,410	783,294	2,195,830	2,828,343
1	412	1,024,224	986,782	3,182,612	2,045,049
0	413	1,215,547	1,058,267	4,240,879	1,058,267

\*Numbers were calculated using the Area and Volume Statistics tool in 3D Analyst.

### Wynne Lake – Estimated Lake Volumes\*

Depth (m)	Approximate Elevation (m)	Surface Area (m <sup>2</sup> )	Incremental Volume (m <sup>3</sup> )	Cumulative Volume (bottom to surface) (m <sup>3</sup> )	Cumulative Volume (surface to bottom) (m <sup>3</sup> )
16	402	32,947	3,801	3,801	9,949,124
15	403	54,525	43,874	47,675	9,945,324
14	404	104,271	69,549	117,223	9,901,449
13	405	258,773	150,157	267,381	9,831,901
12	406	337,852	300,719	568,099	9,681,743
11	407	452,680	377,367	945,467	9,381,025
10	408	570,997	507,621	1,453,088	9,003,657
9	409	623,610	596,722	2,049,810	8,496,036
8	410	691,461	648,233	2,698,043	7,899,314
7	411	780,141	734,389	3,432,432	7,251,081
6	412	824,775	799,195	4,231,628	6,516,692
5	413	870,364	841,666	5,073,294	5,717,497
4	414	909,402	884,331	5,957,625	4,875,830
3	415	958,764	923,221	6,880,846	3,991,499
2	416	1,019,267	980,829	7,861,676	3,068,278
1	417	1,054,851	1,028,515	8,890,191	2,087,449
0	418	1,078,983	1,058,933	9,949,124	1,058,933

\*Numbers were calculated using the Area and Volume Statistics tool in 3D Analyst

## Tributary Streamflow

LAKE DATA flow		flow		flow		flow		flow	
		Sabin Inlet= PM-23		Wynne NW inlet = PM-24		Wynne SE inlet = PM-25		Wynne outlet	
Parameter		cfs		cfs		estimate only		cfs	
7/9/2009		NA (data file was lost)		1.04		not enough flow for MM		31.9	
7/29/2009	0.87" on 7/21	38.2		1.90		0.2 to 0.8 L/s		54.2	
8/21/2009		82.8		5.74				40.1	
9/22/2009		12.1		0.76				14.6	
11/4/2009		84.8	MM not operating properly			0.2 to 0.5 L/s		82.0	
Avg. (1/2 DL for ND)		54.5							
Std. Dev.		35.5							
min		12.1							
max		84.8							

3,980,084 m3	epilimnion
29567	min flow (m3/d)
207428	max flow
4.5 T (months), min	
19 T (days), max	

## Flushing Rates (Estimated)

Date, stratification	Sabin Lake		Wynne Lake	
	Flushing Rate (times/month)	Hydraulic Residence Time (days)	Flushing Rate (times/month)	Hydraulic Residence Time (days)
6/25/2009, 0-4m	4.9	6.3	3.9	7.7
7/29/2009, 0-4m	0.85	36	0.83	37
8/21/09, 0-6m	1.5	20	0.46	67
9/23/09, 0-6m	0.23	135	0.55	56
11/4/09, whole lake	1.5	20	0.61	50
Average		43.4		43.3
St. Deviation		52.1		22.6

## **ATTACHMENT C**

### **Listing of Data from Additional Baseline Monitoring in 2009 by Sample Location and Sampling Date**

Table 1 – Streams (Sites PM11, PM12, PM13, PM19, PM20)

Table 2 – Lakes and Tributary Streams (Sites PM21, PM22, PM23, PM24, PM25)

Table 3 – Sulfur Isotope Data Summary

**Table 1  
Stream Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

Sys Loc Code Sample Date Sample Type Code			PM-11 7/9/2009 N	PM-11 7/21/2009 N      FD		PM-11 7/28/2009 N      FD		PM-11 8/20/2009 FD	PM-11 8/20/2009 N
Chemical Name	Total or Dissolved	Analysis Location							
General Parameters									
Carbon, dissolved organic	Dissolved	NTS	11.7 mg/l	9.8 mg/l	9.8 mg/l	12.0 mg/l	11.0 mg/l	12.1 mg/l	12.1 mg/l
Chloride	Dissolved	NTS	--	--	--	--	--	--	--
Chloride	Total	NTS	8.71 mg/l	10.4 mg/l	10.4 mg/l	11.5 mg/l	11.5 mg/l	14.3 mg/l	14.2 mg/l
Color	Total	NTS	--	--	--	--	--	70 color units	70 color units
Phosphate, Ortho	Total	NTS	< 0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l
Phosphorus, total	Dissolved	NTS	0.009 mg/l	0.008 mg/l	0.007 mg/l	0.007 mg/l	0.007 mg/l	0.012 mg/l	0.013 mg/l
Solids, total suspended	Total	NTS	< 1 mg/l	2.4 mg/l	2.4 mg/l	4 mg/l	2.4 mg/l	2.4 mg/l	6 mg/l
Sulfate	Dissolved	NTS	--	--	--	--	--	--	--
Sulfate	Total	NTS	147 mg/l	151 mg/l	150 mg/l	150 mg/l	150 mg/l	141 mg/l	140 mg/l
Sulfide	Total	CAS	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l
Metals									
Iron	Dissolved	NTS	106 ug/l	80 ug/l	86.5 ug/l	133 ug/l	122 ug/l	168 ug/l	178 ug/l
Mercury	Dissolved	NTS	1.4 ng/l	1.9 ng/l	1.4 ng/l	1.6 ng/l	1.3 ng/l	1.2 ng/l	2.5 ng/l
Mercury Blank, field filters *	Dissolved	NTS	< 0.5 ng/l	< 0.5 ng/l		< 0.5 ng/l			< 0.5 ng/l
Mercury methyl	Dissolved	CAS	0.21 ng/l	< 0.1 ng/l	0.11 ng/l	0.14 ng/l	0.15 ng/l	0.31 ng/l	0.30 ng/l

\* NTS lab water passed through filter (Nalgene 0.45 um #166-0045) in the field.

**Table 1  
Stream Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

Sys Loc Code			PM-11		PM-11	PM-11
Sample Date			8/26/2009		9/10/2009	9/10/2009
Sample Type Code			N	FD	FD	N
Chemical Name	Total or Dissolved	Analysis Location				
General Parameters						
Carbon, dissolved organic	Dissolved	NTS	13.3 mg/l	13.3 mg/l	12.6 mg/l	12.0 mg/l
Chloride	Dissolved	NTS	14.3 mg/l	14.2 mg/l	--	--
Chloride	Total	NTS	14.4 mg/l	14.4 mg/l	17.4 mg/l	17.4 mg/l
Color	Total	NTS	70 color units	70 color units	70 color units	70 color units
Phosphate, Ortho	Total	NTS	< 0.02 mg/l	0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l
Phosphorus, total	Dissolved	NTS	0.013 mg/l	0.011 mg/l	0.01 mg/l	0.012 mg/l
Solids, total suspended	Total	NTS	< 1 mg/l	2.8 mg/l	< 1 mg/l	1.6 mg/l
Sulfate	Dissolved	NTS	124 mg/l	122 mg/l	--	--
Sulfate	Total	NTS	124 mg/l	--	155 mg/l	155 mg/l
Sulfide	Total	CAS	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l
Metals						
Iron	Dissolved	NTS	218 ug/l	214 ug/l	190 ug/l	185 ug/l
Mercury	Dissolved	NTS	1.1 ng/l	1.7 ng/l	1.4 ng/l	1.6 ng/l
Mercury Blank, field filters *	Dissolved	NTS	< 0.5 ng/l			< 0.5 ng/l
Mercury methyl	Dissolved	CAS	0.55 ng/l	0.24 ng/l	0.13 ng/l	0.19 ng/l

\* NTS lab water passed through filter (Nalgene 0.45 um #166-0045) in the field.

**Table 1  
Stream Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

Sys Loc Code Sample Date Sample Type Code			PM-11 10/13/2009		PM-11 11/3/2009		PM-12 7/9/2009	PM-12 7/21/2009	PM-12 7/28/2009
			N	FD	N	FD	N	N	N
Chemical Name	Total or Dissolved	Analysis Location							
General Parameters									
Carbon, dissolved organic	Dissolved	NTS	8.7 mg/l	8.8 mg/l	10.5 mg/l	10.6 mg/l	24.8 mg/l	20.2 mg/l	24.4 mg/l
Chloride	Dissolved	NTS	--	--	--	--	--	--	--
Chloride	Total	NTS	25.4 mg/l	25.4 mg/l	19.9 mg/l	19.9 mg/l	3.85 mg/l	7.72 mg/l	5.05 mg/l
Color	Total	NTS	40 color units	45 color units	75 color units	75 color units	--	--	--
Phosphate, Ortho	Total	NTS	< 0.07 mg/l	< 0.07 mg/l	< 0.02 mg/l	< 0.02 mg/l	0.03 mg/l	0.03 mg/l	0.02 mg/l
Phosphorus, total	Dissolved	NTS	0.005 mg/l	0.006 mg/l	0.007 mg/l	0.008 mg/l	0.024 mg/l	0.016 mg/l	0.016 mg/l
Solids, total suspended	Total	NTS	< 1 mg/l	1.6 mg/l	1.6 mg/l	2.4 mg/l	2.5 mg/l	2.4 mg/l	3.2 mg/l
Sulfate	Dissolved	NTS	--	--	--	--	--	--	--
Sulfate	Total	NTS	188 mg/l	188 mg/l	159 mg/l	160 mg/l	< 1 mg/l	< 1 mg/l	1.05 mg/l
Sulfide	Total	CAS	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l
Metals									
Iron	Dissolved	NTS	81.6 ug/l	82.9 ug/l	240 * ug/l	363 * ug/l	2490 ug/l	2090 ug/l	2500 ug/l
Mercury	Dissolved	NTS	0.6 ng/l	0.8 ng/l	1.6 ng/l	1.7 ng/l	3.3 ng/l	2.6 ng/l	4.3 ng/l
Mercury Blank, field filters *	Dissolved	NTS	< 0.5 ng/l		< 0.5 ng/l		< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l
Mercury methyl	Dissolved	CAS	0.13 ng/l	0.12 ng/l	0.19 ng/l	0.12 ng/l	0.57 ng/l	0.54 ng/l	0.65 ng/l

\* NTS lab water passed through filter (Nalgene 0.45 um #166-0045) in the field.

**Table 1  
Stream Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

Sys Loc Code			PM-12	PM-12	PM-12	PM-12	PM-12	PM-13	PM-13
Sample Date			8/20/2009	8/26/2009	9/10/2009	10/13/2009	11/3/2009	7/9/2009	7/21/2009
Sample Type Code			N	N	N	N	N	N	N
Chemical Name	Total or Dissolved	Analysis Location							
General Parameters									
Carbon, dissolved organic	Dissolved	NTS	27.2 mg/l	29.0 mg/l	22.8 mg/l	15.6 mg/l	21.1 mg/l	20.7 mg/l	17.6 mg/l
Chloride	Dissolved	NTS	--	5.9 mg/l	--	--	--	--	--
Chloride	Total	NTS	5.46 mg/l	6.1 mg/l	5.86 mg/l	7.41 mg/l	6 mg/l	3.08 mg/l	4.12 mg/l
Color	Total	NTS	200 color units	400 color units	200 color units	140 color units	200 color units	--	--
Phosphate, Ortho	Total	NTS	0.02 mg/l	0.03 mg/l	0.02 mg/l	< 0.07 mg/l	< 0.02 mg/l	0.03 mg/l	0.02 mg/l
Phosphorus, total	Dissolved	NTS	0.035 mg/l	0.029 mg/l	0.026 mg/l	0.01 mg/l	0.014 mg/l	0.018 mg/l	0.009 mg/l
Solids, total suspended	Total	NTS	4 mg/l	1.2 mg/l	< 1 mg/l	2 mg/l	1.2 mg/l	8 mg/l	8.4 mg/l
Sulfate	Dissolved	NTS	--	1.07 mg/l	--	--	--	--	--
Sulfate	Total	NTS	1.73 mg/l	< 1 mg/l	1.18 mg/l	1.4 mg/l	3.61 mg/l	47.2 mg/l	48.3 mg/l
Sulfide	Total	CAS	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l
Metals									
Iron	Dissolved	NTS	2350 ug/l	4290 ug/l	3740 ug/l	1200 ug/l	968 ug/l	1850 ug/l	878 ug/l
Mercury	Dissolved	NTS	5.0 ng/l	4.3 ng/l	3.2 ng/l	1.5 ng/l	3.7 ng/l	2.9 ng/l	3.1 ng/l
Mercury Blank, field filters *	Dissolved	NTS	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l
Mercury methyl	Dissolved	CAS	0.63 ng/l	2.7 ng/l	0.32 ng/l	0.21 ng/l	0.12 ng/l	0.37 ng/l	0.27 ng/l

\* NTS lab water passed through filter (Nalgene 0.45 um #166-0045) in the field.

