CONCENTRATIONS AND LOADS OF MERCURY SPECIES IN THE GUADALUPE RIVER, SAN JOSE, CALIFORNIA:

WATER YEAR 2010

Prepared for the Santa Clara Valley Water District by San Francisco Estuary Institute

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Acknowledgements

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Executive Summary

Sampling of the Guadalupe River was undertaken during Water Year 2010 (October 1st 2009 to April 30th 2010) at the USGS gauge near Highway 101 and the USGS gauge near Almaden Expressway. The goal of this sampling was to assess progress in attaining the legacy and urban stormwater runoff mass loading allocations assigned by the San Francisco Bay mercury TMDL and the Guadalupe River Watershed TMDL. The objective was to characterize mercury concentrations during a range of flow conditions and use these data along with flow records to calculate loads. Comparisons to data collected in other water years were made, and the loads of mercury associated with sources in the watershed between the two locations were determined.

Summary of results and findings for water Year 2010:

- Concentrations of total mercury measured near Highway 101 ranged from 5-1290 ng/L. These were lower than those observed near Almaden Expressway (7.4-3590 ng/L).
- Concentrations of total methylmercury ranged from 0.06-2.51 ng/L at the lower (Highway 101) site and from 0.21-2.38 ng/L at the upper site.
- Concentrations of total and dissolved mercury and methylmercury at a given discharge were higher at the upper site than the lower site. The proportion of total mercury that was methylmercury was also higher at the upper site.
- Concentrations of total mercury and total methylmercury were elevated during high flow conditions.
- In contrast, dissolved mercury and dissolved methylmercury concentrations were greater under lower flow conditions.
- Particulate organic carbon was strongly related to suspended sediment concentration and turbidity, and correlated to total mercury and total methylmercury.
- Dissolved organic carbon was correlated to dissolved mercury and dissolved methylmercury.
- Dissolved oxygen, conductivity, pH, and temperature variation were low during the study, and unlikely affect processes known to affect mercury methylation.
- The ratio of total mercury to SSC is a good proxy for the particulate fraction of mercury.
- There was a highly significant relationship between total mercury and SSC at both the upper and lower sites. The relationship was stronger at the upper site.

Summary of estimated mercury and suspended sediment loads:

- Daily loads of suspended sediment varied from 0.278-1973 metric tonnes at the lower site and from 0.028-1127 metric tonnes at the upper site.
- Daily loads of total mercury varied from 0.3 g to 5.4 kg at the lower site and 0.04 g to 6.7 kg at the upper site.
- Maximum daily loads occurred on January 20th, 2010, the largest flow of the year. Measured concentrations of total mercury peaked during this storm at 1290 ng/L at the lower site and 3590 ng/L at the upper site.
- During the first storm, a disproportional amount of both suspended sediment and total mercury was transported through the system relative to discharge (called the seasonal first flush).
- In total, 6829 metric tonnes and 2563 metric tonnes of suspended sediment were transported through the lower and upper sites for the winter season, respectively.

- In total 14.8 kg and 12.3 kg of total mercury were transported through the lower and upper sites for the winter season, respectively.
- On average <0.44% of total mercury was transported as methylmercury at each site.
- On average, 97.7% and 96.4% of mercury transport was associated with particles at the lower and the upper sites, respectively which supports the hypotheses that the majority of mercury is associated with particulate material.

Data on suspended sediments has been collected at the lower Highway 101 site since WY 2003 (eight water years). Suspended sediment loads have varied from 2280-11768 metric tonnes annually. Total mercury loads have been measured during five of the last eight years and varied from 8-116 kg annually. The load of total mercury was the highest during water year 2003 when rainfall distribution throughout the season and intensity during specific storms appeared to have caused a greater release of mercury. During all years of observations, methylmercury and the dissolved fractions made up a small component of loads.

It is estimated that 2.5 kg of total mercury and 5.4 g of total methylmercury was sourced from the area and the channel systems between the two gauges. Land use in this area is 89% urban. Normalizing the loads by area, it is estimated that this represents about 15.6 µg of total mercury per m^2 of land area and 0.034 µg of methylmercury per m^2 of land area. These estimates fall within the range observed in other watersheds with urban land use influences despite known channel erosion associated with the multistage channel construction just downstream from the upper sampling site.

Recommendations

- Future sampling design should include the use of continuous turbidity measurement using the same time interval as discharge measurement (15 minutes). There was instrument failure for part of the year at the Highway 101 site. Even though instruments were checked and serviced prior to the start of the rainy season by the USGS, the failure still occurred.

- Future sampling and analyses should incorporate quality control samples such as duplicate field samples, field blanks, laboratory duplicates, certified reference material comparisons, and matrix spikes to provide high confidence in the data quality. Quality Assurance samples are crucial to validating the usability of any data set and identifying quality issues with data. Quality Assurance samples should be continued at the same frequency as the current project. High sensitivity methods such as EPA 1631 for total mercury and EPA 1630 should be used, especially if there remains an interest in concentrations during smaller floods and low flow conditions.

- It is recommended that the ratio of total mercury concentration to suspended sediment concentration is a reasonable surrogate for particulate mercury concentrations as a stable measure of trends in relation to TMDL targets.

- If estimated loads derived from the urban portion of the watershed are desired, continued monitoring of both sampling locations (Highway 101 and Almaden Expressway) appears to provide robust data for determination of urban loads by subtraction.

- For the purposes of monitoring for loads and trends of mercury species, it is recommended that organic carbon, DO, conductivity, temperature, pH monitoring be discontinued.

- For loads and trends analysis on an annual basis, a turbidity surrogate regression estimator using 16 samples collected over 4 storms seems most cost effective. Sampling should occur during a large early season storm, a large mid-season (December or January) storm, and several later season storms to get a representation of a whole winter season.

- The largest remaining gaps in our understanding of annual loads are for periods with rainfall intensities and runoff greater than or equal to WY 2003. Annual high effort monitoring of the Guadalupe River could therefore be discontinued and replaced with response based sampling design that would augment lower levels of effort, with RMP possibly providing a stable structure for budgeting and planning such sampling. In addition, given there is considerable effort to remove mass and implement urban best management practices, additional sampling in relation to management effort has merit. From the point of view of improving estimates of annual loading in the Guadalupe River, we see no argument for continuing high effort level every year.

- The Highway 101 location is more suitable for continued monitoring to address a greater number of questions, particularly for urban derived pollutants such as PCBs and copper, with previous data for multiple MRP POCs 2003-2006 & 2010 (dioxin 2010 only). However, for measuring trends in response to management in and adjacent to the historic mining area, with the upper station has slightly more merit given its proximity.

Introduction

Importance of stormwater as contaminant loading pathway to SF Bay

Mercury is a toxic heavy metal that accumulates to concentrations of concern in the Bay food web. Mercury exposure is one of the primary drivers behind the existing interim sport fish consumption advisory for San Francisco Bay (Office of Environmental Health Hazard Assessment, 1999). Consumption of Bay caught sportfish is allowed but the advisory recommends that adults should not eat more than two meals of San Francisco Bay caught fish per month. The advisory is more restrictive for pregnant women and children. Certain species such as herring and salmon are exempted from the advisory. Mercury is also one of the primary pollutants causing impairment of San Francisco Bay and the Guadalupe River watershed, both of which are listed as impaired on the State 303(d) list in compliance with the Clean Water Act. Mercury reaches higher concentrations in higher levels of the aquatic food web through a process called biomagnification. Predatory fish, birds, and mammals (including humans that consume fish) at the top of the food web are most vulnerable to mercury exposure. Mercury is a neurotoxicant, and is particularly hazardous to nervous system development in unborn children and children under the age of eight. Mercury enters the Bay via multiple pathways and information presently available suggests that stormwater transport via small and large tributaries accounts for the majority of annual loads.

The Guadalupe River Watershed (the Watershed) at the southern extent of San Francisco Bay, contains multiple land uses, with forest (35%) and residential (30%) land-use being predominant (Santa Clara Valley Urban Runoff Pollution Prevention Program web site). The upper portions of the watershed are less developed, while the lower portions of the watershed are more urban (Figure 1). The Guadalupe River transports water, sediment and pollutants from both the lower and upper watershed, to San Francisco Bay. The upper watershed contains the historic New Almaden Mercury Mining District. Evidence summarized in the Guadalupe River Watershed Total Maximum Daily Load (TMDL) Report (Austin et al., 2008) and San Francisco Bay Mercury TMDL report (RWQCB, 2006) suggests that, on average,106.5 kg per year of total mercury is transported to San Francisco Bay from this watershed. The majority of total mercury in the Watershed (92 kg per year or about 86%) is estimated to emanate from the historic mining district via stormwater runoff that passes down the Guadalupe Flood Control Channel, a District facility.

Regulatory/management drivers for improved loading estimates

TMDLs estimate current mercury loads from various pathways and allocate load reduction requirements, to be attained over a 20 year time frame, that will meet water quality standards. The current total mercury loading estimate for the Guadalupe River Watershed is 106.5 kg per year. The TMDL load allocation is 9.4 kg per year, which translates to a required 91% reduction in mercury loads and is based on achieving a particulate concentration of 0.2 mg Hg per kg of sediment discharged from the watershed. The implementation plan of the TMDL calls for source control in various areas of the Watershed, including mercury mining areas, reservoirs and lakes, and urban stormwater runoff (Austin et al., 2008; Basin Plan Amendment, 2008). Source control includes implementation of urban best management practices (BMPs), methylmercury controls, and erosion control measures in the mining areas.