**Table 1  
Stream Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

Sys Loc Code			PM-13	PM-13	PM-13	PM-13	PM-13	PM-13	PM-19
Sample Date			7/28/2009	8/20/2009	8/26/2009	9/10/2009	10/13/2009	11/3/2009	7/9/2009
Sample Type Code			N	N	N	N	N	N	N
Chemical Name	Total or Dissolved	Analysis Location							
General Parameters									
Carbon, dissolved organic	Dissolved	NTS	22.0 mg/l	29.6 mg/l	27.2 mg/l	24.7 mg/l	16.3 mg/l	21.5 mg/l	16.8 mg/l
Chloride	Dissolved	NTS	--	--	4.55 mg/l	--	--	--	--
Chloride	Total	NTS	4.17 mg/l	4.03 mg/l	4.54 mg/l	5.06 mg/l	6.81 mg/l	6.77 mg/l	9.43 mg/l
Color	Total	NTS	--	260 color units	240 color units	200 color units	140 color units	170 color units	--
Phosphate, Ortho	Total	NTS	0.03 mg/l	0.03 mg/l	0.03 mg/l	0.03 mg/l	< 0.07 mg/l	< 0.02 mg/l	0.03 mg/l
Phosphorus, total	Dissolved	NTS	0.012 mg/l	0.021 mg/l	0.02 mg/l	0.018 mg/l	0.01 mg/l	0.028 mg/l	0.022 mg/l
Solids, total suspended	Total	NTS	8 mg/l	6.7 mg/l	9.2 mg/l	8.8 mg/l	2.8 mg/l	2.4 mg/l	19.5 mg/l
Sulfate	Dissolved	NTS	--	--	31.4 mg/l	--	--	--	--
Sulfate	Total	NTS	37.3 mg/l	25.9 mg/l	31.4 mg/l	27.4 mg/l	44.2 mg/l	45.8 mg/l	10.1 mg/l
Sulfide	Total	CAS	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l
Metals									
Iron	Dissolved	NTS	1330 ug/l	--	1640 ug/l	1770 ug/l	1010 ug/l	812 ug/l	331 ug/l
Mercury	Dissolved	NTS	3.3 ng/l	3.1 ng/l	4.1 ng/l	3.4 ng/l	1.5 ng/l	3.5 ng/l	1.8 ng/l
Mercury Blank, field filters *	Dissolved	NTS	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l
Mercury methyl	Dissolved	CAS	0.29 ng/l	0.62 ng/l	0.76 ng/l	0.46 ng/l	0.27 ng/l	0.23 ng/l	0.60 ng/l

\* NTS lab water passed through filter (Nalgene 0.45 um #166-0045) in the field.



**Table 1  
Stream Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

Sys Loc Code			PM-19	PM-19	PM-19	PM-19	PM-19	PM-19	PM-19
Sample Date			7/21/2009	7/28/2009	8/20/2009	8/26/2009	9/10/2009	10/13/2009	11/3/2009
Sample Type Code			N	N	N	N	N	N	N
Chemical Name	Total or Dissolved	Analysis Location							
General Parameters									
Carbon, dissolved organic	Dissolved	NTS	13.7 mg/l	16.2 mg/l	17.7 mg/l	17.2 mg/l	15.7 mg/l	11.1 mg/l	15.6 mg/l
Chloride	Dissolved	NTS	--	--	--	9.59 mg/l	--	--	--
Chloride	Total	NTS	8.75 mg/l	8.95 mg/l	9.27 mg/l	9.79 mg/l	11.4 mg/l	17.3 mg/l	16.4 mg/l
Color	Total	NTS	--	--	85 color units	100 color units	70 color units	50 color units	90 color units
Phosphate, Ortho	Total	NTS	0.02 mg/l	< 0.02 mg/l	0.02 mg/l	< 0.02 mg/l	0.02 mg/l	< 0.07 mg/l	< 0.02 mg/l
Phosphorus, total	Dissolved	NTS	0.016 mg/l	0.015 mg/l	0.028 mg/l	0.023 mg/l	0.02 mg/l	0.014 mg/l	0.015 mg/l
Solids, total suspended	Total	NTS	2.4 mg/l	2.4 mg/l	5.2 mg/l	< 1 mg/l	< 1 mg/l	10 mg/l	1.2 mg/l
Sulfate	Dissolved	NTS	--	--	--	8.3 mg/l	--	--	--
Sulfate	Total	NTS	18.4 mg/l	15.9 mg/l	7.82 mg/l	6.91 mg/l	7.69 mg/l	33.6 mg/l	40.6 mg/l
Sulfide	Total	CAS	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l
Metals									
Iron	Dissolved	NTS	318 ug/l	306 ug/l	355 ug/l	314 ug/l	422 ug/l	242 ug/l	259 ug/l
Mercury	Dissolved	NTS	1.4 ng/l	2.1 ng/l	1.8 ng/l	1.8 ng/l	1.4 ng/l	0.6 ng/l	1.9 ng/l
Mercury Blank, field filters *	Dissolved	NTS	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l
Mercury methyl	Dissolved	CAS	0.35 ng/l	0.55 ng/l	0.36 ng/l	0.67 ng/l	0.15 ng/l	< 0.1 ng/l	< 0.1 ng/l

\* NTS lab water passed through filter (Nalgene 0.45 um #166-0045) in the field.

**Table 1  
Stream Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

Sys Loc Code Sample Date Sample Type Code			PM-20 7/9/2009 N	PM-20 7/21/2009 N	PM-20 7/28/2009 N	PM-20 8/20/2009 N	PM-20 8/26/2009 N	PM-20 9/10/2009 N	PM-20 10/13/2009 N
Chemical Name	Total or Dissolved	Analysis Location							
General Parameters									
Carbon, dissolved organic	Dissolved	NTS	14.9 mg/l	13.3 mg/l	24.2 mg/l	20.7 mg/l	24.1 mg/l	18.4 mg/l	14.1 mg/l
Chloride	Dissolved	NTS	--	--	--	--	1.66 mg/l	--	--
Chloride	Total	NTS	< 0.5 mg/l	< 0.5 mg/l	1.57 mg/l	1.36 mg/l	1.62 mg/l	1.49 mg/l	1.89 mg/l
Color	Total	NTS	--	--	--	140 color units	200 color units	140 color units	130 color units
Phosphate, Ortho	Total	NTS	0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l	0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l	< 0.07 mg/l
Phosphorus, total	Dissolved	NTS	0.008 mg/l	0.008 mg/l	0.012 mg/l	0.012 mg/l	0.012 mg/l	0.011 mg/l	0.009 mg/l
Solids, total suspended	Total	NTS	2.4 mg/l	2.4 mg/l	2.4 mg/l	5.2 mg/l	2 mg/l	1.2 mg/l	5.5 mg/l
Sulfate	Dissolved	NTS	--	--	--	--	1.23 mg/l	--	--
Sulfate	Total	NTS	1.11 mg/l	1.27 mg/l	< 1 mg/l	1.82 mg/l	1.07 mg/l	1.35 mg/l	1.39 mg/l
Sulfide	Total	CAS	< 0.1 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	--	< 0.10 mg/l	< 0.10 mg/l
Metals									
Iron	Dissolved	NTS	1240 ug/l	289 ug/l	1850 ug/l	1140 ug/l	2060 ug/l	1260 ug/l	892 ug/l
Mercury	Dissolved	NTS	1.7 ng/l	1.5 ng/l	3.4 ng/l	2.6 ng/l	3.1 ng/l	2.0 ng/l	1.3 ng/l
Mercury Blank, field filters *	Dissolved	NTS	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l	< 0.5 ng/l
Mercury methyl	Dissolved	CAS	0.57 ng/l	0.19 ng/l	0.51 ng/l	0.23 ng/l	0.40 ng/l	0.16 ng/l	0.14 ng/l

\* NTS lab water passed through filter (Nalgene 0.45 um #166-0045) in the field.

**Table 1  
Stream Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

Sys Loc Code Sample Date Sample Type Code			PM-20 11/3/2009 N	Relative Percent Difference average	Relative Percent Difference count	Relative Percent Difference std. dev.	Relative Percent Difference min	Relative Percent Difference max
Chemical Name	Total or Dissolved	Analysis Location		%	%	%	%	%
General Parameters								
Carbon, dissolved organic	Dissolved	NTS	<b>23.4 mg/l</b>	<b>2.2</b>	7	3.3	0	8.7
Chloride	Dissolved	NTS	--	<b>0.7</b>	1			
Chloride	Total	NTS	<b>1.84 mg/l</b>	<b>0.10</b>	7	0.26	0	0.70
Color	Total	NTS	<b>200 color units</b>	<b>2.4</b>	5	5.4	0	12
Phosphate, Ortho	Total	NTS	< 0.02 mg/l					
Phosphorus, total	Dissolved	NTS	<b>0.014 mg/l</b>	<b>12</b>	7	6.6	0	18
Solids, total suspended	Total	NTS	<b>3.6 mg/l</b>	<b>44</b>	4	35	0	86
Sulfate	Dissolved	NTS	--					
Sulfate	Total	NTS	<b>2.05 mg/l</b>	<b>0.33</b>	6	0.37	0	0.71
Sulfide	Total	CAS	< 0.10 mg/l					
Metals								
Iron	Dissolved	NTS	<b>1160 ug/l</b>	<b>4.7</b>	6	3.1	1.6	8.6
Mercury	Dissolved	NTS	<b>4 ng/l</b>	<b>30</b>	7	21	6.1	70
Mercury Blank, field filters *	Dissolved	NTS	< 0.5 ng/l					
Mercury methyl	Dissolved	CAS	<b>0.13 ng/l</b>	<b>30</b>	6	29	3.3	78

\* NTS lab water passed through filter (Nalgene 0.45 um #166-0045) in the field.

**Table 2  
Lakes Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

Sys Loc Code			PM-21 (Sabin L.)		PM-21 (Sabin L.)	PM-21 (Sabin L.)	PM-21 (Sabin L.)	PM-21 (Sabin L.)
Sample Date			7/9/2009		7/9/2009	7/9/2009	7/29/2009	7/29/2009
Depth Interval			0 - 0	0 - 0	6.5 - 6.5	9.5 - 9.5	0 - 0	5 - 5
Depth Unit			m	m	m	m	m	m
Sample Type Code			N	FD	N	N	N	N
Chemical Name	Total or Dissolved	Analysis Location						
General Parameters								
Carbon, total organic	Dissolved	NTS	--	--	--	--	--	--
Carbon, total organic	Total	NTS	<b>19.1 mg/l</b>	<b>19.0 mg/l</b>	<b>19.3 mg/l</b>	<b>19.0 mg/l</b>	<b>17.4 mg/l</b>	<b>18.0 mg/l</b>
Chloride	Total	NTS	<b>2.97 mg/l</b>	<b>2.99 mg/l</b>	<b>2.85 mg/l</b>	<b>2.73 mg/l</b>	<b>3.14 mg/l</b>	<b>3.13 mg/l</b>
Chloride	Dissolved	NTS	--	--	--	--	--	--
Chlorophyll a	Total	NTS	<b>0.004 mg/l</b>	<b>0.006 mg/l</b>	--	--	<b>0.012 mg/l</b>	--
Color	Total	NTS	<b>170 color units</b>	<b>180 color units</b>	--	--	<b>140 color units</b>	--
Phosphate, Ortho	Total	NTS	< 0.02 mg/l	<b>0.02 mg/l</b>	<b>0.02 mg/l</b>	<b>0.02 mg/l</b>	< 0.02 mg/l	< 0.02 mg/l
Phosphorus, total	Total	NTS	<b>0.015 mg/l</b>	<b>0.014 mg/l</b>	<b>0.018 mg/l</b>	<b>0.03 mg/l</b>	<b>0.014 mg/l</b>	<b>0.016 mg/l</b>
Solids, total suspended	Total	NTS	<b>2.0 mg/l</b>	<b>2.5 mg/l</b>	<b>1.2 mg/l</b>	<b>2.0 mg/l</b>	<b>3.2 mg/l</b>	<b>1.2 mg/l</b>
Sulfate	Total	NTS	<b>22.5 mg/l</b>	<b>23.8 mg/l</b>	<b>20.2 mg/l</b>	<b>15.8 mg/l</b>	<b>24 mg/l</b>	<b>24.3 mg/l</b>
Sulfate	Dissolved	NTS	--	--	--	--	--	--
Sulfide	Total	CAS	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l
Metals								
Iron	Total	NTS	<b>1390 ug/l</b>	<b>1420 ug/l</b>	<b>1650 ug/l</b>	<b>1100 ug/l</b>	<b>1330 ug/l</b>	<b>1520 ug/l</b>
Mercury	Total	NTS	<b>5.5 ng/l</b>	<b>4.0 ng/l</b>	<b>7.7 b ng/l</b>	<b>7.3 b ng/l</b>	<b>3.2 ng/l</b>	<b>5.3 b ng/l</b>
Mercury methyl	Total	CAS	<b>0.50 ng/l</b>	<b>0.26 ng/l</b>	<b>0.36 ng/l</b>	<b>0.37 ng/l</b>	<b>0.34 ng/l</b>	<b>0.24 ng/l</b>

**Table 2  
Lakes Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

		Sys Loc Code	PM-21 (Sabin L.)	PM-21 (Sabin L.)	PM-21 (Sabin L.)	PM-21 (Sabin L.)	PM-21 (Sabin L.)	PM-21 (Sabin L.)
		Sample Date	7/29/2009	7/29/2009	8/21/2009	8/21/2009	8/21/2009	8/21/2009
		Depth Interval	7 - 7	10.5 - 10.5	0 - 0	7 - 7	10.5 - 10.5	6 - 6
		Depth Unit	m	m	m	m	m	m
		Sample Type Code	N	N	N	N	N	N
Chemical Name	Total or Dissolved	Analysis Location						
General Parameters								
Carbon, total organic	Dissolved	NTS	--	--	--	--	--	--
Carbon, total organic	Total	NTS	<b>18.3 mg/l</b>	<b>19.0 mg/l</b>	<b>19.0 mg/l</b>	<b>19.3 mg/l</b>	<b>20.7 mg/l</b>	<b>19.2 mg/l</b>
Chloride	Total	NTS	<b>2.95 mg/l</b>	<b>2.81 mg/l</b>	<b>3.55 mg/l</b>	<b>3.39 mg/l</b>	<b>3.08 mg/l</b>	<b>3.64 mg/l</b>
Chloride	Dissolved	NTS	--	--	--	--	--	--
Chlorophyll a	Total	NTS	--	--	<b>0.004 mg/l</b>	--	--	--
Color	Total	NTS	--	--	<b>140 color units</b>	<b>140 color units</b>	<b>140 color units</b>	<b>140 color units</b>
Phosphate, Ortho	Total	NTS	< 0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l
Phosphorus, total	Total	NTS	<b>0.019 mg/l</b>	<b>0.022 mg/l</b>	<b>0.018 mg/l</b>	<b>0.029 mg/l</b>	<b>0.023 mg/l</b>	<b>0.024 mg/l</b>
Solids, total suspended	Total	NTS	<b>2.4 mg/l</b>	<b>2.8 mg/l</b>	<b>2.0 mg/l</b>	<b>3.2 mg/l</b>	<b>1.6 mg/l</b>	<b>2.4 mg/l</b>
Sulfate	Total	NTS	<b>22.3 mg/l</b>	<b>16.1 mg/l</b>	<b>27 mg/l</b>	<b>24.1 mg/l</b>	<b>15.2 mg/l</b>	<b>26.8 mg/l</b>
Sulfate	Dissolved	NTS	--	--	--	--	--	--
Sulfide	Total	CAS	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l
Metals								
Iron	Total	NTS	<b>1720 ug/l</b>	<b>1270 ug/l</b>	<b>1260 ug/l</b>	<b>1430 ug/l</b>	<b>984 ug/l</b>	<b>1420 ug/l</b>
Mercury	Total	NTS	<b>5.0 b ng/l</b>	<b>6.4 b ng/l</b>	<b>2.1 ng/l</b>	<b>3.3 b ng/l</b>	<b>4.6 b ng/l</b>	<b>3.8 b ng/l</b>
Mercury methyl	Total	CAS	<b>0.25 ng/l</b>	<b>0.31 ng/l</b>	<b>0.18 ng/l</b>	<b>0.14 ng/l</b>	<b>0.26 ng/l</b>	<b>0.19 ng/l</b>

**Table 2  
Lakes Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

			PM-21 (Sabin L.)		PM-21 (Sabin L.)	PM-21 (Sabin L.)	PM-21 (Sabin L.)	PM-21 (Sabin L.)
			9/23/2009		9/23/2009	9/23/2009	9/23/2009	11/4/2009
			0 - 0	0 - 0	5 - 5	7 - 7	10 - 10	0 - 0
			m	m	m	m	m	m
Sample Type Code			N	FD	N	N	N	N
Chemical Name	Total or Dissolved	Analysis Location						
General Parameters								
Carbon, total organic	Dissolved	NTS	--	--	--	--	--	16.2 mg/l
Carbon, total organic	Total	NTS	18.2 mg/l	18.3 mg/l	18.7 mg/l	19.6 mg/l	19.7 mg/l	16.6 mg/l
Chloride	Total	NTS	4 mg/l	3.94 mg/l	3.91 mg/l	3.81 mg/l	3.25 mg/l	5.2 mg/l
Chloride	Dissolved	NTS	3.56 mg/l	3.76 mg/l	3.78 mg/l	3.65 mg/l	3.1 mg/l	--
Chlorophyll a	Total	NTS	0.011 mg/l	--	--	--	--	0.003 mg/l
Color	Total	NTS	130 color units	140 color units	150 color units	200 color units	150 color units	130 color units
Phosphate, Ortho	Total	NTS	< 0.07 mg/l	< 0.07 mg/l	< 0.07 mg/l	< 0.07 mg/l	< 0.07 mg/l	0.02 mg/l
Phosphorus, total	Total	NTS	0.025 mg/l	0.017 mg/l	0.032 mg/l	0.035 mg/l	0.017 mg/l	0.028 mg/l
Solids, total suspended	Total	NTS	1.5 mg/l	2.8 mg/l	2.4 mg/l	4.4 mg/l	< 1 mg/l	6.0 mg/l
Sulfate	Total	NTS	25.7 mg/l	25.7	26.2 mg/l	25.1 mg/l	15.8 mg/l	33.5 mg/l
Sulfate	Dissolved	NTS	22.4 mg/l	24.3 mg/l	25 mg/l	24 mg/l	14.9 mg/l	--
Sulfide	Total	CAS	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l
Metals								
Iron	Total	NTS	1230 ug/l	1210	1520 ug/l	1890 ug/l	450 ug/l	1510 ug/l
Mercury	Total	NTS	2.2 ng/l	2.4 ng/l	600 b ng/l	520 b ng/l	360 b ng/l	3.3 ng/l
Mercury methyl	Total	CAS	0.11 ng/l	0.14 ng/l	0.27 ng/l	0.17 ng/l	0.35 ng/l	0.16 ng/l

**Table 2  
Lakes Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

			Sys Loc Code	PM-21 (Sabin L.)	PM-21 (Sabin L.)	PM-21 (Sabin L.)	PM-22 (Wynne L.)	PM-22 (Wynne L.)	PM-22 (Wynne L.)
			Sample Date	11/4/2009	11/4/2009	11/4/2009	7/9/2009	7/9/2009	7/9/2009
			Depth Interval	6 - 6	9 - 9	11 - 11	0 - 0	6.5 - 6.5	9.5 - 9.5
			Depth Unit	m	m	m	m	m	m
			Sample Type Code	N	N	N	N	N	N
Chemical Name	Total or Dissolved	Analysis Location							
General Parameters									
Carbon, total organic	Dissolved	NTS	15.9 mg/l	17.6 mg/l	15.9 mg/l	--	--	--	--
Carbon, total organic	Total	NTS	16.8 mg/l	16.2 mg/l	16.8 mg/l	17.8 mg/l	17.3 mg/l	14.0 mg/l	
Chloride	Total	NTS	5.23 mg/l	5.23 mg/l	5.25 mg/l	3.06 mg/l	3.08 mg/l	4.14 mg/l	
Chloride	Dissolved	NTS	--	--	--	--	--	--	
Chlorophyll a	Total	NTS	--	--	--	0.004 mg/l	--	--	
Color	Total	NTS	140 color units	140 color units	130 color units	180 color units	--	--	
Phosphate, Ortho	Total	NTS	0.02 mg/l	0.02 mg/l	0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l	
Phosphorus, total	Total	NTS	0.035 mg/l	0.021 mg/l	0.028 mg/l	0.011 mg/l	0.01 mg/l	0.011 mg/l	
Solids, total suspended	Total	NTS	2.8 mg/l	2.8 mg/l	2.4 mg/l	1.5 mg/l	1.2 mg/l	< 1 mg/l	
Sulfate	Total	NTS	34.1 mg/l	33.7 mg/l	33.6 mg/l	18.2 mg/l	19.7 mg/l	37.7 mg/l	
Sulfate	Dissolved	NTS	--	--	--	--	--	--	
Sulfide	Total	CAS	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	
Metals									
Iron	Total	NTS	1530 ug/l	--	1480 ug/l	720 ug/l	502 ug/l	370 ug/l	
Mercury	Total	NTS	2.6 b ng/l	2.3 b ng/l	2.9 b ng/l	5.0 ng/l	9.4 b ng/l	7.9 b ng/l	
Mercury methyl	Total	CAS	0.11 ng/l	0.17 ng/l	0.19 ng/l	0.30 ng/l	0.39 ng/l	0.16 ng/l	

**Table 2  
Lakes Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

		Sys Loc Code	PM-22 (Wynne L.)	PM-22 (Wynne L.)	PM-22 (Wynne L.)	PM-22 (Wynne L.)	PM-22 (Wynne L.)	PM-22 (Wynne L.)
		Sample Date	7/29/2009	7/29/2009	7/29/2009	7/29/2009	8/21/2009	8/21/2009
		Depth Interval	0 - 0	5.5 - 5.5	7 - 7	13 - 13	0 - 0	5.5 - 5.5
		Depth Unit	m	m	m	m	m	m
		Sample Type Code	N	N	N	N	N	N
Chemical Name	Total or Dissolved	Analysis Location						
General Parameters								
Carbon, total organic	Dissolved	NTS	--	--	--	--	--	--
Carbon, total organic	Total	NTS	<b>16.3 mg/l</b>	<b>16.6 mg/l</b>	<b>16.3 mg/l</b>	<b>11.5 mg/l</b>	<b>17.0 mg/l</b>	<b>16.4 mg/l</b>
Chloride	Total	NTS	<b>3.16 mg/l</b>	<b>3.15 mg/l</b>	<b>3.34 mg/l</b>	<b>4.64 mg/l</b>	<b>3.55 mg/l</b>	<b>3.54 mg/l</b>
Chloride	Dissolved	NTS	--	--	--	--	--	--
Chlorophyll a	Total	NTS	<b>0.003 mg/l</b>	--	--	--	<b>0.006 mg/l</b>	--
Color	Total	NTS	<b>130 color units</b>	--	--	--	<b>100 color units</b>	<b>100 color units</b>
Phosphate, Ortho	Total	NTS	< 0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l
Phosphorus, total	Total	NTS	<b>0.008 mg/l</b>	<b>0.008 mg/l</b>	<b>0.008 mg/l</b>	<b>0.008 mg/l</b>	<b>0.013 mg/l</b>	<b>0.013 mg/l</b>
Solids, total suspended	Total	NTS	<b>1.5 mg/l</b>	< 1 mg/l	< 1 mg/l	< 1 mg/l	<b>1.2 mg/l</b>	< 1 mg/l
Sulfate	Total	NTS	<b>19.5 mg/l</b>	<b>19.7 mg/l</b>	<b>23 mg/l</b>	<b>46.1 mg/l</b>	<b>22.3 mg/l</b>	<b>22.4 mg/l</b>
Sulfate	Dissolved	NTS	--	--	--	--	--	--
Sulfide	Total	CAS	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l
Metals								
Iron	Total	NTS	<b>696 ug/l</b>	<b>686 ug/l</b>	<b>494 ug/l</b>	<b>263 ug/l</b>	<b>699 ug/l</b>	<b>649 ug/l</b>
Mercury	Total	NTS	<b>3.6 ng/l</b>	<b>7.0 b ng/l</b>	<b>6.7 b ng/l</b>	<b>5.4 b ng/l</b>	<b>2.2 ng/l</b>	<b>3.0 b ng/l</b>
Mercury methyl	Total	CAS	<b>0.25 ng/l</b>	<b>0.16 ng/l</b>	<b>0.16 ng/l</b>	<b>0.12 ng/l</b>	<b>0.22 ng/l</b>	< 0.1 ng/l



**Table 2  
Lakes Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

			PM-22 (Wynne L.)	PM-22 (Wynne L.)	PM-22 (Wynne L.)	PM-22 (Wynne L.)	PM-22 (Wynne L.)	PM-22 (Wynne L.)
Sys Loc Code								
Sample Date			8/21/2009	8/21/2009	9/22/2009	9/22/2009	9/22/2009	9/22/2009
Depth Interval			8 - 8	11 -11	0 - 0	5 - 5	7 - 7	11 - 11
Depth Unit			m	m	m	m	m	m
Sample Type Code			N	N	N	N	N	N
Chemical Name	Total or Dissolved	Analysis Location						
General Parameters								
Carbon, total organic	Dissolved	NTS	--	--	--	--	--	--
Carbon, total organic	Total	NTS	<b>14.4 mg/l</b>	<b>12.6 mg/l</b>	<b>16.4 mg/l</b>	<b>15.8 mg/l</b>	<b>14.1 mg/l</b>	<b>11.3 mg/l</b>
Chloride	Total	NTS	<b>4.18 mg/l</b>	<b>4.83 mg/l</b>	<b>3.6 mg/l</b>	<b>3.81 mg/l</b>	<b>4.19 mg/l</b>	<b>5.15 mg/l</b>
Chloride	Dissolved	NTS	--	--	<b>3.81 mg/l</b>	<b>3.63 mg/l</b>	<b>3.99 mg/l</b>	<b>4.87 mg/l</b>
Chlorophyll a	Total	NTS	--	--	<b>0.003 mg/l</b>	--	--	--
Color	Total	NTS	<b>80 color units</b>	<b>70 color units</b>	--	--	--	<b>150 color units</b>
Phosphate, Ortho	Total	NTS	< 0.02 mg/l	< 0.02 mg/l	< 0.07 mg/l	< 0.07 mg/l	< 0.07 mg/l	< 0.07 mg/l
Phosphorus, total	Total	NTS	<b>0.012 mg/l</b>	<b>0.013 mg/l</b>	<b>0.008 mg/l</b>	<b>0.009 mg/l</b>	<b>0.012 mg/l</b>	<b>0.014 mg/l</b>
Solids, total suspended	Total	NTS	< 1 mg/l	<b>1.2 mg/l</b>	< 1 mg/l	< 1 mg/l	<b>1.2 mg/l</b>	<b>1.6 mg/l</b>
Sulfate	Total	NTS	<b>33.9 mg/l</b>	<b>44.5 mg/l</b>	<b>24.8 mg/l</b>	<b>25.3 mg/l</b>	<b>31.5 mg/l</b>	<b>47.7 mg/l</b>
Sulfate	Dissolved	NTS	--	--	<b>23.2 mg/l</b>	<b>23.9 mg/l</b>	<b>29.7 mg/l</b>	<b>45.4 mg/l</b>
Sulfide	Total	CAS	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l
Metals								
Iron	Total	NTS	<b>358 ug/l</b>	<b>265 ug/l</b>	<b>668 ug/l</b>	<b>648 ug/l</b>	<b>386 ug/l</b>	<b>562 ug/l</b>
Mercury	Total	NTS	<b>3.1 b ng/l</b>	<b>2.5 b ng/l</b>	<b>2.8 ng/l</b>	<b>130 b ng/l</b>	<b>340 b ng/l</b>	<b>65 b ng/l</b>
Mercury methyl	Total	CAS	<b>0.21 ng/l</b>	<b>0.11 ng/l</b>	<b>0.17 ng/l</b>	<b>0.20 ng/l</b>	<b>0.21 ng/l</b>	<b>0.18 ng/l</b>