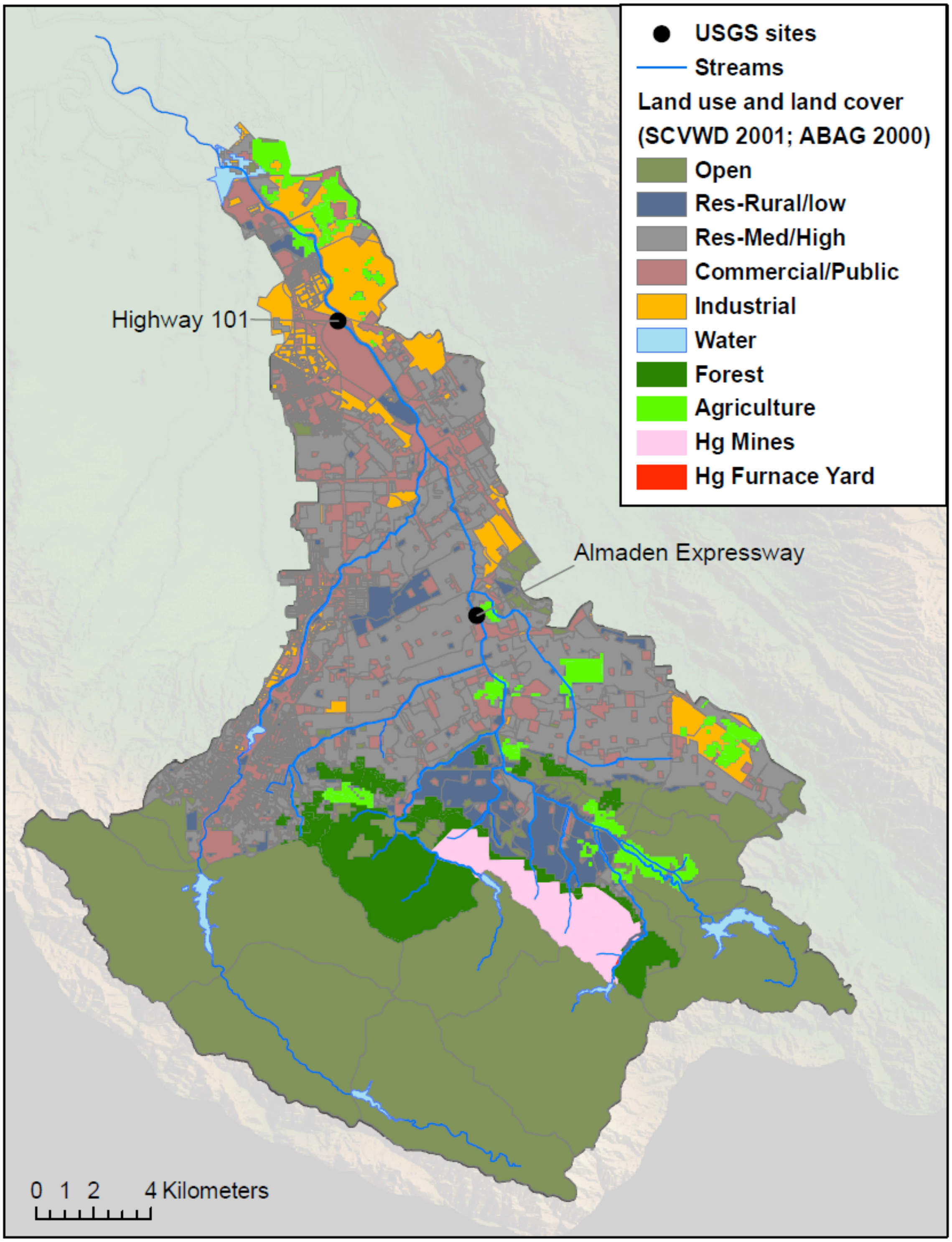

Figure 1. Map of the Guadalupe River watershed, main drainages, Almaden Expressway and Highway 101 sampling locations, and land-use/land cover. Source: Combination of ABAG 2000 and SCVWD's land use data sets.

The Santa Clara Valley Water District (SCVWD) and others are required to implement a monitoring program to measure mercury loadings from the Guadalupe River to San Francisco Bay in order to gauge progress in the attainment of total mercury load allocations identified in the San Francisco Bay and Guadalupe River Watershed Mercury TMDL reports.

The monitoring program undertaken by the District includes two locations along the Guadalupe River: one location in the upper watershed (USGS gauge station 11167800 at Almaden Expressway) and one location below San Jose (USGS gauge station 11169025 at Highway 101). The monitoring performed in Water Year 2010 (October 1, 2009 to April 30, 2010) by SFEI and described in this report fulfills the first winter season sampling of the multi-season effort.

Study objectives

The objective of this season of data collection was to characterize concentrations of mercury and its various species during a range of flow conditions at two locations and use these data, along with USGS discharge records, to calculate loads of mercury. These data and loads are compared to data that SFEI collected in water years 2003-2006. In addition, we provide an analysis of trends in loads and particle concentrations in relation to the TMDL objectives. A secondary objective was to determine the load of mercury associated with mercury sources in the watershed between the two locations.

Methods

Site descriptions

The Guadalupe River Watershed is located in the southernmost portion of San Francisco Bay. There are 50 identifiable creeks within the Watershed and the Guadalupe River is the main drainage of the system. The Guadalupe River, which forms below the confluence of Alamitos and Guadalupe Creeks, drains approximately 170 square miles of watershed (Austin et al., 2008). The Watershed is estimated to be 37% impervious with forest and residential land uses predominant (Santa Clara Valley Urban Runoff Pollution Prevention Program web site). The New Almaden Mercury Mining District, a legacy and current source of mercury, is located in the upper portion of the watershed.

Precipitation varies both within the watershed and over time. The majority of precipitation in the Watershed falls between October 1 and April 30 of each water year. Due to orographic lift, precipitation is generally higher in the upper portions of the Watershed. Total precipitation in WY 2010 at Mount Umunhum (3090 feet above sea level) was 59.3 inches (22% above the 10 year average) while precipitation in the City of San Jose was 14.5 inches (1% above the 134 year average) (Santa Clara Valley Water District precipitation data). The mean daily discharge over the sampling period was 43 ft^3/second (cfs) at the Almaden Expressway site (USGS unpublished data) and 106 cfs at the Highway 101 site.

Sample and data collection

Water samples were collected during 16 rain events and two dry weather periods during Water Year 2010 at the two Guadalupe River monitoring locations (USGS gauge station 11167800 at Almaden Expressway and USGS gauge station 1169025 at Highway 101). Samples were collected during base flow, rise, peak, and fall of 16 storm hydrographs (including the first storm of the year on 10/13/2009 – 10/14/2009) and base flow of 2 dry weather events. Samples were collected for analysis of water chemistry in the thalweg within 1 m of the turbidity probe (described below) using clean-hands protocols (Bloom, 1995). Samples were analyzed for total mercury, dissolved mercury, total methylmercury, and dissolved methylmercury, suspended sediment concentration (SSC), particulate organic carbon (POC) and dissolved organic carbon (DOC) in water.

During high river flow when wading into the center of flow is unsafe, a Teflon coated D-95 depth-integrating sampler (utilizing laboratory trace element cleaned Teflon bottle, cap, and nozzle) was deployed from the bridge platform in a single vertical deployment within 1 meter of the turbidity sensor using a b-reel attached to a four-wheel-boom-truck and crane assembly. During the wade-in stages of river flow, water samples were collected, mid channel, using a handheld DH-81 (utilizing laboratory trace element cleaned Teflon bottle, cap, and nozzle). Previous data demonstrated that sampling from the center of the channel provides a representative sample within 2% of the cross-section average (McKee et al., 2004).

Water samples were poured from the 1.0 L Teflon collection bottle into precleaned 1.0 L amber glass bottles (mercury speciation), 250 mL amber glass bottles (SSC), and 1.0 L plastic bottles (POC/DOC). Samples were labeled and placed in coolers on wet and blue ice immediately after sampling. Samples were returned to SFEI and placed in a commercial refrigerator (5°C) until shipment to the lab. All water samples for organic carbon determination were filtered for fractionation of organic carbon within 48 hours of collection time in the SFEI preparation laboratory. All samples analyzed for methylmercury and dissolved mercury were received at the laboratory within 48 hours of collection time.

The USGS maintains continuous turbidity, gauge height, and discharge monitoring equipment at the two sampling locations. Turbidity measurements were collected using a Forest Technology Systems Limited (FTS) model DTS-12 turbidity sensor equipped with an optical wiper that was installed in the thalweg using a depth-proportional boom (Eads & Thomas, 1983). The turbidity sensor was installed at the Highway 101 site and slightly downstream of the Almaden Expressway site in the weir pool of the District gauge. A Design Analyses Assoc. Inc. data logger and pressure transducer (model H350-XL) in the gauge house at the top of the left (west) bank communicates with the turbidity sensor every 15 minutes via wiring housed inside a 1 inch galvanized pipe. USGS data are downloaded from the gauge station website and are considered preliminary until the USGS completes their QAQC process. In addition, grab samples were taken during each round of sampling at the Almaden Expressway sampling site and measured for turbidity with a Hach 2100P portable turbidimeter.

Continuous ancillary water quality measurements for pH, dissolved oxygen (D0), temperature, and conductivity were taken at the Highway 101 station for the duration of each sampling event. Measurements were made utilizing a hand held YSI 556 Multiparameter Instrument.

Laboratory analytical methods

All samples for mercury and SSC analysis were shipped on ice to Moss Landing Marine Laboratories, Moss Landing, California. For analysis of total and dissolved mercury, water samples were prepared and analyzed by US EPA Method 1631 Revision E (USEPA, 2002). Upon receipt at the lab, samples were aliquoted and dissolved samples were filtered through a 0.45-µm capsule filter. Samples received beyond the 48-hour preservation holding time were retained for total mercury analysis only. Mercury samples were preserved to a final concentration of 0.5% v:v bromine monochloride (BrCl). After preservation, each aliquot was oxidized to Hg(II) with bromine monochloride (BrCL), then sequentially reduced with $NH_2OH{\cdot}HCL$ and stannous chloride to convert it to Hg(0). The Hg(0) was then purged from the solution and collected on gold traps. Finally the Hg(0) was thermally desorbed from the gold trap and carried into a cold-vapor atomic fluorescence spectrometer (CVAFS) for detection and quantification.

For analysis of total and dissolved methylmercury, water samples were prepared and analyzed using a modified US EPA Method 1630 (USEPA, 1998; Modification by MLML). Dissolved samples were filtered through a 0.45-µm capsule filter. Total and dissolved samples were acidified to a final concentration of 0.5% v:v hydrochloric acid (HCl). Methylmercury samples were stored in the dark at 4°C until analysis. Each aliquot was distilled, ethylated using sodium tetraethyl borate, and separated by purging onto a graphitic carbon trap, thermally desorbed, and pyrolytically decomposed for detection and quantification by CVAFS.

For analysis of suspended sediment concentration (SSC), water samples were prepared and analyzed using Marine Pollution Studies Lab Method 103 (MPSL, 2006). SSC samples were stored in the dark at 4°C until analysis. Glass fiber filters were prepared by rinsing with deionized water and heating for 2 hours and then preweighed. Samples were vigorously mixed, and their volume was measured with a graduated cylinder. The entire sample was passed through the filter using a vacuum pump. The filter was placed in a drying oven for 2 hours at 103-105°C, and the final filter weight was recorded and the SSC was calculated.

All water samples for particulate organic carbon (POC) and dissolved organic carbon (DOC) were filtered in the SFEI lab within 48 hours of sampling time before shipping on ice to Columbia Analytical Services (Kelso, Oregon). The particulate fraction was filtered on a pre-ashed 0.45-µm glass fiber filter (GFF) using a vacuum pump. The filtrate was collected in a clean glass graduated flask. Filters with the particulate sample fraction were wrapped in aluminum foil and placed in a freezer until shipment to the analytical laboratory. The weight of the pre-ashed filters and the volume filtered were recorded in the laboratory logbook. The filtrate from the filtered sample was poured into pre-weighed polypropylene bottles with sulfuric acid preservative. Total organic carbon (TOC) (dissolved fraction) was determined using EPA method 9060 (EPA, 2007). The method measures release of carbon dioxide by chemical oxidation of the non-volatile portion of the sample. Inorganic carbon in the sample is removed by acidification, sodium persulfate is added to the sample as an oxidant, and the sample is heated to 100°C to form carbon dioxide. Carbon dioxide is purged from solution, concentrated, and measured (by mass) with a pre-calibrated infrared detector.

Particulate organic carbon was determined using ASTM method D4192-82 modified for sediment matrices. The filter with sample was acidified to remove the inorganic carbon.

Samples were combusted in oxygen, and the combustion product gases were passed through a barium chromate catalyst/scrubber to oxidize the organic carbon to carbon dioxide. The gases were then passed through a series of scrubbers to remove interfering gases such as sulfur dioxide and NO_x. The carbon dioxide was passed into a coulometer cell filled with a partially aqueous medium containing ethanolamine and a colorimetric indicator. The solution absorbs carbon dioxide which then reacts to form a strong titratable acid. The coulometric titration was detected and measured by the colorimetric indicator.