**Table 2  
Lakes Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

			Sys Loc Code	PM-22 (Wynne L.)	PM-22 (Wynne L.)	PM-22 (Wynne L.)	PM-22 (Wynne L.)	PM-23 (Emb. R.)	PM-23 (Emb. R.)
			Sample Date	11/4/2009	11/4/2009	11/4/2009	11/4/2009	7/9/2009	7/28/2009
			Depth Interval	0 - 0	6 - 6	9 - 9	11 - 11	0 - 0	0 - 0
			Depth Unit	m	m	m	m	m	m
			Sample Type Code	N	N	N	N	N	N
Chemical Name	Total or Dissolved	Analysis Location							
<b>General Parameters</b>									
Carbon, total organic	Dissolved	NTS	15.2 mg/l	15.4 mg/l	15.2 mg/l	14.6 mg/l	--	--	
Carbon, total organic	Total	NTS	15.6 mg/l	15.3 mg/l	14.7 mg/l	15.2 mg/l	19.9 mg/l	20.5 mg/l	
Chloride	Total	NTS	4.07 mg/l	4.04 mg/l	4.03 mg/l	3.98 mg/l	2.76 mg/l	4.34 mg/l	
Chloride	Dissolved	NTS	--	--	--	--	--	--	
Chlorophyll a	Total	NTS	0.002 mg/l	--	--	--	--	--	
Color	Total	NTS	100 color units	100 color units	100 color units	100 color units	--	--	
Phosphate, Ortho	Total	NTS	< 0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l	0.02 mg/l	0.02 mg/l	
Phosphorus, total	Total	NTS	0.017 mg/l	0.025 mg/l	0.021 mg/l	0.014 mg/l	0.024 mg/l	0.022 mg/l	
Solids, total suspended	Total	NTS	1.2 mg/l	1.6 mg/l	< 1 mg/l	1.6 mg/l	3.2 mg/l	4.4 mg/l	
Sulfate	Total	NTS	29 mg/l	28.2 mg/l	28 mg/l	27 mg/l	34.7 mg/l	32.9 mg/l	
Sulfate	Dissolved	NTS	--	--	--	--	--	--	
Sulfide	Total	CAS	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	--	< 0.10 mg/l	
<b>Metals</b>									
Iron	Total	NTS	703 ug/l	735 ug/l	762 ug/l	786 ug/l	3090 ug/l	2250 ug/l	
Mercury	Total	NTS	2.0 ng/l	2.5 b ng/l	2.2 b ng/l	2.2 b ng/l	2.7 ng/l	3.1 ng/l	
Mercury methyl	Total	CAS	0.11 ng/l	0.14 ng/l	0.12 ng/l	0.16 ng/l	0.32 ng/l	0.24 ng/l	

**Table 2  
Lakes Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

Sys Loc Code			PM-23 (Embarrass R.)		PM-23 (Emb. R.)	PM-23 (Emb. R.)	PM-23 (Emb. R.)	PM-24 (Narrows)
Sample Date			8/21/2009		9/23/2009	11/4/2009	7/9/2009	7/28/2009
Depth Interval			0 - 0	0 - 0	0 - 0	0 - 0	0 - 0	0 - 0
Depth Unit			m	m	m	m	m	m
Sample Type Code			N	FD	N	N	N	N
Chemical Name	Total or Dissolved	Analysis Location						
General Parameters								
Carbon, total organic	Dissolved	NTS	--	--	--	21.9 mg/l	--	--
Carbon, total organic	Total	NTS	26.1 mg/l	25.1 mg/l	16.3 mg/l	22.1 mg/l	24.4 mg/l	18.6 mg/l
Chloride	Total	NTS	4.62 mg/l	4.65 mg/l	4.03 mg/l	6.33 mg/l	1.18 mg/l	0.96 mg/l
Chloride	Dissolved	NTS	--	--	3.9 mg/l	--	--	--
Chlorophyll a	Total	NTS	--	--	--	--	--	--
Color	Total	NTS	250 color units	250 color units	150 color units	200 color units	--	--
Phosphate, Ortho	Total	NTS	0.02 mg/l	0.02 mg/l	< 0.07 mg/l	0.03 mg/l	0.02 mg/l	< 0.02 mg/l
Phosphorus, total	Total	NTS	0.035 mg/l	0.035 mg/l	0.029 mg/l	0.043 mg/l	0.032 mg/l	0.026 mg/l
Solids, total suspended	Total	NTS	8.4 mg/l	8.4 mg/l	4.0 mg/l	15.2 mg/l	2.0 mg/l	2.4 mg/l
Sulfate	Total	NTS	26.9 mg/l	26.9 mg/l	14.4 mg/l	39.5 mg/l	1.76 mg/l	1.83 mg/l
Sulfate	Dissolved	NTS	--	--	13.8 mg/l	--	--	--
Sulfide	Total	CAS	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l
Metals								
Iron	Total	NTS	2920 ug/l	2920 ug/l	3320 ug/l	2090 ug/l	1980 ug/l	1970 ug/l
Mercury	Total	NTS	3.8 ng/l	3.1 ng/l	1.9 ng/l	4.8 ng/l	4.3 ng/l	3.4 ng/l
Mercury methyl	Total	CAS	0.61 ng/l	0.65 ng/l	0.12 ng/l	0.23 ng/l	0.89 ng/l	0.39 ng/l

**Table 2  
Lakes Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

		Sys Loc Code	PM-24 (Narrows)	PM-24 (Narrows)	PM-24 (Narrows)	PM-25	PM-25	PM-25
		Sample Date	8/21/2009	9/23/2009	11/4/2009	7/28/2009	8/21/2009	11/4/2009
		Depth Interval	0 - 0	0 - 0	0 - 0	0 - 0	0 - 0	0 - 0
		Depth Unit	m	m	m	m	m	m
		Sample Type Code	N	N	N	N	N	N
Chemical Name	Total or Dissolved	Analysis Location						
General Parameters								
Carbon, total organic	Dissolved	NTS	--	--	17 mg/l	--	--	--
Carbon, total organic	Total	NTS	20.9 mg/l	22.9 mg/l	16.9 mg/l	10.5 mg/l	14.0 mg/l	14 mg/l
Chloride	Total	NTS	0.95 mg/l	1.69 mg/l	0.61 mg/l	0.68 mg/l	0.78 mg/l	1.51 mg/l
Chloride	Dissolved	NTS	--	1.56 mg/l	--	--	--	--
Chlorophyll a	Total	NTS	--	--	--	--	--	--
Color	Total	NTS	200 color units	150 color units	130 color units	--	70 color units	80 color units
Phosphate, Ortho	Total	NTS	0.02 mg/l	< 0.07 mg/l	< 0.02 mg/l	< 0.02 mg/l	< 0.02 mg/l	0.04 mg/l
Phosphorus, total	Total	NTS	0.042 mg/l	0.034 mg/l	0.021 mg/l	0.012 mg/l	0.023 mg/l	0.037 mg/l
Solids, total suspended	Total	NTS	8.8 mg/l	2.0 mg/l	2 mg/l	< 1 mg/l	2.4 mg/l	12.4 mg/l
Sulfate	Total	NTS	2.14 mg/l	3.29 mg/l	3.03 mg/l	6.42 mg/l	5.68 mg/l	11 mg/l
Sulfate	Dissolved	NTS	--	3.03 mg/l	--	--	--	--
Sulfide	Total	CAS	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l	< 0.10 mg/l
Metals								
Iron	Total	NTS	3270 ug/l	2170 ug/l	929 ug/l	143 ug/l	283 ug/l	681 ug/l
Mercury	Total	NTS	3.2 ng/l	3.5 ng/l	3.4 ng/l	4.9 ng/l	6.4 ng/l	8.1 ng/l
Mercury methyl	Total	CAS	0.77 ng/l	0.53 ng/l	0.19 ng/l	< 0.1 ng/l	0.11 ng/l	< 0.1 ng/l

**Table 2  
Lakes Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

		Sys Loc Code	Relative Percent Difference	Relative Percent Difference	Relative Percent Difference	Relative Percent Difference	Relative Percent Difference	Field Blank (NTS lab water)
		Sample Date						
		Depth Interval						
		Depth Unit						
		Sample Type Code	average	count	std. dev.	min	max	11/4/2009
Chemical Name	Total or Dissolved	Analysis Location	%	%	%	%	%	
General Parameters								
Carbon, total organic	Dissolved	NTS						
Carbon, total organic	Total	NTS	<b>1.7</b>	3	1.9	0.52	3.9	<1 mg/L
Chloride	Total	NTS	<b>0.94</b>	3	0.49	0.65	1.5	<0.5 mg/l
Chloride	Dissolved	NTS	<b>5.5</b>	1				
Chlorophyll a	Total	NTS	<b>40</b>	1				
Color	Total	NTS	<b>4.4</b>	3	3.9	0	7.4	< 5 color units
Phosphate, Ortho	Total	NTS	<b>0.0</b>	1				<0.02 mg/l
Phosphorus, total	Total	NTS	<b>15</b>	3	20	0	38	<0.004 mg/l
Solids, total suspended	Total	NTS	<b>27</b>	3	30	0	60	<1 mg/l
Sulfate	Total	NTS	<b>1.9</b>	3	3.2	0	5.6	<1 mg/l
Sulfate	Dissolved	NTS	<b>8.1</b>	1				
Sulfide	Total	CAS						< 0.10 mg/l
Metals								
Iron	Total	NTS	<b>1.2</b>	3	1.1	0	2.1	<50 ug/l
Mercury	Total	NTS	<b>20</b>	3	12	8.7	32	<0.5 ng/l
Mercury methyl	Total	CAS	<b>31</b>	3	29	6.3	63	<0.1 ng/l

**Table 2  
Lakes Data  
Monitoring for Sulfate and Methyl Mercury  
In the Embarrass River Watershed**

		Sys Loc Code	Field Blank
		Sample Date	(NTS lab water)
		Depth Interval	
		Depth Unit	
		Sample Type Code	9/22/2009
Chemical Name	Total or Dissolved	Analysis Location	
General Parameters			
Carbon, total organic	Dissolved	NTS	
Carbon, total organic	Total	NTS	<1 mg/L
Chloride	Total	NTS	<0.5 mg/l
Chloride	Dissolved	NTS	
Chlorophyll a	Total	NTS	
Color	Total	NTS	< 5 color units
Phosphate, Ortho	Total	NTS	<0.07 mg/l
Phosphorus, total	Total	NTS	<0.004 mg/l
Solids, total suspended	Total	NTS	<1 mg/l
Sulfate	Total	NTS	<1 mg/l
Sulfate	Dissolved	NTS	
Sulfide	Total	CAS	< 0.10 mg/l
Metals			
Iron	Total	NTS	<50 ug/l
Mercury	Total	NTS	<0.5 ng/l
Mercury methyl	Total	CAS	<0.1 ng/l

Data Qualifiers/Footnotes	
Qualifier	Definition
--	Not analyzed/not available.
a	Estimated value, calculated using some or all values that are estimates.
b	Potential false positive value based on blank data validation procedures.
c	Coeluting compound.
e	Estimated value, exceeded the instrument calibration range.
h	EPA recommended sample preservation, extraction or analysis holding time was exceeded.
l	Indeterminate value based on failure of blind duplicate data to meet quality assurance criteria.
j	Reported value is less than the stated laboratory quantitation limit and is considered an estimated value.
p	Relative percent difference is >40% (25% CLP pesticides) between primary and confirmation GC columns.
pp	Small peak in chromatogram below method detection limit.
r	The presence of the compound is suspect based on the ID criteria of the retention time and relative retention time obtained from the examination of the chromatograms.
s	Potential false positive value based on statistical analysis of blank sample data.
*	Estimated value, QA/QC criteria not met.
**	Unusable value, QA/QC criteria not met.
N	Sample Type: Normal
FD	Sample Type: Field Duplicate
AT	Sample chromatogram is noted to be atypical of a petroleum product.
DLND	Not detected, detection limit not determined.
DNF	Did not flash
EMPC	Estimated maximum possible concentration.
NA – (Not applicable)	NA indicates that a fractional portion of the sample is not part of the analytical testing or field collection procedures.
ND	Not detected.
TIC	Tentatively identified compound

**Attachment C, Table 3**  
**Streams and Lakes Data**  
**Monitoring for <sup>34</sup>S Isotope in the Embarrass Watershed**

		$\delta^{34}\text{S SO}_4^{2-}, \text{‰}$								
Monitoring Location*	depth (m)	7/8/2009	7/21/2009	7/28/2009	8/20/2009	8/26/2009	9/10/2009	9/22/2009	10/13/2009	11/3/2009
PM-12		**	**	**	**	**	**		**	**
PM-20		**	**	**	**	**	**		**	**
PM-19		**	40.5	**	**	**	**		33.5	20.4
PM-11		13.5	13.6	13.9	15.5	15.6	15.0		13.2	9.5
PM-11 duplicate			14.5	14.1	15.6	15.7	14.5		13.4	9.7
PM-13		11.4	11.8	14.2	**	14.6	14.2		18.2	11.7
PM-23		11.8		14.3	13.2			14.7		10.7
PM-24		**		**	**			**		**
PM-25				**	**					4.9
PM-21	0	10.1		11.0	**			12.1		12.4
PM-21 duplicate	0	9.6						12.7		
PM-21	5-6			10.9	**			12.7		12.1
PM-21	6.5-9	9.7		10.3	**			12.4		15.1
PM-21	9.5-11	10.0		*	**			9.5		13.9
PM-22	0	8.8		8.3	**			11.1		9.8
PM-22	5-6			8.8				10.2		9.8
PM-22	6.5-9	8.9		7.8	7.9			7.7		10.4
PM-22	9.5-13	7.6		6.8	7.6			7.3		10.2

\* Not all locations were sampled on all dates

\*\* Due to low sulfate concentration, isotope data unavailable.



Filtered vs. unfiltered DOC/TOC comparison

Sabin and Wynne Lakes, Nov. 4th, 2009, Neal Hines, Barr Engineering, NTS is the lab

Nov. 4th 2009

Sample	TOC mg/L	DOC (0.45um Nalgene filter) mg/L	% Diff.
lake data			
PM21 0m Sabin	16.6	16.2	2.4%
PM21 6m	16.8	15.9	5.5%
PM21 9m	16.2	17.6	-8.3%
PM21 11m	16.8	15.9	5.5%
PM22 Wynne	15.6	15.2	2.6%
PM22 6m	15.3	15.4	-0.7%
PM22 9m	14.7	15.2	-3.3%
PM22 11m	15.2	14.6	4.0%
inlets to lakes			
PM23 Sabin Inlet	22.1	21.9	0.9%
PM24 NW inlet to Wynne	16.9	17.0	-0.6%

(Just for comparisons, temporally)

Higher Lake Productivity

Aug. 21 2009

TOC

mg/L

---

---

19

19.2

19.3

20.7

17

16.4

14.4

12.6

26.1

20.9

# **ATTACHMENT D**

## **Statistical Analysis Results**

## Attachment D

### **PolyMet Stream and Lake Surface Water Samples Collected in 2009 from Sites with Low Sulfate (Background) and Elevated Sulfate:**

#### **Statistical Analysis of Methylmercury Concentrations and Percent that is Methylmercury**

1	Pair-wise Analyses.....	2
1.1	Individual Site Comparisons.....	2
1.2	Power Tests.....	15
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# 1 Pair-wise Analyses

## 1.1 Individual Site Comparisons

### Assumptions for individual site comparisons

PM12 and PM20 are low sulfate sites; PM11 and PM19 are high sulfate sites

PM12 is upstream; PM13 is downstream

All analyses are paired

### 1.1.1 Methylmercury Concentrations

#### Paired analysis of PM11 and PM19 – high sulfate sites [MeHg concentration]

```
> shapiro.test(MeHg[location=="PM11"]-MeHg[location=="PM19"])
```

Shapiro-Wilk normality test

data: MeHg[location == "PM11"] - MeHg[location == "PM19"]

W = 0.8848, p-value = **0.2092**

*No deviation from normality*

```
> t.test(MeHg[location=="PM11"],MeHg[location=="PM19"],paired=TRUE,conf.level=0.95)
```

Paired t-test

data: MeHg[location == "PM11"] and MeHg[location == "PM19"]

t = -2.048, df = 7, p-value = **0.07977**

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

**-0.32453856 0.02328856**

sample estimates:

mean of the differences

-0.150625

*The two sites do not have significantly different MeHg concentrations at p=0.05 level*

```
> t.test(MeHg[location=="PM11"],MeHg[location=="PM19"],paired=TRUE,conf.level=0.9)
```

Paired t-test

data: MeHg[location == "PM11"] and MeHg[location == "PM19"]

t = -2.048, df = 7, p-value = 0.07977

alternative hypothesis: true difference in means is not equal to 0

90 percent confidence interval:

**-0.28996761 -0.01128239**

sample estimates:

mean of the differences

-0.150625

*The two sites have marginally different MeHg concentrations at p=0.1 level*

#### Paired analysis of PM12 and PM20 – low sulfate sites [MeHg concentration]

```
> shapiro.test(MeHg[location=="PM12"]-MeHg[location=="PM20"])
```

Shapiro-Wilk normality test

data: MeHg[location == "PM12"] - MeHg[location == "PM20"]

W = 0.5945, p-value = **0.0001371**  
*Significant deviation from normality*

```
> t.test(MeHg[location=="PM12"],MeHg[location=="PM20"],paired=TRUE,conf.level=0.95)
```

Paired t-test

data: MeHg[location == "PM12"] and MeHg[location == "PM20"]

t = 1.5622, df = 7, p-value = **0.1622**

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

**-0.2189492 1.0714492**

sample estimates:

mean of the differences

0.42625

```
> t.test(MeHg[location=="PM12"],MeHg[location=="PM20"],paired=TRUE,conf.level=0.9)
```

Paired t-test

data: MeHg[location == "PM12"] and MeHg[location == "PM20"]

t = 1.5622, df = 7, p-value = 0.1622

alternative hypothesis: true difference in means is not equal to 0

90 percent confidence interval:

**-0.09069499 0.94319499**

sample estimates:

mean of the differences

0.42625

```
> wilcox.test(MeHg[location=="PM12"],MeHg[location=="PM20"],paired=TRUE,conf.level=0.95)
```

Wilcoxon signed rank test with continuity correction

data: MeHg[location == "PM12"] and MeHg[location == "PM20"]

V = 27, p-value = **0.03461**

alternative hypothesis: true location shift is not equal to 0

*The two sites have significantly different MeHg concentrations when using the non-parametric test*

### **Paired analysis of PM11 and PM12 [MeHg concentration]**

```
> shapiro.test(MeHg[location=="PM11"]-MeHg[location=="PM12"])
```

Shapiro-Wilk normality test

data: MeHg[location == "PM11"] - MeHg[location == "PM12"]

W = 0.6623, p-value = **0.000839**

*Significant deviation from normality is evident*

```
t.test(MeHg[location=="PM11"],MeHg[location=="PM12"],paired=TRUE,conf.level=0.95)
```

Paired t-test

data: MeHg[location == "PM11"] and MeHg[location == "PM12"]

t = -1.9778, df = 7, p-value = **0.08847**

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

**-1.1430875 0.1018375**

sample estimates:

mean of the differences

**-0.520625**

```
> t.test(MeHg[location=="PM11"],MeHg[location=="PM12"],paired=TRUE,conf.level=0.9)
  Paired t-test
data: MeHg[location == "PM11"] and MeHg[location == "PM12"]
t = -1.9778, df = 7, p-value = 0.08847
alternative hypothesis: true difference in means is not equal to 0
90 percent confidence interval:
-1.01935292 -0.02189708
sample estimates:
mean of the differences
-0.520625

> wilcox.test(MeHg[location=="PM11"],MeHg[location=="PM12"],paired=TRUE,conf.level=0.95)
  Wilcoxon signed rank test
data: MeHg[location == "PM11"] and MeHg[location == "PM12"]
V = 1, p-value = 0.01563
alternative hypothesis: true location shift is not equal to 0
The two sites are significantly different at the p = 0.05 level when using the non-parametric test
```

#### **Paired analysis of PM11 and PM20 [MeHg concentration]**

```
> shapiro.test(MeHg[location=="PM11"]-MeHg[location=="PM20"])
  Shapiro-Wilk normality test
data: MeHg[location == "PM11"] - MeHg[location == "PM20"]
W = 0.7914, p-value = 0.02313
Deviation from normality

> t.test(MeHg[location=="PM11"],MeHg[location=="PM20"],paired=TRUE,conf.level=0.95)
  Paired t-test
data: MeHg[location == "PM11"] and MeHg[location == "PM20"]
t = -1.5405, df = 7, p-value = 0.1673
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-0.23923732 0.05048732
sample estimates:
mean of the differences
-0.094375

> t.test(MeHg[location=="PM11"],MeHg[location=="PM20"],paired=TRUE,conf.level=0.9)
  Paired t-test
data: MeHg[location == "PM11"] and MeHg[location == "PM20"]
t = -1.5405, df = 7, p-value = 0.1673
alternative hypothesis: true difference in means is not equal to 0
90 percent confidence interval:
-0.21044124 0.02169124
sample estimates:
mean of the differences
-0.094375

> wilcox.test(MeHg[location=="PM11"],MeHg[location=="PM20"],paired=TRUE,conf.level=0.95)
  Wilcoxon signed rank test with continuity correction
data: MeHg[location == "PM11"] and MeHg[location == "PM20"]
```

V = 7, p-value = **0.2719**  
alternative hypothesis: true location shift is not equal to 0  
*No significant difference*

**Paired analysis of PM19 and PM12 [MeHg concentration]**

> shapiro.test(MeHg[location=="PM19"]-MeHg[location=="PM12"])

Shapiro-Wilk normality test

data: MeHg[location == "PM19"] - MeHg[location == "PM12"]

W = 0.5486, p-value = **3.941e-05**

*Significant deviation from normality*

> t.test(MeHg[location=="PM19"],MeHg[location=="PM12"],paired=TRUE,conf.level=0.95)

Paired t-test

data: MeHg[location == "PM19"] and MeHg[location == "PM12"]

t = -1.5466, df = 7, p-value = **0.1659**

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-0.9356947 0.1956947

sample estimates:

mean of the differences

**-0.37**

> t.test(MeHg[location=="PM19"],MeHg[location=="PM12"],paired=TRUE,conf.level=0.9)

Paired t-test

data: MeHg[location == "PM19"] and MeHg[location == "PM12"]

t = -1.5466, df = 7, p-value = 0.1659

alternative hypothesis: true difference in means is not equal to 0

90 percent confidence interval:

**-0.8232446 0.0832446**

sample estimates:

mean of the differences

-0.37

> wilcox.test(MeHg[location=="PM19"],MeHg[location=="PM12"],paired=TRUE,conf.level=0.95)

Wilcoxon signed rank test

data: MeHg[location == "PM19"] and MeHg[location == "PM12"]

V = 1, p-value = **0.01563**

alternative hypothesis: true location shift is not equal to 0

*The MeHg concentrations at the sites are significantly different when using the non-parametric test*

**Paired analysis of PM19 and PM20 [MeHg concentration]**

> shapiro.test(MeHg[location=="PM19"]-MeHg[location=="PM20"])

Shapiro-Wilk normality test

data: MeHg[location == "PM19"] - MeHg[location == "PM20"]

W = 0.9483, p-value = **0.6938**

*No significant deviation from normality*

> t.test(MeHg[location=="PM19"],MeHg[location=="PM20"],paired=TRUE,conf.level=0.95)

Paired t-test



```
data: MeHg[location == "PM19"] and MeHg[location == "PM20"]
t = 1.2857, df = 7, p-value = 0.2394
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-0.04720231 0.15970231
sample estimates:
mean of the differences
0.05625
No significant difference
```

```
> t.test(MeHg[location=="PM19"],MeHg[location=="PM20"],paired=TRUE,conf.level=0.9)
Paired t-test
data: MeHg[location == "PM19"] and MeHg[location == "PM20"]
t = 1.2857, df = 7, p-value = 0.2394
alternative hypothesis: true difference in means is not equal to 0
90 percent confidence interval:
-0.02663781 0.13913781
sample estimates:
mean of the differences
0.05625
```

### MeHg by location (upstream/downstream)

#### Paired analysis of downstream (PM13) and upstream (PM12)

```
> shapiro.test(MeHgLocDiff)
Shapiro-Wilk normality test
data: MeHgLocDiff
W = 0.6642, p-value = 0.0008801
Data violates assumption of normality
```

```
> t.test(MeHgDown,MeHgUp,paired=TRUE,conf.level=0.95)
Paired t-test
data: MeHgDown and MeHgUp
t = -1.276, df = 7, p-value = 0.2427
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-0.8809283 0.2634283
sample estimates:
mean of the differences
-0.30875
```

```
> t.test(MeHgDown,MeHgUp,paired=TRUE,conf.level=0.8)
Paired t-test
data: MeHgDown and MeHgUp
t = -1.276, df = 7, p-value = 0.2427
alternative hypothesis: true difference in means is not equal to 0
80 percent confidence interval:
-0.65112523 0.03362523
sample estimates:
mean of the differences
-0.30875
```

```
> wilcox.test(MeHgDown,MeHgUp,paired=TRUE,conf.level=0.95)
Wilcoxon signed rank test
data: MeHgDown and MeHgUp
V = 9, p-value = 0.25
alternative hypothesis: true location shift is not equal to 0
Median difference between MeHg concentrations at upstream and downstream sites is statistically indistinguishable from zero
```

### **MeHg by location Paired analysis of downstream (PM13) and upstream (PM12) during normal conditions**

```
> shapiro.test(MeHgLocNFDiff)
Shapiro-Wilk normality test
data: MeHgLocNFDiff
W = 0.8855, p-value = 0.3349

> t.test(MeHgDownNF,MeHgUpNF,paired=TRUE,conf.level=0.95)
Paired t-test
data: MeHgDownNF and MeHgUpNF
t = 0.3301, df = 4, p-value = 0.7579
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-0.1481985 0.1881985
sample estimates:
mean of the differences
0.02
```

```
> t.test(MeHgDownNF,MeHgUpNF,paired=TRUE,conf.level=0.8)
Paired t-test
data: MeHgDownNF and MeHgUpNF
t = 0.3301, df = 4, p-value = 0.7579
alternative hypothesis: true difference in means is not equal to 0
80 percent confidence interval:
-0.07288244 0.11288244
sample estimates:
mean of the differences
0.02

Mean difference between MeHg concentrations at upstream and downstream sites is statistically indistinguishable from zero during normal conditions
```