Laboratory quality assurance and quality control

There was no blank contamination measured for mercury or methylmercury in any analytical batch. All SSC and mercury data were reported above the detection limit except for one SSC sample (a base flow sample at the season start). Four SSC samples were within 3 times the MDL, causing lower confidence in these concentrations. These data were flagged and were not used in the analysis. All mercury data passed QAQC review and were used in data analysis. Average precision for field duplicates ranged from 4% for dissolved mercury to 18% for dissolved methylmercury (Table 1). All field precision results were within the RSD target of 35% for all mercury fractions. The RSD was at or below 13% for laboratory duplicates and 10% for matrix spikes (Table 1). Certified Reference Material (CRM) and Matrix Spike (MS) percent recoveries were between 94% and 104%, again within acceptance criteria for all mercury fractions. Dissolved to total ratios averaged 12% for total mercury and 35% for methylmercury in the raw data.

No lab blanks reported any contamination for POC/DOC analyses. Precision results on lab and field replicates were within the measurement Quality Objectives (MQOs) of 5% and 10% for DOC and POC respectively. Average accuracy was 3% and 7% error in the DOC and POC blank spike samples respectively. Matrix spike samples on the dissolved fraction (DOC) had a 4% average error.

Table 1. Summary of data validation. RSD=relative standard deviation.

AnalyteName	FractionName	RSD Lab Duplicates	RSD Field Duplicates	RSD CertifiedReference Material	%Recovery CRM	RSD MatrixSpike	%Recovery MatrixSpike
Mercury	Dissolved	3.38%	3.69%			8.26%	96.82%
Mercury	Total	5.76%	9.70%	5.68%	97.22%	7.49%	94.43%
Mercury, Methyl	Dissolved	13.34%	17.92%			8.28%	100.79%
Mercury, Methyl	Total	7.94%	12.18%			10.11%	104.40%

Load estimation methods

Suspended Sediment

Loads for each analyte, at each site, were calculated for the winter months of WY 2010. Loads were estimated using the data collected during this study, in combination with 15-minute discharge and turbidity data provided by the USGS. Discharge and turbidity were used as surrogates to estimate continuous (15 minute) suspended sediment concentrations (SSC) via linear interpolation and/or regression equations (turbidity vs. SSC and discharge vs. SSC) of 15-minute USGS data and empirical data. In this study, suspended sediment loads were determined by combining the 15-minute SSC estimates derived from turbidity measurements with 15-minute discharge. The estimate of suspended sediment load is considered very accurate because the sampling regime was at a time interval sufficient to characterize almost all variability in concentrations and focused on storms when most loads are transported. There were however some notable equipment failures that impacted accuracy. Non storm loads accuracy was diminished from October 1st 2009 to January 13th 10:45 am, 2010 at the lower (Highway 101) site due to a turbidity probe malfunction. Non storm loads during this period were estimated using a discharge versus SSC regression estimator (in a similar way to the USGS standard “GCLASS” method). There was a loss of continuous discharge and turbidity data at the Almaden Expressway site from January 19th at 3:30 pm to January 20th at 3:30 pm. In this case there were spot data obtained at 1:15 am, 5 am, 10:15 am, and 1:30 pm. Linear interpolation was used to fill the data gaps between the spot data. These two exceptions impact the calculation of loads of mercury also.

Mercury species

Total mercury loads were calculated by using linear interpolation guided by changes in SSC relative to discharge (preferred method) and a combination of regression equations (turbidity vs. total mercury and SSC vs. total mercury). Knowledge of rainfall distribution and timing in addition to changes in turbidity/SSC relative to discharge were used to make decisions on the best method of interpolation. This approach goes beyond the simple application of mathematical interpolation methodologies such as combining average or weighted concentration with monthly or annual flow. Mercury concentrations estimated in these ways were then combined with 15-minute discharges to calculate loads that were then summed for each day, month, and the wet season as a whole. The method used to calculate loads of each mercury form differed depending largely on individual relationships with SSC and are less accurate than the estimate of suspended sediment load.

Total methylmercury loads were calculated by using a combination of linear interpolation (preferred and best method) and regression equations (turbidity vs. total methylmercury and SSC vs. total methylmercury). Dissolved mercury and dissolved methylmercury loads were calculated using linear interpolation and power regression equations between % dissolved concentrations and discharge.

Results

Concentrations of SSC and Mercury

Mercury mean concentrations, ranges, and detection frequencies

During water Year 2010, concentrations of total mercury measured at the lower gauge site (Highway 101) ranged between 5 and 1290 ng/L. These concentrations were lower than those observed at the upper location (Almaden Expressway) which ranged between 7.4 and 3590 ng/L (Table 2). As expected, methylmercury formed only a small component of the total mercury in the water column. Concentrations of total methylmercury ranged between 0.06 and 2.51 ng/L at the lower site and between 0.21 and 2.38 ng/L at the upper site. Only a small portion of total mercury was found be in the dissolved phase; greater than 61 percent was particulate mercury under all flow conditions. Complete measurements of turbidity and discharge, over the sampling period, with notation of when samples for mercury analysis were collected, are shown in

Figures 10-13. Peak discharge at the Highway 101 station, for each water year, is shown in Figure 14.

Influence of hydrology on concentrations

Concentrations of suspended sediments, total mercury, and methylmercury varied in direct response to rainfall-induced runoff (Figures 2 through 7). Concentrations of all of these parameters were greater during high flow, although there was some scatter about the regression relationships. In a similar manner, the portion of mercury in the particulate phase was greater during high flow conditions (Figure 8, 9). In contrast to these patterns, concentration of dissolved methylmercury was not correlated with flow.

Table 2. Summary of mercury concentrations in water for the Highway 101 and Almaden Expressway sampling sites for water year 2010. FWMC = flow-weighted mean concentration.

	Highway 101 (Lower site)	**Almaden Expressway (Upper site)**
Total mercury (ng/L)		
Minimum	5.2	7.4
Maximum	1290	3590
FWMC	274	553
Total dissolved mercury (ng/L)		
Minimum	0.64	2.1
Maximum	21.5	27.5
FWMC	6.3	20
Total methylmercury (ng/L)		
Minimum	0.06	0.21
Maximum	2.51	2.38
FWMC	0.47	0.90
Dissolved methylmercury (ng/L)		
Minimum	0.028	0.05
Maximum	0.179	0.77
FWMC	0.079	0.18

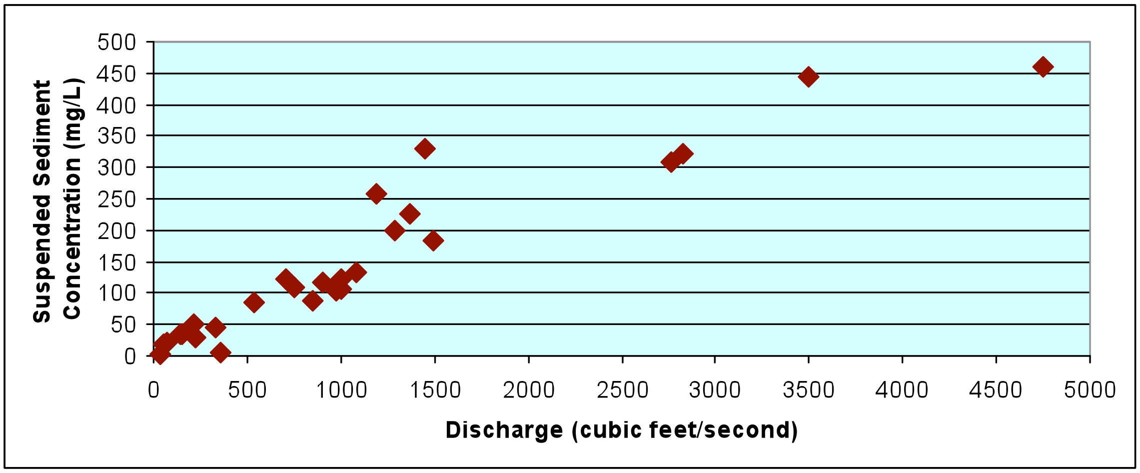

Figure 2. Discharge and suspended sediment concentration at the Highway 101 station, Water Year 2010.

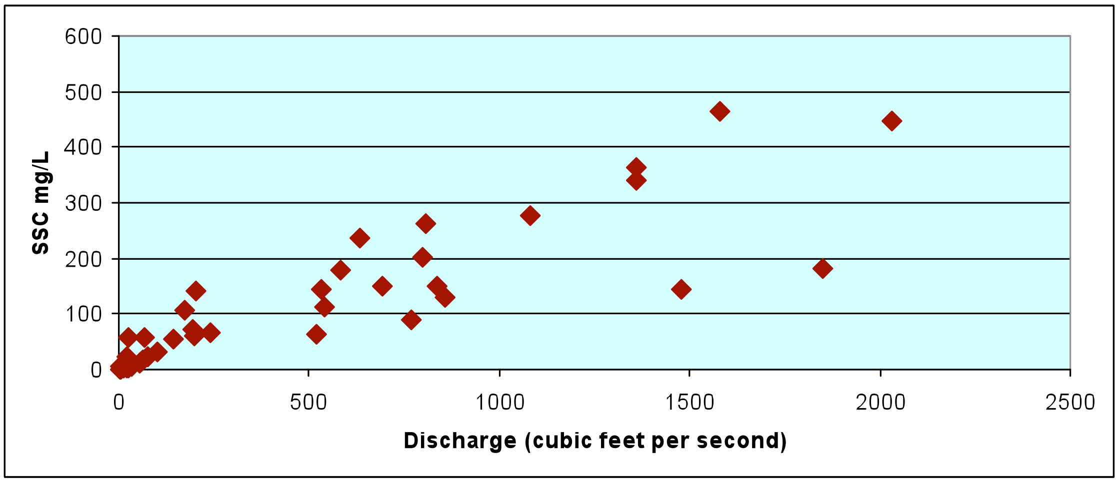

Figure 3. Discharge and suspended sediment concentration (SSC) at the Almaden Expressway USGS gauge station, Water Year 2010.

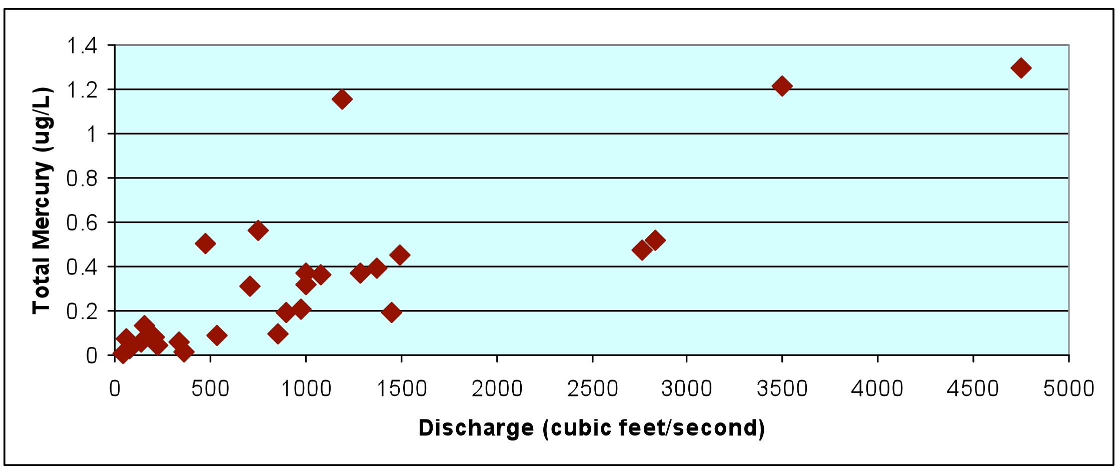

Figure 4. Discharge and total mercury concentration at the Highway 101 USGS gauge station, Water Year 2010.