### **MeHg by location Paired analysis of downstream (PM13) and upstream (PM12) during rain (storm) events**

```
> shapiro.test(MeHgLocFIDiff)
Shapiro-Wilk normality test
data: MeHgLocFIDiff
W = 0.7903, p-value = 0.09154

> t.test(MeHgDownFl,MeHgUpFl,paired=TRUE,conf.level=0.95)
Paired t-test
```

data: MeHgDownFl and MeHgUpFl  
t = -1.5797, df = 2, p-value = **0.2549**  
alternative hypothesis: true difference in means is not equal to 0  
95 percent confidence interval:  
**-3.189950 1.476616**  
sample estimates:  
mean of the differences  
-0.8566667

```
> t.test(MeHgDownFl,MeHgUpFl,paired=TRUE,conf.level=0.8)
Paired t-test
```

data: MeHgDownFl and MeHgUpFl  
t = -1.5797, df = 2, p-value = **0.2549**  
alternative hypothesis: true difference in means is not equal to 0  
80 percent confidence interval:  
**-1.879217 0.165884**  
sample estimates:  
mean of the differences  
-0.8566667

*Mean difference between MeHg concentrations at upstream and downstream sites is zero during rain (storm) events*

## 1.1.2 Percent that is Methylmercury

### Paired analysis of PM11 and PM19 – high sulfate sites [percent that is methyl]

```
> shapiro.test(pctMe[location=="PM11"]-pctMe[location=="PM19"])
```

Shapiro-Wilk normality test

data: pctMe[location == "PM11"] - pctMe[location == "PM19"]

W = 0.9265, p-value = **0.4844**

*No deviation from normality*

```
> t.test(pctMe[location=="PM11"],pctMe[location=="PM19"],paired=TRUE,conf.level=0.95)
Paired t-test
```

data: pctMe[location == "PM11"] and pctMe[location == "PM19"]

t = -1.5804, df = 7, p-value = **0.1580**

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

**-15.900082 3.160526**

sample estimates:

mean of the differences

-6.369778

*The two sites do not have significantly different percent that is methyl*

```
> t.test(pctMe[location=="PM11"],pctMe[location=="PM19"],paired=TRUE,conf.level=0.9)
```

Paired t-test

data: pctMe[location == "PM11"] and pctMe[location == "PM19"]

t = -1.5804, df = 7, p-value = 0.1580

alternative hypothesis: true difference in means is not equal to 0

90 percent confidence interval:

**-14.005625 1.266069**

sample estimates:

mean of the differences

-6.369778

### **Paired analysis of PM12 and PM20 – low sulfate sites [percent that is methyl]**

```
> shapiro.test(pctMe[location=="PM12"]-pctMe[location=="PM20"])
```

Shapiro-Wilk normality test

data: pctMe[location == "PM12"] - pctMe[location == "PM20"]

W = 0.7425, p-value = **0.006744**

*Significant deviation from normality is evident*

```
> t.test(pctMe[location=="PM12"],pctMe[location=="PM20"],paired=TRUE,conf.level=0.95)
```

Paired t-test

data: pctMe[location == "PM12"] and pctMe[location == "PM20"]

t = 0.9463, df = 7, p-value = **0.3755**

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

**-9.522488 22.229360**

sample estimates:

mean of the differences

6.353436

```
> t.test(pctMe[location=="PM12"],pctMe[location=="PM20"],paired=TRUE,conf.level=0.9)
```

Paired t-test

data: pctMe[location == "PM12"] and pctMe[location == "PM20"]

t = 0.9463, df = 7, p-value = 0.3755

alternative hypothesis: true difference in means is not equal to 0

90 percent confidence interval:

**-6.366634 19.073506**

sample estimates:

mean of the differences

6.353436

```
> wilcox.test(pctMe[location=="PM12"],pctMe[location=="PM20"],paired=TRUE,conf.level=0.95)
```

Wilcoxon signed rank test

data: pctMe[location == "PM12"] and pctMe[location == "PM20"]

V = 28, p-value = **0.1953**

alternative hypothesis: true location shift is not equal to 0

*The two sites do not have significantly different percent that is methyl*

### **Paired analysis of PM11 and PM12 [percent that is methyl]**

```
> shapiro.test(pctMe[location=="PM11"]-pctMe[location=="PM12"])
```

Shapiro-Wilk normality test

data: pctMe[location == "PM11"] - pctMe[location == "PM12"]

W = 0.811, p-value = 0.03753

*Violation of normality*

```
> t.test(pctMe[location=="PM11"],pctMe[location=="PM12"],paired=TRUE,conf.level=0.95)
```

Paired t-test

data: pctMe[location == "PM11"] and pctMe[location == "PM12"]

t = -1.118, df = 7, p-value = **0.3005**

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

**-16.869717 6.038424**

sample estimates:

mean of the differences

**-5.415647**

```
> t.test(pctMe[location=="PM11"],pctMe[location=="PM12"],paired=TRUE,conf.level=0.9)
```

Paired t-test

data: pctMe[location == "PM11"] and pctMe[location == "PM12"]

t = -1.118, df = 7, p-value = 0.3005

alternative hypothesis: true difference in means is not equal to 0

90 percent confidence interval:

**-14.592850 3.761557**

sample estimates:

mean of the differences

-5.415647

```
> wilcox.test(pctMe[location=="PM11"],pctMe[location=="PM12"],paired=TRUE,conf.level=0.95)
```

Wilcoxon signed rank test

data: pctMe[location == "PM11"] and pctMe[location == "PM12"]

V = 14, p-value = **0.6406**

alternative hypothesis: true location shift is not equal to 0

*No significant difference is detected*

### **Paired analysis of PM11 and PM20 [percent that is methyl]**

```
> shapiro.test(pctMe[location=="PM11"]-pctMe[location=="PM20"])
```

Shapiro-Wilk normality test

data: pctMe[location == "PM11"] - pctMe[location == "PM20"]

W = 0.9454, p-value = **0.6649**

*No deviation from normality*

```
> t.test(pctMe[location=="PM11"],pctMe[location=="PM20"],paired=TRUE,conf.level=0.95)
```

Paired t-test

data: pctMe[location == "PM11"] and pctMe[location == "PM20"]

t = 0.2465, df = 7, p-value = **0.8123**

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-8.057158 9.932737

sample estimates:

mean of the differences

0.9377896

*No significant difference*

```
> t.test(pctMe[location=="PM11"],pctMe[location=="PM20"],paired=TRUE,conf.level=0.9)
```

Paired t-test

```
data: pctMe[location == "PM11"] and pctMe[location == "PM20"]
t = 0.2465, df = 7, p-value = 0.8123
alternative hypothesis: true difference in means is not equal to 0
90 percent confidence interval:
-6.269121 8.144700
sample estimates:
mean of the differences
0.9377896
```

**Paired analysis of PM19 and PM12 [percent that is methyl]**

```
> shapiro.test(pctMe[location=="PM19"]-pctMe[location=="PM12"])
Shapiro-Wilk normality test
data: pctMe[location == "PM19"] - pctMe[location == "PM12"]
W = 0.9088, p-value = 0.3459
No deviation from normality
```

```
> t.test(pctMe[location=="PM19"],pctMe[location=="PM12"],paired=TRUE,conf.level=0.95)
Paired t-test
data: pctMe[location == "PM19"] and pctMe[location == "PM12"]
t = 0.2122, df = 7, p-value = 0.838
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-9.680576 11.588839
sample estimates:
mean of the differences
0.9541315
No significant difference
```

```
> t.test(pctMe[location=="PM19"],pctMe[location=="PM12"],paired=TRUE,conf.level=0.9)
Paired t-test
data: pctMe[location == "PM19"] and pctMe[location == "PM12"]
t = 0.2122, df = 7, p-value = 0.838
alternative hypothesis: true difference in means is not equal to 0
90 percent confidence interval:
-7.566583 9.474846
sample estimates:
mean of the differences
0.9541315
```

**Paired analysis of PM19 and PM20 [percent that is methyl]**

```
> shapiro.test(pctMe[location=="PM19"]-pctMe[location=="PM20"])
Shapiro-Wilk normality test
data: pctMe[location == "PM19"] - pctMe[location == "PM20"]
W = 0.8933, p-value = 0.251
No significant deviation from normality
```

```
> t.test(pctMe[location=="PM19"],pctMe[location=="PM20"],paired=TRUE,conf.level=0.95)
Paired t-test
data: pctMe[location == "PM19"] and pctMe[location == "PM20"]
```

t = 2.2713, df = 7, p-value = **0.05737**  
alternative hypothesis: true difference in means is not equal to 0  
95 percent confidence interval:  
-0.3002701 14.9154054  
sample estimates:  
mean of the differences  
7.307568  
*No significant difference at the p=0.05 level*

```
> t.test(pctMe[location=="PM19"],pctMe[location=="PM20"],paired=TRUE,conf.level=0.9)
Paired t-test
data: pctMe[location == "PM19"] and pctMe[location == "PM20"]
t = 2.2713, df = 7, p-value = 0.05737
alternative hypothesis: true difference in means is not equal to 0
90 percent confidence interval:
1.212034 13.403101
sample estimates:
mean of the differences
7.307568
Marginal difference at the p=0.1 level
```

**Percent that is methyl by location (upstream/downstream)**  
**Paired analysis of downstream (PM13) and upstream (PM12)**

```
> shapiro.test(pctMeLocDiff)
Shapiro-Wilk normality test
data: pctMeLocDiff
W = 0.7565, p-value = 0.00963
Data violates the assumption of normality
```

```
> t.test(pctMeDown,pctMeUp,paired=TRUE,conf.level=0.95)
Paired t-test
data: pctMeDown and pctMeUp
t = -1.0333, df = 7, p-value = 0.3359
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-20.100539 7.875895
sample estimates:
mean of the differences
-6.112322
```

```
> t.test(pctMeDown,pctMeUp,paired=TRUE,conf.level=0.8)
Paired t-test
data: pctMeDown and pctMeUp
t = -1.0333, df = 7, p-value = 0.3359
alternative hypothesis: true difference in means is not equal to 0
80 percent confidence interval:
-14.482473 2.257829
sample estimates:
mean of the differences
-6.112322
```

```
> wilcox.test(pctMeDown,pctMeUp,paired=TRUE,conf.level=0.95)
Wilcoxon signed rank test
data: pctMeDown and pctMeUp
V = 12, p-value = 0.4609
alternative hypothesis: true location shift is not equal to 0
Median difference between percent that is methyl at upstream and downstream sites is statistically indistinguishable from zero
```

**Percent that is methyl by location Paired analysis of downstream (PM13) and upstream (PM12) during normal conditions**

```
> shapiro.test(pctMeLocDiff[flushing==0])
Shapiro-Wilk normality test
data: pctMeLocDiff[flushing == 0]
W = 0.8492, p-value = 0.192
```

```
> t.test(pctMeDown[flushing==0],pctMeUp[flushing==0],paired=TRUE,conf.level=0.95)
Paired t-test
data: pctMeDown[flushing == 0] and pctMeUp[flushing == 0]
t = 1.4018, df = 4, p-value = 0.2336
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-2.695330 8.192726
sample estimates:
mean of the differences
2.748698
```

```
> t.test(pctMeDown[flushing==0],pctMeUp[flushing==0],paired=TRUE,conf.level=0.8)
Paired t-test
data: pctMeDown[flushing == 0] and pctMeUp[flushing == 0]
t = 1.4018, df = 4, p-value = 0.2336
alternative hypothesis: true difference in means is not equal to 0
80 percent confidence interval:
-0.2575988 5.7549950
sample estimates:
mean of the differences
2.748698
```

*Mean difference between percent that is methyl at upstream and downstream sites is statistically indistinguishable from zero during normal conditions*

**Percent that is methyl by location Paired analysis of downstream (PM13) and upstream (PM12) during rain (storm) events**

```
> shapiro.test(pctMeLocDiff[flushing==1])
Shapiro-Wilk normality test
data: pctMeLocDiff[flushing == 1]
W = 0.8604, p-value = 0.2686
```

```
> t.test(pctMeDown[flushing==1],pctMeUp[flushing==1],paired=TRUE,conf.level=0.95)
Paired t-test
```



data: pctMeDown[flushing == 1] and pctMeUp[flushing == 1]  
t = -1.7691, df = 2, p-value = **0.2189**  
alternative hypothesis: true difference in means is not equal to 0  
95 percent confidence interval:  
**-71.66592 29.90454**  
sample estimates:  
mean of the differences  
-20.88069

```
> t.test(pctMeDown[flushing==1],pctMeUp[flushing==1],paired=TRUE,conf.level=0.8)
```

Paired t-test

data: pctMeDown[flushing == 1] and pctMeUp[flushing == 1]  
t = -1.7691, df = 2, p-value = **0.2189**  
alternative hypothesis: true difference in means is not equal to 0  
80 percent confidence interval:  
**-43.137086 1.375709**  
sample estimates:  
mean of the differences  
-20.88069

*Mean difference between percent that is methyl at upstream and downstream sites is statistically indistinguishable from zero during rain (storm) events*

## 1.2 Power Tests

### Power tests for pair-wise analyses

*For n=8*

```
> power.t.test(n=8,delta=1,sig.level=0.05,type="paired",alternative="two.sided",strict=TRUE)
```

Paired t test power calculation

n = 8

delta = 1

sd = 1

sig.level = 0.05

power = **0.680834**

alternative = two.sided

NOTE: n is number of \*pairs\*, sd is std.dev. of \*differences\* within pairs

```
> power.t.test(n=8,delta=1,sig.level=0.1,type="paired",alternative="two.sided",strict=TRUE)
```

Paired t test power calculation

n = 8

delta = 1

sd = 1

sig.level = 0.1

power = **0.8150305**

alternative = two.sided

*For n=5*

```
> power.t.test(n=5,delta=1,sig.level=0.05,type="paired",alternative="two.sided",strict=TRUE)
```

Paired t test power calculation

n = 5

delta = 1

sd = 1

sig.level = 0.05

power = **0.4013899**

alternative = two.sided

NOTE: n is number of \*pairs\*, sd is std.dev. of \*differences\* within pairs

```
> power.t.test(n=5,delta=1,sig.level=0.1,type="paired",alternative="two.sided",strict=TRUE)
```

Paired t test power calculation

n = 5

delta = 1

sd = 1

sig.level = 0.1

power = **0.5799045**

alternative = two.sided

NOTE: n is number of \*pairs\*, sd is std.dev. of \*differences\* within pairs

*For n=3*

```
> power.t.test(n=3,delta=1,sig.level=0.05,type="paired",alternative="two.sided",strict=TRUE)
```

Paired t test power calculation

n = 3

```
delta = 1
sd = 1
sig.level = 0.05
power = 0.1792554
alternative = two.sided
```

NOTE: n is number of \*pairs\*, sd is std.dev. of \*differences\* within pairs

```
> power.t.test(n=3,delta=1,sig.level=0.1,type="paired",alternative="two.sided",strict=TRUE)
```

Paired t test power calculation

```
n = 3
delta = 1
sd = 1
sig.level = 0.1
power = 0.3231872
alternative = two.sided
```

NOTE: n is number of \*pairs\*, sd is std.dev. of \*differences\* within pairs

## 2 Analysis of Variance

### 2.1 Methylmercury Concentration

#### 2.1.1 Analysis by Sulfate Status

```
> shapiro.test(MeHg[location=="PM11"])
Shapiro-Wilk normality test
data: MeHg[location == "PM11"]
W = 0.8869, p-value = 0.219
```

```
> shapiro.test(MeHg[location=="PM19"])
Shapiro-Wilk normality test
data: MeHg[location == "PM19"]
W = 0.9037, p-value = 0.3121
```

```
> shapiro.test(MeHg[location=="PM12"])
Shapiro-Wilk normality test
data: MeHg[location == "PM12"]
W = 0.6468, p-value = 0.0005562
```

```
> shapiro.test(MeHg[location=="PM20"])
Shapiro-Wilk normality test
data: MeHg[location == "PM20"]
W = 0.8405, p-value = 0.07619
```

*Data from PM12 violated the assumption of normality; however, repeated measures ANOVA is robust to such violations*

#### One-way repeated measures ANOVA (parametric analysis)

If PM11 and PM19 represent high sulfate, and PM20 and PM12 represent low sulfate

```
> aov.mod1<-aov(MeHg~impact+Error(date/impact),data=W)
> summary(aov.mod1)
```

```
Error: date
      Df  Sum Sq  Mean Sq  F value  Pr(>F)
Residuals  7    2.5178    0.35968
Error: date:impact
      Df  Sum Sq  Mean Sq  F value  Pr(>F)
impact  1    0.43129    0.43129    4.1204  0.08193 .
Residuals  7    0.73269    0.10467
```

```
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
Error: Within
```

```
      Df  Sum Sq  Mean Sq  F value  Pr(>F)
Residuals  16    3.0536    0.19085
```

*Sulfate status does not have a significant effect on the mean MeHg concentration at the p=0.05 level.*

```
> print(model.tables(aov.mod1,"means"),digits=3)
```

Tables of means

Grand mean

0.3882812

impact

**impact**

0 1

**0.504 0.272**

*The direction of the non-significant effect is negative. High sulfate sites have lower MeHg concentrations.*

## 2.1.2 Analysis by Mining Status and Rain (storm) Event Status

Mine status ("mine impact") = 0 for background sites; 1 for elevated sulfate concentration

Storm status = 0 for non-storm sampling event; 1 for storm event sampling

### Two-way ANOVA with one repeated measure (parametric analysis)

If PM11 and PM19 represent high sulfate sites, and PM20 and PM12 represent low sulfate sites

```
> aov.mod3<-aov(MeHg~impact*flushing+Error(date/impact),data=W)
```

```
> summary(aov.mod3)
```

Error: date

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
flushing	1	0.84714	0.84714	3.0424	0.1317
Residuals	6	1.67065	0.27844		

Error: date:impact

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
impact	1	0.43129	0.43129	5.5201	<b>0.0571 .</b>
impact:flushing	1	0.26391	0.26391	3.3777	<b>0.1157</b>
Residuals	6	0.46879	0.07813		

---

Signif. codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

Error: Within

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Residuals	16	3.0536	0.19085		

*The likelihood of a sulfate status effect increases after accounting for flushing events, but this is statistically insignificant. Additionally, mining status interacting with flushing status does not have a significant effect on the mean MeHg concentration.*

```
> print(model.tables(aov.mod3,"means"),digits=3)
```

Tables of means

Grand mean

0.3882812

impact

impact

0 1

0.504 0.272

flushing

flushing

0 1

```
0.262 0.598
impact:flushing
      flushing
impact 0      1
      0 0.308 0.832
      1 0.216 0.365
```

*The direction of the non-significant interactive effect maximizes the differences in MeHg concentration between high-sulfate and low-sulfate sites*

## 2.2 Percent that is Methylmercury

### 2.2.1 Analysis by Sulfate Status

```
> shapiro.test(pctMe[location=="PM11"])
Shapiro-Wilk normality test
data: pctMe[location == "PM11"]
W = 0.9296, p-value = 0.5121
```

```
> shapiro.test(pctMe[location=="PM19"])
Shapiro-Wilk normality test
data: pctMe[location == "PM19"]
W = 0.9556, p-value = 0.7669
```

```
> shapiro.test(pctMe[location=="PM12"])
Shapiro-Wilk normality test
data: pctMe[location == "PM12"]
W = 0.697, p-value = 0.002081
```

```
> shapiro.test(pctMe[location=="PM20"])
Shapiro-Wilk normality test
data: pctMe[location == "PM20"]
W = 0.803, p-value = 0.03086
```

*Data from PM12 and PM20 violated the assumption of normality; however, repeated measures ANOVA is robust to such violations*

#### One-way repeated measures ANOVA (parametric analysis)

If PM11 and PM19 represent high sulfate sites, and PM20 and PM12 represent low sulfate sites

```
> aov.mod4<-aov(pctMe~impact+Error(date/impact),data=W)
> summary(aov.mod4)
```

```
Error: date
      Df  Sum Sq  Mean Sq  F value  Pr(>F)
Residuals  7    2498.8    356.96
Error: date:impact
      Df  Sum Sq  Mean Sq  F value  Pr(>F)
impact  1     7.159    7.1587  0.4977  0.5033
Residuals  7    100.677    14.3824
Error: Within
      Df  Sum Sq  Mean Sq  F value  Pr(>F)
Residuals  16    2040.7    127.55
```

*Sulfate status does not have a significant effect on the mean percent that is methyl.*

```
> print(model.tables(aov.mod4,"means"),digits=3)
Tables of means
Grand mean
```

```
16.77028
  impact
impact
0      1
16.30 17.24
```

## 2.2.2 Analysis by Mining Status and Rain (Storm) Event Status

Mine status ("mine impact") = 0 for background sites; 1 for elevated sulfate concentration  
 Storm status = 0 for non-storm sampling event; 1 for storm event sampling

### Two-way ANOVA with one repeated measure (parametric analysis)

```
> summary(aov.mod6)
```

```
Error: date
```

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
flushing	1	643.63	643.63	2.0817	0.1992
Residuals	6	1855.12	309.19		

```
Error: date:impact
```

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
impact	1	7.159	7.1587	0.5610	<b>0.4822</b>
impact:flushing	1	24.107	24.1074	1.8891	<b>0.2184</b>
Residuals	6	76.570	12.7616		

```
Error: Within
```

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Residuals	16	2040.7	127.55		

*None of the factors investigated has a significant effect on the mean percent that is methyl. Including the interaction reduces the likelihood of rejecting the null hypothesis that impact status has an effect on methylmercury concentrations.*

```
> print(model.tables(aov.mod6,"means"),digits=3)
```

```
Tables of means
```

```
Grand mean
```

```
16.77028
  impact
  impact
0      1
16.30 17.24
```

```
flushing
```

```
flushing
```

```
0      1
```

```
13.30 22.56
```

```
impact:flushing
```

```
  flushing
```

```
impact 0      1
```

```
  0  12.15 23.21
```

```
  1  14.44 21.91
```

*The interactive effect does not significantly change the relationship between impact status and percent that is methyl.*



### 3 Trends in Concentrations in the Embarrass River (Upstream / Downstream)

#### 3.1 Methylmercury Concentration

Determination that use of surface MeHg concentration at PM21 and PM22 is representative of MeHg throughout water column

##### PM 21

*The data from 7/9/2009 was left out of this analysis because of a missing value that unbalanced the repeated-measures ANOVA*

```
> shapiro.test(MeHg[depth.prox=="a"])
      Shapiro-Wilk normality test
data:  MeHg[depth.prox == "a"]
W = 0.8501, p-value = 0.1949
```

```
> shapiro.test(MeHg[depth.prox=="b"])
      Shapiro-Wilk normality test
data:  MeHg[depth.prox == "b"]
W = 0.9965, p-value = 0.9967
```

```
> shapiro.test(MeHg[depth.prox=="c"])
      Shapiro-Wilk normality test
data:  MeHg[depth.prox == "c"]
W = 0.8519, p-value = 0.2004
```

```
> shapiro.test(MeHg[depth.prox=="d"])
      Shapiro-Wilk normality test
data:  MeHg[depth.prox == "d"]
W = 0.98, p-value = 0.9022
```

*None of the depths violated the assumption of normality*

```
> mlm.depth.PM21.aov<-
Anova(mlm.depth.PM21, idata=data.frame(depth.factor), idesign=~depth.factor, type="III")
> summary(mlm.depth.PM21.aov, multivariate=FALSE)
```

Univariate Type III Repeated-Measures ANOVA Assuming Sphericity						
	SS	num Df	Error SS	den Df	F	Pr(>F)
(Intercept)	0.74822	1	0.035725	3	62.8321	0.004187 **
depth.factor	0.02107	3	0.026375	9	2.3972	<b>0.135567</b>

---  
Signif. codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

Mauchly Tests for Sphericity

	Test statistic	p-value
depth.factor	0.00035355	<b>0.036157</b>

Greenhouse-Geisser and Huynh-Feldt Corrections  
for Departure from Sphericity

GG eps	Pr(>F[GG])
--------	------------

```
depth.factor    0.40734    0.2078
                HF eps    Pr(>F[HF])
depth.factor    0.54144    0.1882
```

*There is no statistically significant trend in MeHg concentration over the depth of the lake (PM21). We use the Greenhouse-Geisser correction here because sphericity is violated and the epsilon is below 0.75.*

## PM22

```
> shapiro.test(MeHg[depth.prox=="a"])
  Shapiro-Wilk normality test
data:  MeHg[depth.prox == "a"]
W = 0.9905, p-value = 0.9814
```

```
> shapiro.test(MeHg[depth.prox=="b"])
  Shapiro-Wilk normality test
data:  MeHg[depth.prox == "b"]
W = 0.9166, p-value = 0.5084
```

```
> shapiro.test(MeHg[depth.prox=="c"])
  Shapiro-Wilk normality test
data:  MeHg[depth.prox == "c"]
W = 0.8788, p-value = 0.3040
```

```
> shapiro.test(MeHg[depth.prox=="d"])
  Shapiro-Wilk normality test
data:  MeHg[depth.prox == "d"]
W = 0.9157, p-value = 0.513
```

*None of the depths violated the assumption of normality*

```
> mlm.depth.PM22.aov<-
Anova(mlm.depth.PM22,idata=data.frame(depth.factor),idesign=~depth.factor,type="III")
> summary(mlm.depth.PM22.aov,multivariate=FALSE)
Univariate Type III Repeated-Measures ANOVA Assuming Sphericity
```

	SS	num Df	Error SS	den Df	F	Pr(>F)
(Intercept)	0.41281	1	0.0078688	3	157.3844	0.001092 **
depth.factor	0.00717	3	0.0244563	9	0.8794	<b>0.487388</b>

---  
Signif. codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

Mauchly Tests for Sphericity

	Test statistic	p-value
depth.factor	0.16835	<b>0.7326</b>

Greenhouse-Geisser and Huynh-Feldt Corrections  
for Departure from Sphericity

	GG eps	Pr(>F[GG])
depth.factor	0.54744	0.45
	HF eps	Pr(>F[HF])
depth.factor	1.1218	0.4874

Warning message:

In summary.Anova.mlm(mlm.depth.PM22.aov, multivariate = FALSE) :

HF eps > 1 treated as 1

*There is no statistically significant trend in MeHg concentration over the depth of the lake (PM22)*

### Determination of the relationship between sulfate and MeHg in PM21 and PM22

#### PM21

```
> MeHgSO4.PM21.mod<-lm(MeHg~SO4,data=lake.depth.wSO4[1:20,])
> summary(MeHgSO4.PM21.mod)
```

Call:

```
lm(formula = MeHg ~ SO4, data = lake.depth.wSO4[1:20, ])
```

Residuals:

Min	1Q	Median	3Q	Max
-0.105229	-0.034361	-0.003187	0.040898	0.125069

Coefficients:

	Estimate	Std. Error	t value	Pr(> t )
(Intercept)	0.49134	0.06221	7.899	4.34e-07 ***
SO4	-0.01021	0.00246	-4.152	<b>0.000668</b> ***

---

Signif. codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.06465 on 17 degrees of freedom

(1 observation deleted due to missingness)

Multiple R-squared: 0.5035, Adjusted R-squared: 0.4743

F-statistic: 17.24 on 1 and 17 DF, p-value: 0.0006677

*Linear regression shows a significant negative relationship between SO4 concentration and MeHg concentration in PM21.*

#### PM22

```
> MeHgSO4.PM22.mod<-lm(MeHg~SO4,data=lake.depth.wSO4[21:40,])
> summary(MeHgSO4.PM22.mod)
```

Call:

```
lm(formula = MeHg ~ SO4, data = lake.depth.wSO4[21:40, ])
```

Residuals:

Min	1Q	Median	3Q	Max
-0.151068	-0.040646	-0.003875	0.039029	0.180137

Coefficients:

	Estimate	Std. Error	t value	Pr(> t )
(Intercept)	0.274028	0.055674	4.922	0.000129 ***
SO4	-0.003257	0.001842	-1.769	<b>0.094903</b> .