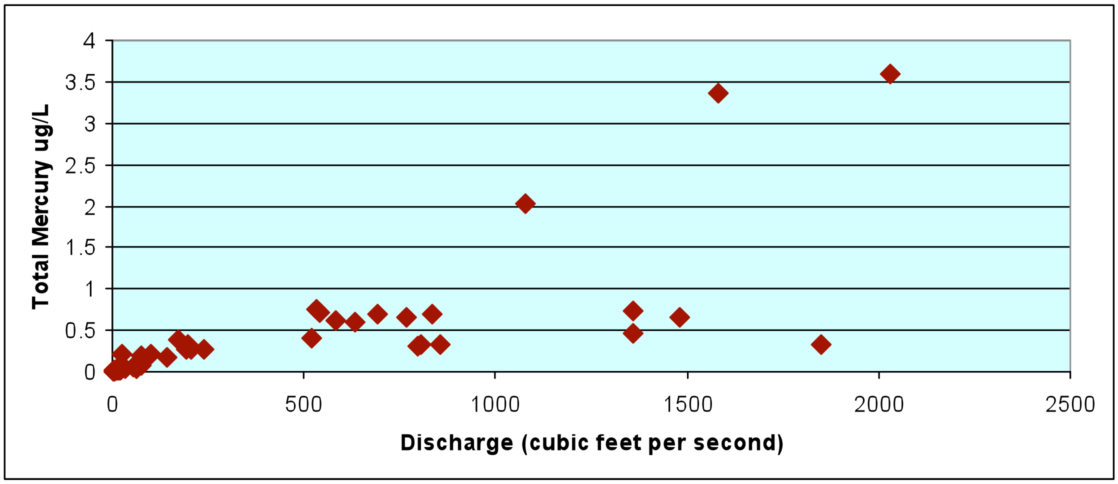

Figure 5. Discharge and total mercury concentration at the Almaden Expressway USGS gauge station, Water Year 2010.

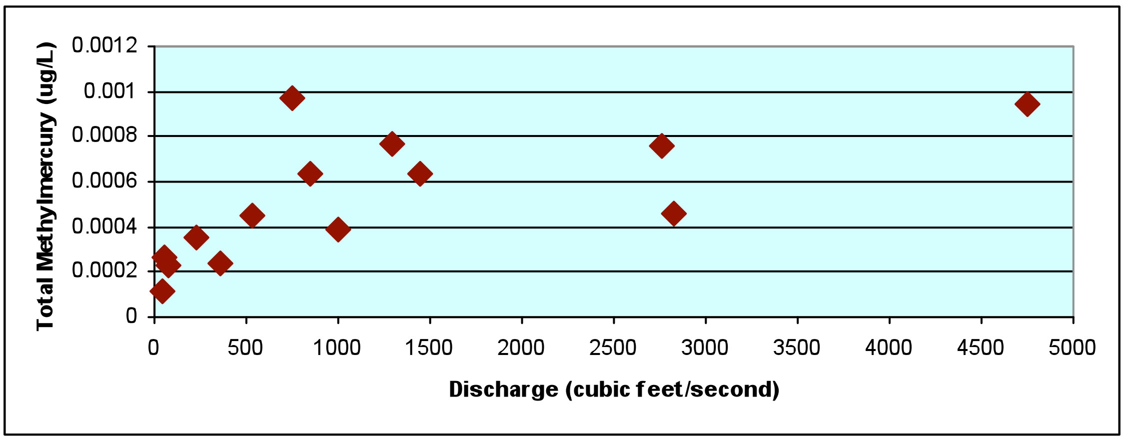

Figure 6. Discharge and total methylmercury concentration at the Highway 101 USGS gauge station, Water Year 2010.

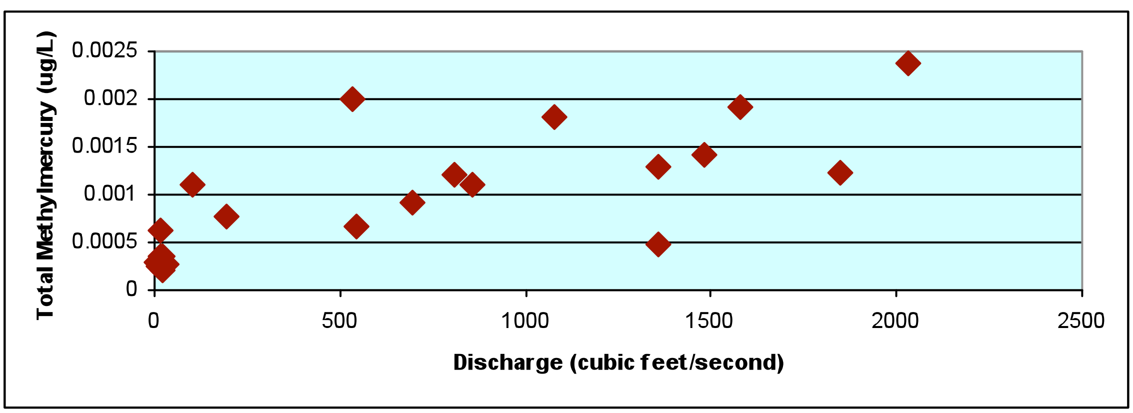

Figure 7. Discharge and total methylmercury concentration at the Almaden Expressway USGS gauge station, Water Year 2010.

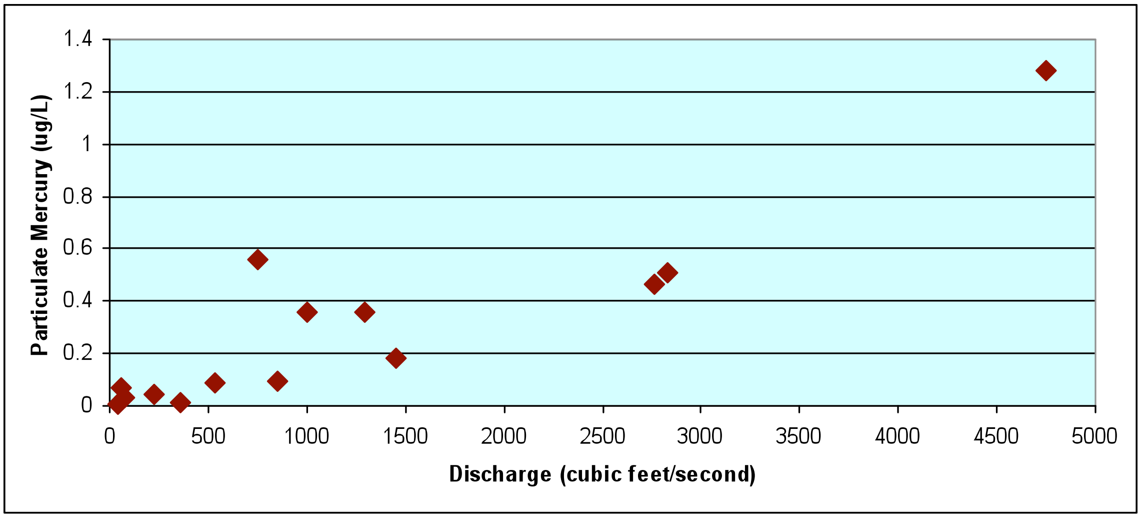

Figure 8. Discharge and particulate mercury concentration at the Highway 101 USGS gauge station, Water Year 2010.

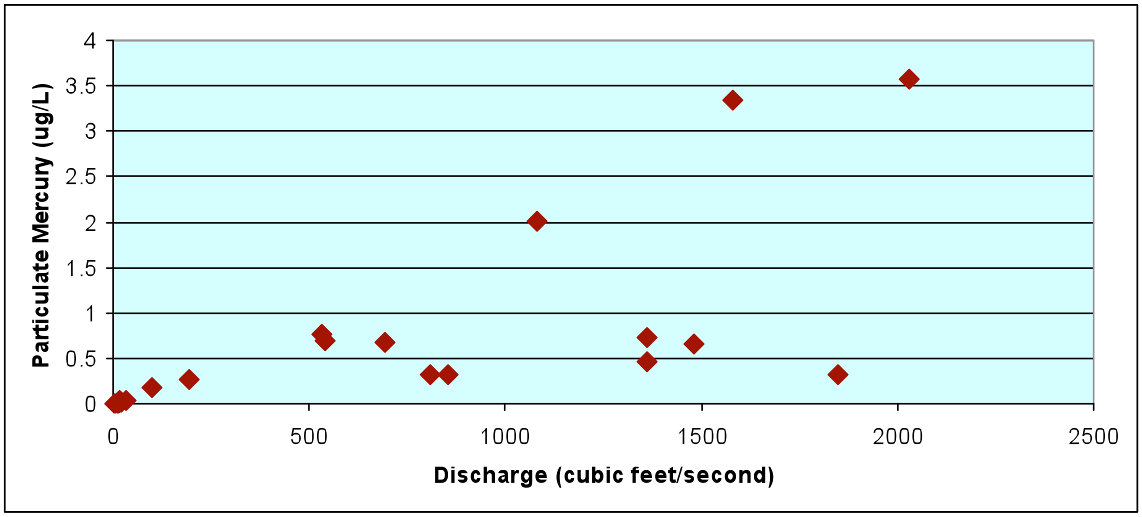

Figure 9. Discharge and particulate mercury concentration at the Almaden Expressway USGS gauge station, Water Year 2010.

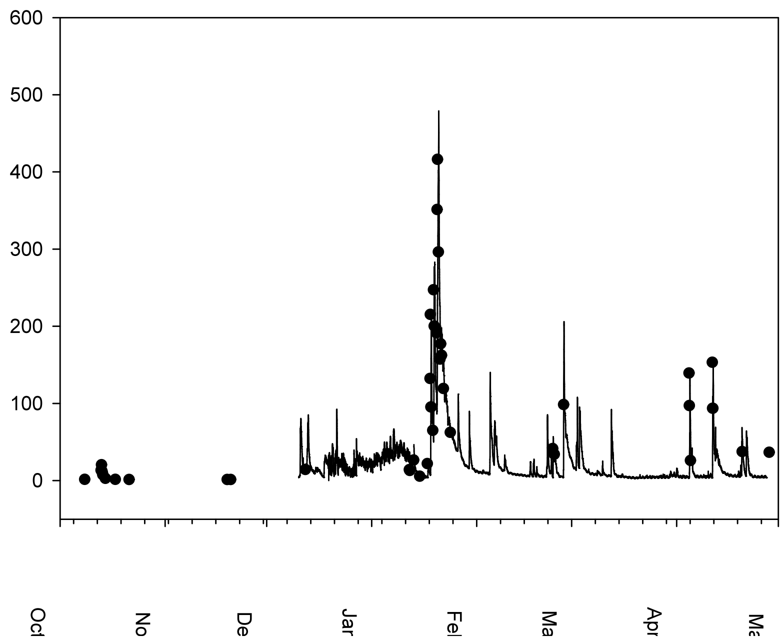

Figure 10. USGS continuous (15 minute interval) turbidity measurements (line) over the sampling period at the Highway 101 station. Black dots note where mercury samples were collected. Note turbidity measurements not available from October 1 – December 11, 2011 due to instrument malfunction.

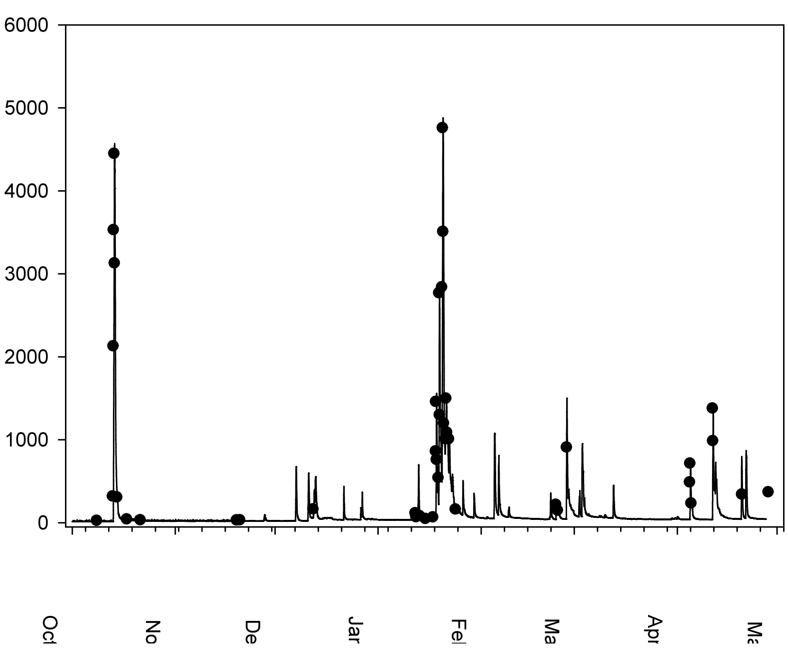

Figure 11. USGS continuous (15 minute interval) discharge measurements (line) over the sampling period at the Highway 101 station. Black dots note where mercury samples were collected.

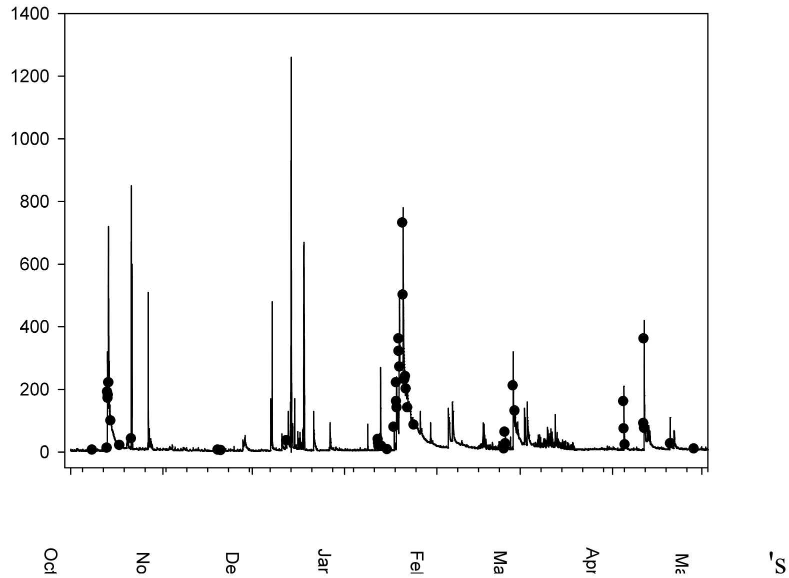

Figure 12. USGS continuous (15 minute interval) turbidity measurements (line) over the sampling period at the Almaden Expressway station. Black dots note where mercury samples were collected.

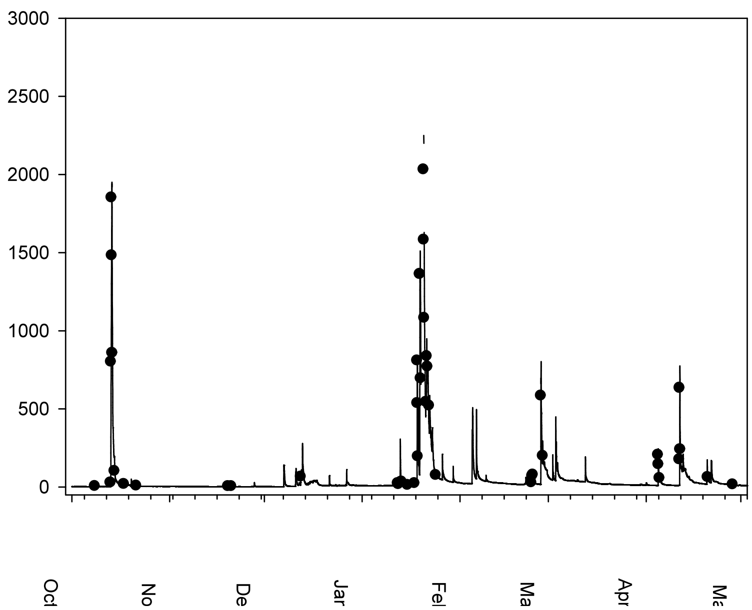

Figure 13. USGS continuous (15 minute interval) discharge measurements (line) over the sampling period at the Almaden Expressway station. Black dots note where mercury samples were collected.

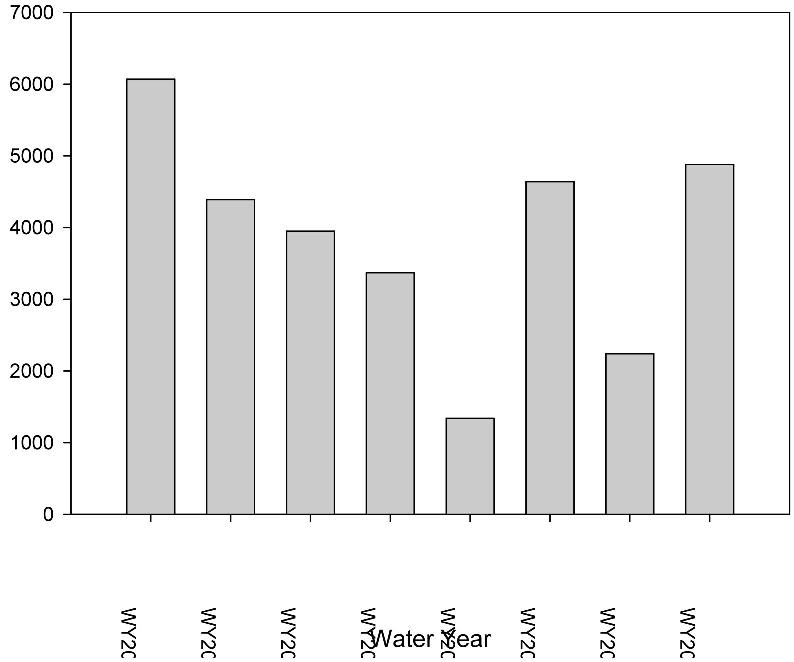

Figure 14. Peak discharge, for each Water Year, at the Highway 101 site over the monitoring period.

Influence of SSC on mercury concentrations

Regression relationships were developed between suspended sediment concentration and each component of total mercury to enable calculation of mercury loads during periods having limited or no sampling. The regression relationship between total mercury and suspended sediment concentration is steeper at the upper site compared to the lower site (Figure 15). This pattern likely occurs since sediments from the upper watershed (adjacent to mining areas) are generally more contaminated with mercury while sediments measured at the lower site have been diluted with less mercury contaminated sediments. Regardless of these complexities, the relationship between suspended sediment and mercury concentration are highly significant at both sites (Table 3). Regression relationships were stronger between mercury species and turbidity than relationships between mercury species and flow (Table 3). This is because concentrations of both mercury and suspended sediments are typically different on the rising stage versus the falling stage at similar discharges, termed hysteresis. Mercury loads calculations using regression relationships with turbidity (a surrogate measurement of suspended sediments) take into account hysteresis, and are thus more accurate than averaging methods such as combining average or weighted concentration with monthly or annual flow.

Load Estimates

During water year 2010, daily loads of suspended sediment varied from 278 kg to 1973 metric tonnes at the lower site and from 28 kg to 1127 metric tonnes at the upper site. Daily loads of total mercury varied from 0.3 g to 5.4 kg at the lower site and 0.04 g to 6.7 kg at the upper site. Maximum daily loads occurred on January 20th, 2010. These maximum loads were associated with the largest flow of the year (4880 cfs at the lower site at 1:15 pm and 2410 cfs at the upper site at 10:45 am – USGS provisional data) and with a 6-hour rainfall intensity of 2.68 inches (measured at the New Almaden gauge). Concentrations of total mercury peaked during this storm at 1290 ng/L at the lower site and 3590 ng/L at the upper site.

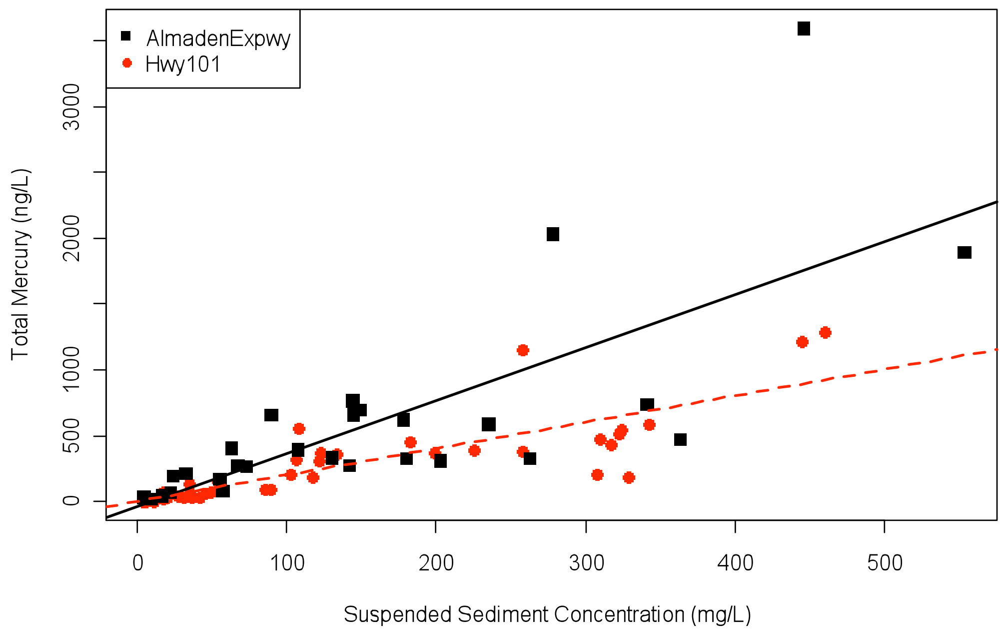

Figure 15. Linear regression of SSC (empirical data) and total mercury (empirical data) at the two sampling sites. ■ Guadalupe River near Almaden Expressway ● Guadalupe River at Highway 101.

Table 3. Summary statistics for linear regression analysis of mercury.

Highway 101	Slope parameter	y-intercept	r^2	p value
Turbidity and Total Mercury	0.0031		0.78	<0.0001
SSC and Total Mercury	0.002	0.0037	0.68	<0.0001
SSC and Total Methylmercury	0.0017	0.3132	0.26	0.01
Discharge and Total Mercury	0.0002	0.0778	0.59	<0.0001
Discharge and Total Methylmercury	0.0001	0.4211	0.12	0.1008
Almaden Expressway				
Turbidity and Total Mercury	0.0036		0.78	<0.0001
SSC and Total Mercury	0.0046	-0.0633	0.65	<0.0001
SSC and Total Methylmercury	0.0031	0.5147	0.6	<0.0001
Discharge and Total Mercury	0.001	0.0074	0.53	<0.0001
Discharge and Total Methylmercury	0.0007	0.4634	0.58	<0.0001

The majority of mass transport occurs in the watershed during flood flow; as a result, months with high rainfall and flow had greater loads (Table 4 and 5). January, the month with the highest runoff, transported 58% and 73% of the annual suspended sediment load at the lower and upper stations respectively. Similarly, 64% and 81% of the annual total mercury load was transported during January at the lower and upper stations respectively. California's climate, typified by winter and spring precipitation and summer drought, creates a long period for pollutant build-up. The initial storms of the winter season usually have higher suspended sediment and pollutant concentrations, which is called a seasonal first flush. In addition, this manifests as a disproportionally higher mass loading rate relative to storm magnitude in early season storms relative to later season storms in any given water year (Lee et al., 2004).