---

Signif. codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.07202 on 17 degrees of freedom

(1 observation deleted due to missingness)

Multiple R-squared: 0.1554, Adjusted R-squared: 0.1057

F-statistic: 3.128 on 1 and 17 DF, p-value: 0.0949

*Linear regression shows a marginally significant negative relationship between SO4 concentration and MeHg concentration in PM22.*

**One-way repeated measures ANOVA (parametric analysis) of upstream-downstream trend**

*Note: Data from sampling on 7/21/2009, 8/26/2009, and 10/13/2009 were removed from the PM12 and PM13 series. Additionally, it was assumed that the 9/10/2009 data for these sites could be matched to the 9/16/2009 data at PM23, PM21, and PM22. Both of these steps were done in order to be able to properly match the data by date (repeated measures analysis).*

```
> shapiro.test(MeHg[loc.num==1])
      Shapiro-Wilk normality test
data:  MeHg[loc.num == 1]
W = 0.8592, p-value = 0.2255
```

```
> shapiro.test(MeHg[loc.num==2])
      Shapiro-Wilk normality test
data:  MeHg[loc.num == 2]
W = 0.9618, p-value = 0.8208
```

```
> shapiro.test(MeHg[loc.num==3])
      Shapiro-Wilk normality test
data:  MeHg[loc.num == 3]
W = 0.868, p-value = 0.2584
```

```
> shapiro.test(MeHg[loc.num==4])
      Shapiro-Wilk normality test
data:  MeHg[loc.num == 4]
W = 0.859, p-value = 0.2247
```

```
> shapiro.test(MeHg[loc.num==5])
      Shapiro-Wilk normality test
data:  MeHg[loc.num == 5]
W = 0.9905, p-value = 0.9814
```

*No sampling sites violate the assumption of normality at the p = 0.05 level.*

```
> mlm1.aov<-Anova(mlm1,ldata=data.frame(loc.factor),idesign=~loc.factor,type="III")
> summary(mlm1.aov,multivariate=FALSE)
```

Univariate Type III Repeated-Measures ANOVA Assuming Sphericity

	SS	num Df	Error SS	den Df	F	Pr(>F)
(Intercept)	2.58245	1	0.26664	4	38.7412	0.003393 **
loc.factor	0.21822	4	0.26342	16	3.3135	0.037028 *

```
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Mauchly Tests for Sphericity

	Test statistic	p-value
loc.factor	0.00021653	<b>0.038286</b>

Greenhouse-Geisser and Huynh-Feldt Corrections for Departure from Sphericity

	GG eps	Pr(>F[GG])
loc.factor	0.61782	0.07224 .

```
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
      HF eps      Pr(>F[HF])
```

loc.factor 1.6936 **0.03703** \*

---

Signif. codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

*Assumption of sphericity is violated. Pr(>F[HF]) gives p-value corrected for non-sphericity*

> mlm1

Call:

lm(formula = MatrixMeHg ~ 1)

Coefficients:

	[,1]	[,2]	[,3]	[,4]	[,5]
<b>(Intercept)</b>	<b>0.458</b>	<b>0.394</b>	<b>0.308</b>	<b>0.237</b>	<b>0.210</b>

*Location explains much of the variability in the MeHg concentrations. There is a significant negative trend (at the p=0.05 level) from upstream (PM12) to downstream (PM22).*

Removal of PM12 from the series

> mlm3.aov<-Anova(mlm3,idata=data.frame(loc.factor.ex1),idesign=~loc.factor.ex1,type="III")

> summary(mlm3.aov,multivariate=FALSE)

Univariate Type III Repeated-Measures ANOVA Assuming Sphericity

	SS	num Df	Error SS	den Df	F	Pr(>F)
(Intercept)	1.65025	1	0.13783	4	47.8924	0.002288 **
loc.factor.ex1	0.10159	3	0.17995	12	2.2583	0.133968

---

Signif. codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

Mauchly Tests for Sphericity

	Test statistic	p-value
loc.factor.ex1	0.0016991	<b>0.0063709</b>

Greenhouse-Geisser and Huynh-Feldt Corrections

for Departure from Sphericity

	GG eps	Pr(>F[GG])
loc.factor.ex1	0.52961	0.1828
	HF eps	Pr(>F[HF])
loc.factor.ex1	0.82175	<b>0.1506</b>

*Assumption of sphericity is violated. Pr(>F[HF]) gives p-value corrected for non-sphericity*

> mlm3

Call:

lm(formula = MatrixMeHgeX1 ~ 1)

Coefficients:

	[,1]	[,2]	[,3]	[,4]
<b>(Intercept)</b>	<b>0.394</b>	<b>0.308</b>	<b>0.237</b>	<b>0.210</b>

*When PM12 is removed, the significance of an upstream-downstream trend disappears. PM12 may be the major driver of an upstream-downstream MeHg gradient.*

Removal of PM12 and PM 13 from the series – Three station lakes analysis

> mlm4.aov<-Anova(mlm4,idata=data.frame(loc.factor.ex12),idesign=~loc.factor.ex12,type="III")

> summary(mlm4.aov,multivariate=FALSE)

Univariate Type III Repeated-Measures ANOVA Assuming Sphericity

	SS	num Df	Error SS	den Df	F	Pr(>F)
--	----	--------	----------	--------	---	--------

(Intercept)	0.95004	1	0.10730	4	35.4163	0.004001 **
loc.factor.ex12	0.02562	2	0.11676	8	0.8778	<b>0.452210</b>

---

Signif. codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

Mauchly Tests for Sphericity

	Test statistic	p-value
loc.factor.ex12	0.18649	<b>0.080532</b>

Greenhouse-Geisser and Huynh-Feldt Corrections  
for Departure from Sphericity

	GG eps	Pr(>F[GG])
loc.factor.ex12	0.55142	0.4092

	HF eps	Pr(>F[HF])
loc.factor.ex12	0.60648	0.4163

*Sphericity is not violated. Unadjusted p-value is appropriate.*

> mlm4

Call:

lm(formula = MatrixMeHgex12 ~ 1)

Coefficients:

	[,1]	[,2]	[,3]
(Intercept)	<b>0.308</b>	<b>0.237</b>	<b>0.210</b>

*When PM12 and PM13 are removed, the likelihood of a trend is even more substantially reduced.*

### 3.2 Percent that is Methylmercury

#### One-way repeated measures ANOVA (parametric analysis)

*Note: Data from sampling on 7/21/2009, 8/26/2009, and 10/13/2009 were removed from the PM12 and PM13 series. Additionally, it was assumed that the 9/10/2009 data for these sites could be matched to the 9/16/2009 data at PM23, PM21, and PM22. Both of these steps were done in order to be able to properly match the data by date (repeated measures analysis).*

```
> shapiro.test(pctMe[loc.num==1])
      Shapiro-Wilk normality test
data:  pctMe[loc.num == 1]
W = 0.9455, p-value = 0.705
```

```
> shapiro.test(pctMe[loc.num==2])
      Shapiro-Wilk normality test
data:  pctMe[loc.num == 2]
W = 0.9551, p-value = 0.7738
```

```
> shapiro.test(pctMe[loc.num==3])
      Shapiro-Wilk normality test
data:  pctMe[loc.num == 3]
W = 0.9027, p-value = 0.4252
```

```
> shapiro.test(pctMe[loc.num==4])
      Shapiro-Wilk normality test
data:  pctMe[loc.num == 4]
W = 0.9407, p-value = 0.6706
```

```
> shapiro.test(pctMe[loc.num==5])
      Shapiro-Wilk normality test
data:  pctMe[loc.num == 5]
W = 0.7928, p-value = 0.07072
There are no violations of normality
```

```
> mlm2.aov<-Anova(mlm2,ldata=data.frame(loc.factor),idesign=~loc.factor,type="III")
> summary(mlm2.aov,multivariate=FALSE)
```

Univariate Type III Repeated-Measures ANOVA Assuming Sphericity

	SS	num Df	Error SS	den Df	F	Pr(>F)
(Intercept)	2320.10	1	219.62	4	42.2563	0.002889 **
loc.factor	116.85	4	157.25	16	2.9723	<b>0.051756 .</b>

---  
Signif. codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

Mauchly Tests for Sphericity

	Test statistic	p-value
loc.factor	0.0090104	<b>0.35638</b>

Greenhouse-Geisser and Huynh-Feldt Corrections  
for Departure from Sphericity

```

loc.factor      GG eps      Pr(>F[GG])
                0.54546     0.1011
loc.factor      HF eps      Pr(>F[HF])
                1.2250      0.05176 .

```

---

Signif. codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

*Assumption of sphericity is not violated. Unadjusted p-value is applicable.*

```
> mlm2
```

Call:

```
lm(formula = MatrixpctMe ~ 1)
```

Coefficients:

```

          [,1]  [,2]  [,3]  [,4]  [,5]
(Intercept) 11.646 12.329  9.792  7.496  6.903

```

*Location is not a significant predictor of variance in the percent that is methyl at a p=0.05 level. There is a marginally significant negative trend (at the p=0.1 level) from upstream to downstream.*

Removal of PM12 from the series

```
> mlm5.aov<-Anova(mlm5,idata=data.frame(loc.factor.ex1),idesign=~loc.factor.ex1,type="III")
```

```
> summary(mlm5.aov,multivariate=FALSE)
```

Univariate Type III Repeated-Measures ANOVA Assuming Sphericity

	SS	num Df	Error SS	den Df	F	Pr(>F)
(Intercept)	1667.23	1	167.206	4	39.8845	0.003215 **
loc.factor.ex1	91.52	3	91.736	12	3.9907	<b>0.034818</b> *

---

Signif. codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

Mauchly Tests for Sphericity

	Test statistic	p-value
loc.factor.ex1	0.16537	<b>0.45469</b>

Greenhouse-Geisser and Huynh-Feldt Corrections

for Departure from Sphericity

```

loc.factor.ex1  GG eps      Pr(>F[GG])
                0.51768     0.08244 .

```

---

Signif. codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

```

loc.factor.ex1  HF eps      Pr(>F[HF])
                0.78534     0.05076 .

```

---

Signif. codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

*Sphericity is not violated. Uncorrected p-value is appropriate.*

```
> mlm5
```

Call:

```
lm(formula = MatrixpctMeex1 ~ 1)
```

Coefficients:

```

          [,1]  [,2]  [,3]  [,4]
(Intercept) 12.329  9.792  7.496  6.903

```

*When PM12 is removed, the percent that is methyl trend becomes significant at the p=0.05 level.*



Removal of PM12 and PM13 from the series – Three station lakes analysis

```
> mlm6.aov<-Anova(mlm6,idata=data.frame(loc.factor.ex12),idesign=~loc.factor.ex12,type="III")
```

```
> summary(mlm6.aov,multivariate=FALSE)
```

Univariate Type III Repeated-Measures ANOVA Assuming Sphericity

	SS	num Df	Error SS	den Df	F	Pr(>F)
(Intercept)	975.38	1	95.433	4	40.8826	0.003072 **
loc.factor.ex12	23.29	2	57.350	8	1.6243	<b>0.255839</b>

---

Signif. codes: 0 '\*\*\*' 0.001 '\*\*' 0.01 '\*' 0.05 '.' 0.1 ' ' 1

Mauchly Tests for Sphericity

	Test statistic	p-value
loc.factor.ex12	0.45669	<b>0.30862</b>

Greenhouse-Geisser and Huynh-Feldt Corrections  
for Departure from Sphericity

	GG eps	Pr(>F[GG])
loc.factor.ex12	0.64796	0.2683
	HF eps	Pr(>F[HF])
loc.factor.ex12	0.8283	0.2624

*Sphericity is not violated. The uncorrected p-value is appropriate.*

```
> mlm6
```

Call:

```
lm(formula = MatrixpctMeex12 ~ 1)
```

Coefficients:

	[,1]	[,2]	[,3]
<b>(Intercept)</b>	<b>9.792</b>	<b>7.496</b>	<b>6.903</b>

*When PM12 and PM13 are removed, the likelihood that a trend exists in percent that is methyl is drastically reduced.*