There was a first flush effect observed in the watershed. During the first storm, disproportional amounts of both suspended sediment and total mercury were transported through the system relative to discharge. In total, 6829 metric tonnes and 2563 metric tonnes of suspended sediment and 14.8 kg and 12.3 kg of total mercury were transported through the lower and upper sites for the winter season, respectively. While there were variations between months, on average, only 0.17% and 0.16% of this total mercury was transported as methylmercury at the lower and upper sites respectively. On average, at the Highway 101 site, 97.7% of the mercury transported was associated with particles, slightly more than at the Almaden Expressway location (96.4%). This indicates using the ratio of total mercury to suspended sediment as a surrogate for particle concentrations (mg/kg) on average leads to an error of <5%, although the error is larger during lower flow periods.

Table 4. Average monthly discharge, suspended sediment loads and mercury loads for water year 2010 at the Highway 101 site.

	Discharge (Avg cfs)	SS load (metric t)	HgT (kg)	MeHgT (g)	MeHg (% of HgT)	HgD (g)	HgD (%of HgT)	MeHgD (g)	MeHgD (% of HgT)
Oct-09	96	1608	2.51	4.51	0.18	51.9	2.1	0.602	0.02
Nov-09	21	19.4	0.027	0.276	1.01	4.36	16.0	0.090	0.3
Dec-09	65	250	0.479	1.83	0.38	35.0	7.3	0.422	0.09
Jan-10	258	3979	9.48	11.4	0.12	157.5	1.7	1.60	0.017
Feb-10	109	441	1.07	2.85	0.27	41.8	3.9	0.558	0.052
Mar-10	77	169	0.414	1.98	0.48	20.7	5.0	0.451	0.11
Apr-10	102	363	0.836	2.75	0.33	31.8	3.8	0.548	0.07
		6829	14.8	25.6	0.17	343	2.3	4.3	0.029

Table 5. Average monthly discharge, suspended sediment loads and mercury loads for water year 2010 at the Almaden Expressway site.

	Discharge (Avg cfs)	SS load (metric t)	HgT (kg)	MeHgT (g)	MeHg (% of HgT)	HgD (g)	HgD (%of HgT)	MeHgD (g)	MeHgD (% of HgT)
Oct-09	35	334	0.83	2.83	0.34	35.3	4.3	0.478	0.06
Nov-09	3	2	0.0028	0.110	3.87	1.15	40.6	0.068	2.4
Dec-09	17	28	0.094	0.771	0.82	13.0	13.9	0.275	0.29
Jan-10	129	1867	10.01	11.1	0.11	255	2.5	1.67	0.017
Feb-10	49	182	0.79	2.30	0.29	68.5	8.7	0.624	0.079
Mar-10	33	55	0.25	1.45	0.58	31.5	12.5	0.474	0.19
Apr-10	35	96	0.37	1.60	0.44	36.3	9.9	0.478	0.13
		2563	12.3	20.1	0.16	440	3.6	4.1	0.033

Relationships between mercury species and water quality parameters

For this study, eight chemical measurements were obtained: suspended sediment concentrations, turbidity, total organic carbon (TOC), dissolved organic carbon (DOC), total and dissolved mercury, and total and dissolved methylmercury. Pairwise comparisons across these parameters were evaluated using Pearson correlation coefficients (r) to determine the strongest predictors of the mercury species (Table 6). Results were also examined graphically using scatterplot matrices (Figure 16). In this analysis, all parameters were log-transformed to achieve multivariate normality and variance homoskedasticity. Total mercury was strongly related to discharge (r = 0.85), and the various measures of material transport: suspended sediments (r = 0.89), turbidity (0.91), and POC (0.85) (Figure 16). Dissolved mercury was most related to total mercury (0.68) and dissolved organic carbon (0.66). Total methylmercury was strongly related to total mercury, and was also related to SSC, turbidity, and POC (Figure 16). Dissolved methylmercury was related to dissolved mercury (0.69), but was weakly related to most other measures (Figure 16), and was not related to discharge (r = -0.04). Although particulate and dissolved organic carbon was related to most other measurements, the relationships were generally weaker than SSC or turbidity. Similarly, dissolved organic carbon was not strongly associated with measures of proportion of dissolved mercury or proportion of dissolved methylmercury.

Table 6. Pearson correlation coefficients (r) comparing across chemical parameters and discharge for individual measurements in this study.

	Discharge	SS	Turbidity	POC	DOC	HgT	HgD	MeHgT
SS	0.88							
Turbidity	0.88	0.86						
POC	0.78	0.90	0.82					
DOC	0.41	0.46	0.52	0.56				
HgT	0.85	0.89	0.91	0.85	0.56			
HgD	0.39	0.48	0.56	0.48	0.66	0.68		
MeHgT	0.65	0.74	0.80	0.73	0.66	0.85	0.68	
MeHgD	-0.04	0.17	0.13	0.11	0.35	0.30	0.69	0.50

Comparing the two monitoring stations, total mercury regressions to turbidity and discharge showed similar slopes for both sites (Figure 17). This finding is in contrast with the difference in the mercury vs. suspended sediment relationship between the sites (Figure 15). The particle concentration of organic carbon at the upper site is slightly higher (5.1%) than at the lower site (4.6%) which may contribute to the discrepancy. Total methylmercury concentration was also greater at a given total mercury or suspended sediment concentration at the Almaden Expressway site (Figure 18). Dissolved methylmercury concentrations were higher at the Almaden Expressway site than the Highway 101 site, irrespective of dissolved organic carbon or measures of suspended material (Figure 16).

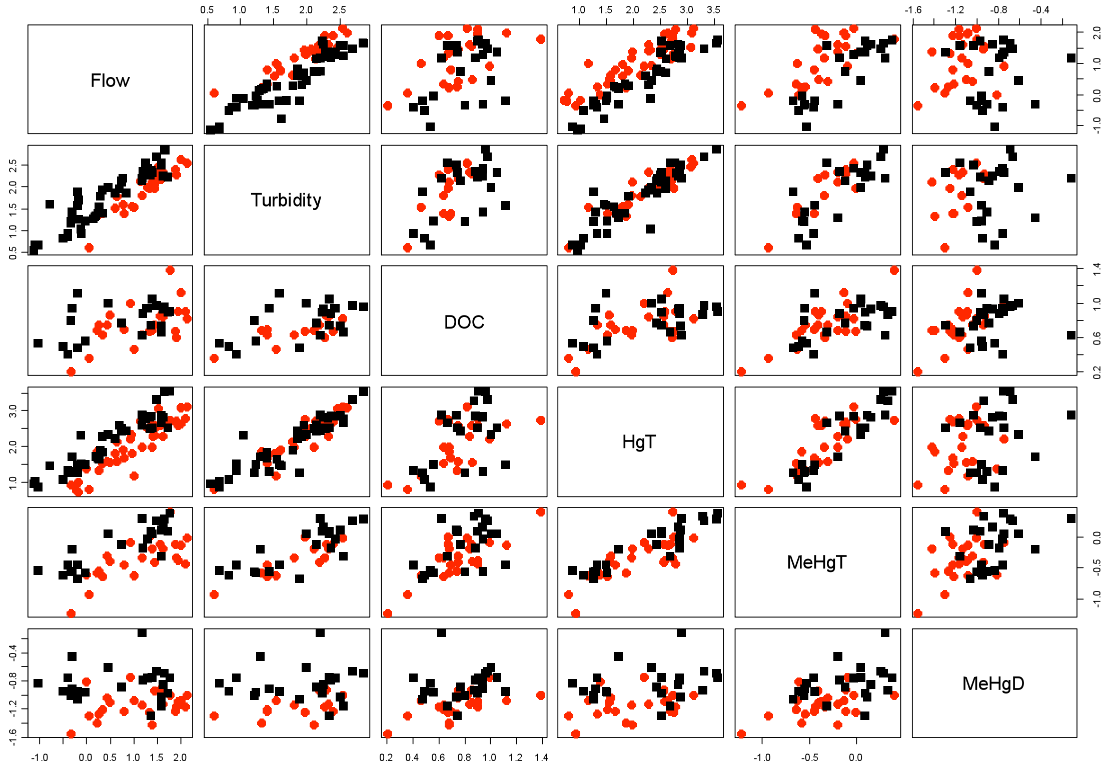

Figure 16. Scatterplot matrix illustrating relationships among flow (i.e., discharge), turbidity, dissolved organic carbon (DOC), total mercury (HgT), total methylmercury (MeHgT), and dissolved methylmercury (MeHgD). ■ Guadalupe River near Almaden Expressway ● Guadalupe River at Highway 101. Note: in this plot all results are plotted on a log-scale to illustrate relationships.

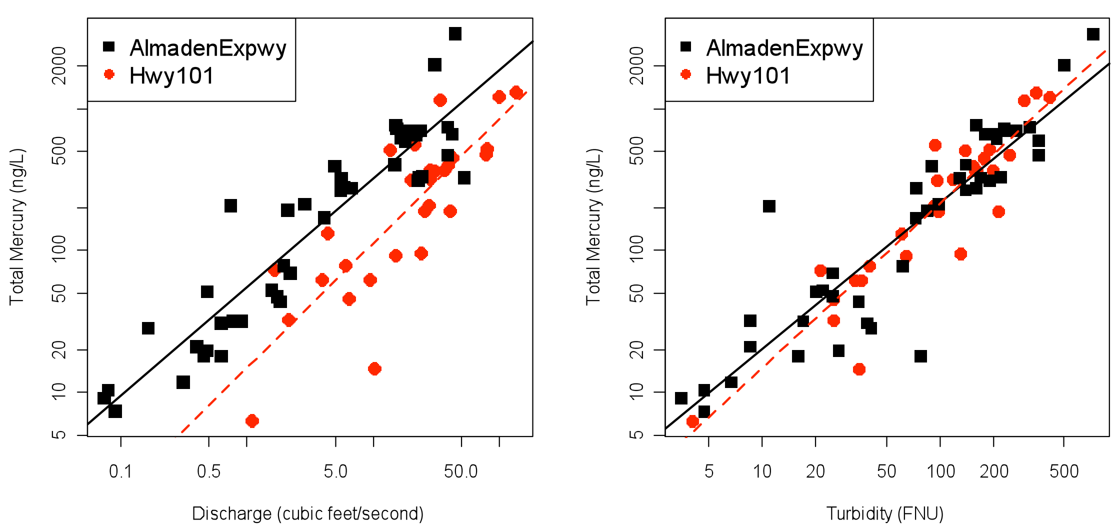

Figure 17. Comparison of total mercury versus discharge (left panel) and turbidity (right panel) at the upper (Almaden Expressway) and lower (Highway 101) monitoring stations.

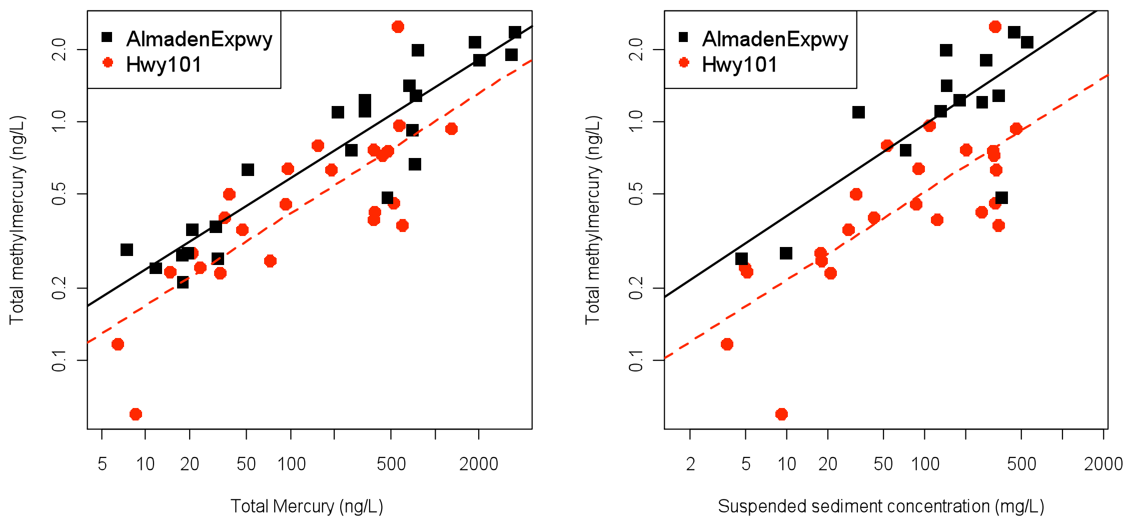

Figure 18. Comparison of total methylmercury versus total mercury (left panel) and suspended sediment concentration (right panel) at the upper (Almaden Expressway) and lower (Highway 101) monitoring stations.

Water Quality Parameters

Water quality parameters were measured at the Highway 101 site during sample collection. Dissolved oxygen (DO), conductivity, temperature, and pH were measured with a hand-held YSI multimeter. There was very little variation in the water quality parameters both within a sampling event and over the sampling season. Surface water dissolved oxygen concentrations ranged from 7 mg/L to 13 mg/L over the season (see Appendix B). There was no incidence where DO fell below 5 mg per liter during the season. This level is the current water quality objective for warm freshwater habitat (cold freshwater habitat water quality objective is 7 mg/L) (California Regional Water Quality Control Board San Francisco Bay Region, 2007). Discharge was not correlated with DO but was negatively correlated with conductivity and pH (see Appendix B). There was minimal within storm variation in temperature but there was seasonal variation in water temperature which reflects decreases in ambient air temperature from October through February. Similarly, there was very little variation in conductivity measurements. Conductivity varied between 0 and 1.0 part per thousand (ppt) which is generally considered to be freshwater. Total mercury and total methylmercury were negatively correlated with conductivity, expected given the association of transport of these contaminants to high freshwater flow storm events. pH ranged from 6.4 to 8.1 over the sampling season. There was minimal variation within a sampling event except for the first storm of the season where the lowest pH was observed and more variation was also observed (range 6.4-7.5).

Interannual trends in mercury and suspended sediment loading

Data on suspended sediments have been collected at the lower Highway 101 site since WY 2003 (eight water years). During that time, flow has varied from 75% of normal to 230% of normal. Suspended sediment loads have varied from 2280 to 11,768 metric t.

Total mercury loads have been measured during five of the last eight years and varied from 8 to 116 kg (Table 7). The load of total mercury was the highest during water year 2003, and was five to ten fold higher than in other years (Table 7). During all years of observations methylmercury and the dissolved fractions made up a small component of loads.

Table 7. Comparisons between data collected this year (Water Year 2010) and other years of observations.

Water Year	Discharge percent of normal from average[1]	Total Hg ng/L	Flow Weighted Mean Total Hg Concentration ng/L	Total Hg Loads Kg	SSC mg/L	Dissolved Hg ng/L	Total MeHg ng/L	Dissolved MeHg ng/L	Description of storms
Highway 101									
2003	111	178- 18,673	2190	116±36	17-1148	NA	NA	NA	Few, high magnitude
2004	96	DL- 1419	329	15±4.5	18-970	NA	NA	NA	Many, low magnitude
2005	133	4-1916	140	8±2.5	6-720	0.93-12.2	0.06-1.89	0.04-0.15	Many, low magnitude
2006	230	6-891	200	22	13-652	0.59-15.3	0.05-2.22	0.02-0.16	Low magnitude
2010	114	5.2-1290	270	14.8	3.7-460	0.64-21.5	0.06-2.51	0.028-0.179	Some higher magnitude
Almaden Expressway									
2010	-	7.4-3590	550	12.3	1.7-533	2.1-27.5	0.21-2.38	0.05-0.77	Some higher magnitude

1. Discharge average based on data from 1971-2000. 2010 is year to date as the water year ends September 30th.

The San Francisco Bay TMDL targets focus on particle corrected mercury concentration (i.e., total mercury:SSC ratio), related to the association between suspended sediment and mercury concentrations. As mentioned above, since most mercury in the system is particulate, the ratio of total mercury to SSC is a reasonable surrogate. Note that for some years (WYs 2005, 2006, and 2010) we have measured particulate mercury data, but in order to include as much data as possible we focus more on the total mercury:SSC ratio. As mercury loads and concentrations are related to discharge and suspended sediments, trends assessment may be performed while accounting for these parameters.

The monthly mercury and suspended sediment loads were compared to monthly discharge, to test for differences among water years. Since the majority of load actually occurs during storms, it would perhaps have been slightly superior to complete this analysis using storm specific data so that more points could have been included for each regression line rather than just 7-8 per year. However, since the objective was to compare loads between years, a monthly aggregated analysis is entirely sufficient; weekly, daily, or storm based aggregates would provide the same conclusion each with differing amount of scatter around the regression lines and level of effort.

A statistically significant effect of water year was observed on the slope of the suspended sediment monthly load vs. discharge relationship (linear model on log-transformed parameters; $p < 0.0001$). Specifically, the slope of the suspended sediment monthly load vs. monthly discharge relationship was higher in 2003 and 2004, than in 2005, 2006, or 2010 (Figure 19).

Similarly, monthly mercury loads were greater in 2003 and 2004 than other water years, evidenced by a significant effect of water year on the intercept of the mercury vs. suspended sediment relationship (linear model on log-transformed parameters; $p < 0.0001$). In 2003, the total mercury loading was substantially higher at a given discharge than other years (Figures 20 and 21).

Methylmercury monthly loads and event-specific concentrations exhibited weaker trends than total mercury and suspended sediments. For the sampling years evaluated where there were data (WYs 2005, 2006, and 2010), there was no significant difference among years in the monthly methylmercury load vs. discharge relationship. Examining across all individual sample collection events, there was a significant but weak interaction

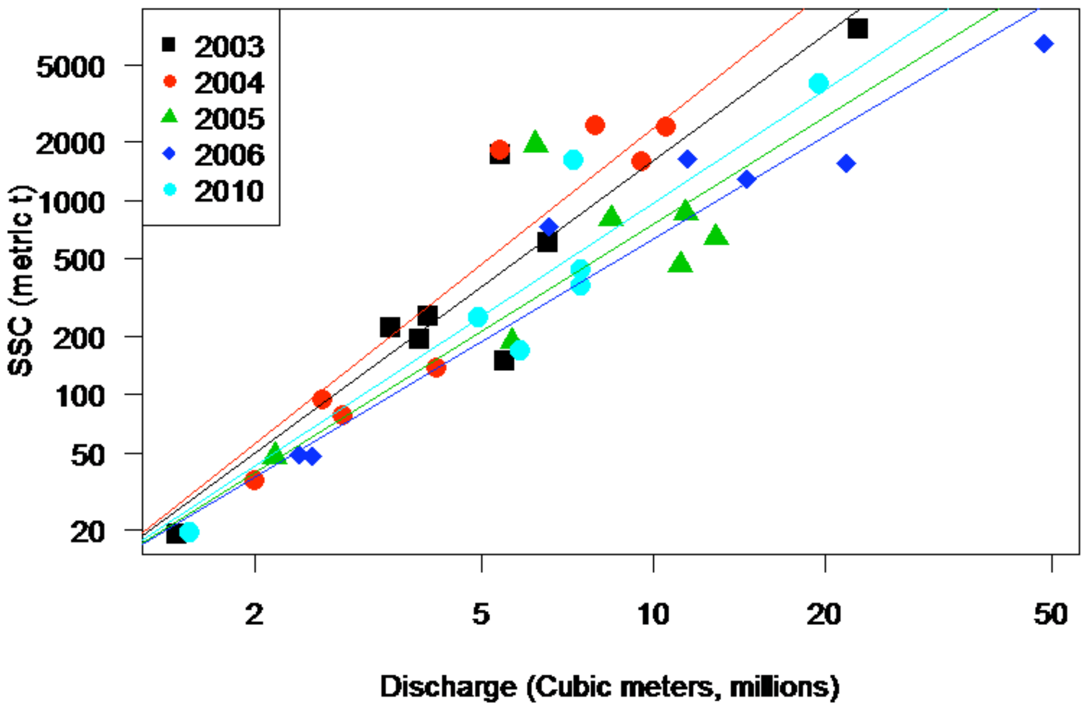

Figure 19. Monthly loads of suspended sediment versus monthly discharge at the Highway 101 monitoring station, over five sampling years. Lines indicate the results of a regression that accounts for annual differences in the relationship.

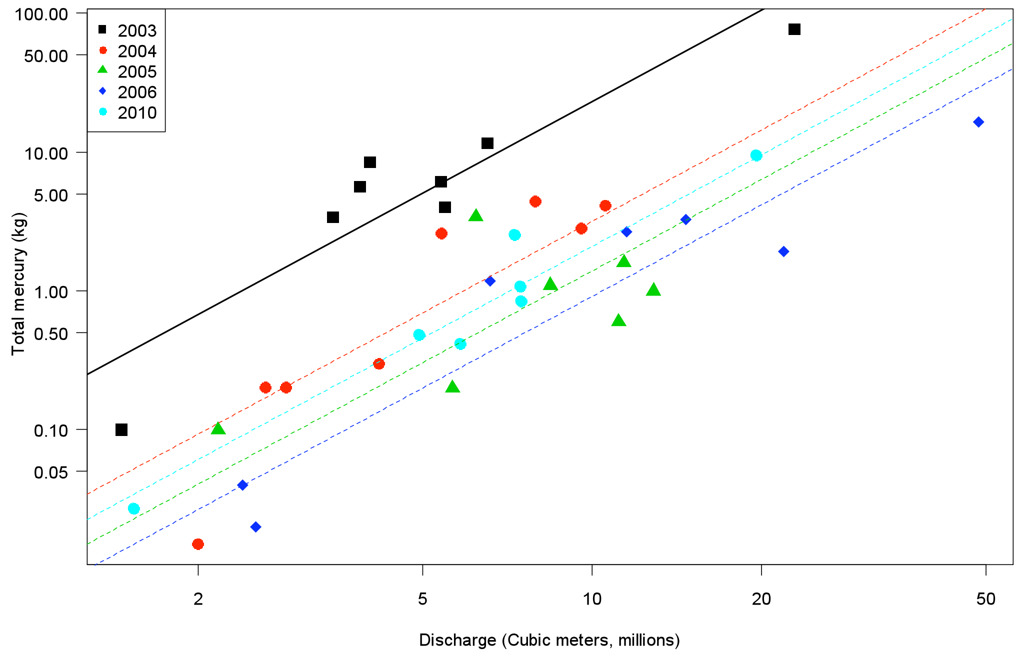

Figure 20. Monthly loads of total mercury versus monthly discharge at the Highway 101 monitoring station, over five sampling years. Lines indicate the results of a regression that accounts for annual differences in the relationship. Note log scale.

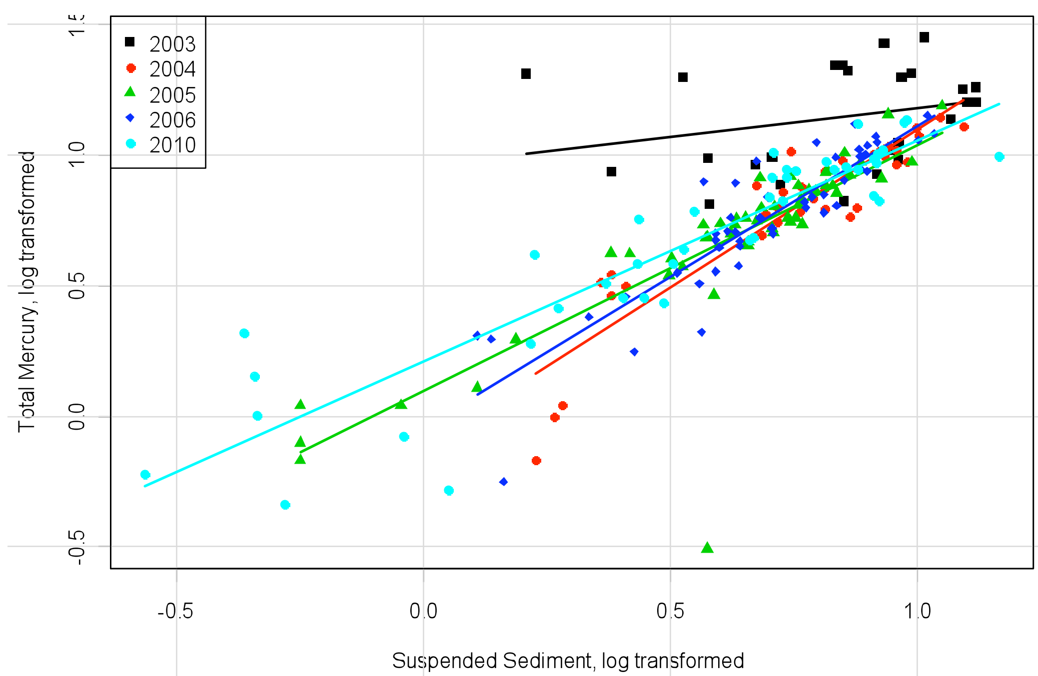

Figure 21. Log-transformed total mercury concentrations in relation to suspended sediment concentrations. Data indicate water year 2003 is significantly different from the other years.

between the total methylmercury vs. suspended sediments relationship and sampling year. Results indicated that in 2010, at higher suspended sediment concentrations, total methylmercury concentrations were lower than in 2005 and 2006. This pattern was not observed at lower suspended sediment concentrations, where total methylmercury was similar across sampling years. Dissolved methylmercury exhibited no significant relationship with suspended sediment concentrations in WYs 2005, 2006, or 2010, indicating that the interannual trends in total mercury or methylmercury do not correspond to similar trends in dissolved methylmercury.

Taking a look at the ratio of total mercury to SSC (Figure 22), overall there is no difference among years with the exception of WY 2003 which is significantly different from the other years. The pattern shows some similarities to a box plot of rainfall intensities observed for each water year (Figure 23). Although in water year 2010, there were two storms that exceeded 2 inches in a 6-hour period; the first storm on October 13th and the largest peak flow storm on January 19th high mercury concentrations were not observed when comparing to similar precipitation events in previous monitoring years (e.g. mercury concentrations were higher in previous years when precipitation amounts exceeded 2 inches in a 6 hour period).

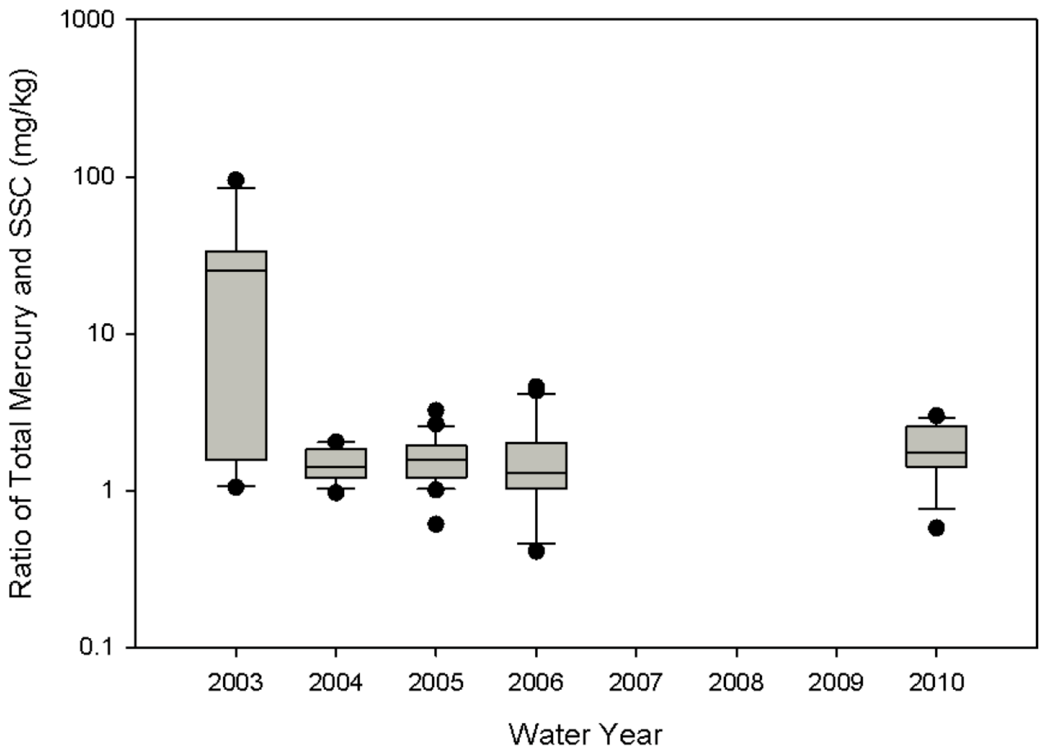

Figure 22. Box plot of the ratio of total mercury and suspended sediment concentration relative to water year. Note log scale.

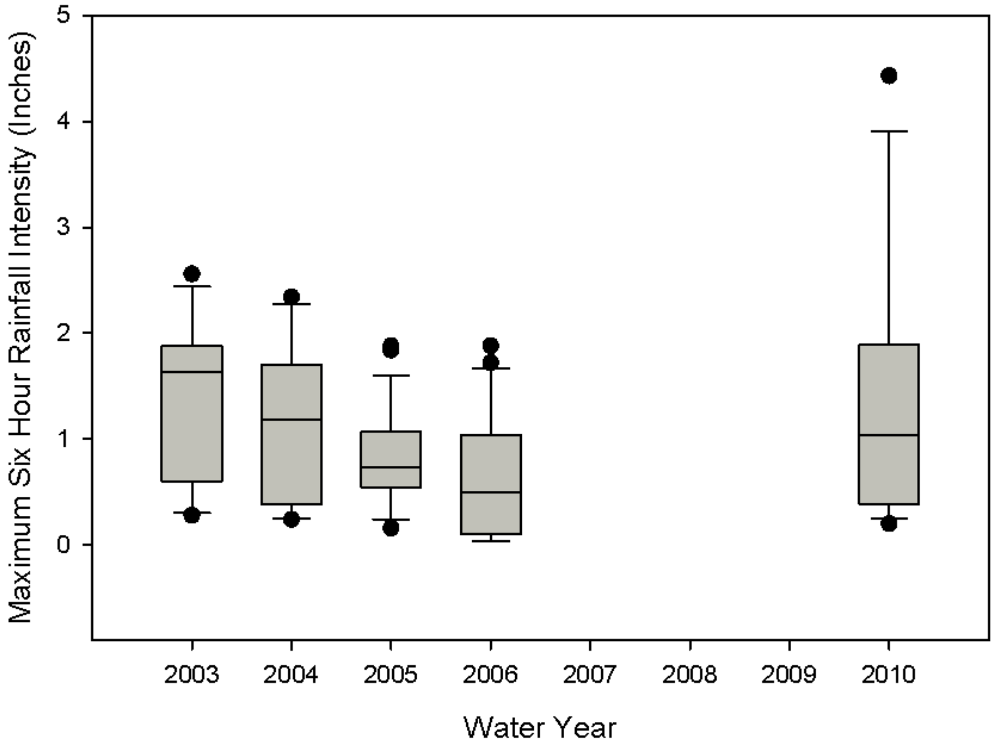

Figure 23. Box plot of maximum 6-hour rainfall intensity measured at the District gauge at New Almaden relative to water year.

Discussion

Data quality

Sampling during water year 2010 was successful with the exception of some data losses associated with malfunction of the automated instrumentation at both sites. This is the first time in eight years that the Highway 101 site has sustained data loss for more than a few hours. Prior to the water year, the turbidity probe was sent back to the manufacturer for service. It was either reinstalled incorrectly or the service caused a malfunction. Luckily, the sampling regime this year (with plenty of samples and diligent sample capture during the largest storms) meant that concentrations during important large storms and the first storm were well described in terms of concentrations. As a result, loads could be confidently calculated using the preferred method of loads calculation (linear interpolation). Should monitoring continue, in future years the probes should not be serviced unless there is clear evidence of a malfunction. Routine servicing of the internal workings and calibration is akin to fixing something that is not broken and in this year's case led to a malfunction and data loss. Routine servicing should include replacing the external wiper components and cleaning the optics with a mild soap.

Mercury and SSC data quality was high. The use of duplicate field samples (1 in 10 samples) captured under a variety of climatic conditions, field blanks, laboratory duplicates, certified reference material comparisons, and matrix spikes provided high confidence in the data quality. Total mercury and total dissolved mercury were analyzed using US EPA Method 1631 Revision E (USEPA, 2002). Total and dissolved methylmercury were analyzed using Modified US EPA Method 1630 (USEPA, 1998). The method detection limits for these methods are 0.2 ng/L and 0.02 ng/L respectively. This year we saw no data below detection limits. In addition, the comparison of both dissolved total and methylmercury to total mercury and total methylmercury provides information on particulate forms and the calculation of the partition coefficient (k_d) giving a further indication of quality assurance. Data with unexplainable high fractions of dissolved forms (low log k_d) are flagged for quality which helped identify some lab transcription errors. Should monitoring continue with an interest in concentrations during smaller floods and low flow conditions, these sensitive methods would be necessary to understand the transport of dissolved and methylated (more bioavailable) species of mercury and provide additional quality assurance.

Comparisons to previous years of data and trend evaluation

At the Highway 101 station, annual and monthly loads of total mercury were substantially greater in water year 2003 than in other water years evaluated. This did not result from increased discharge, which did not deviate from other years in 2003. Increased mercury loads in 2003 did correspond to higher suspended sediment loads. Additionally, water year 2003 showed a significantly different relationship for the slope between SSC and total mercury, with higher mercury concentrations even for moderate SSC concentrations seen in other years.

The exact cause of the dramatic reduction in annual and monthly mercury loads and particle concentrations over the course of the data collection effort is difficult to establish. There are two main plausible reasons for these trends. Although suspended sediment loading declined during this time period, the year with the highest monthly suspended sediment loads (2004) did not have the highest monthly mercury loads, which were in 2003. The first possible hypothesis to explain the reduced monthly mercury loads include management practices designed to reduce contaminated suspended material release from within the watershed are benefitting mercury loading into the system. For example, the District has been aggressively removing mercury from the channel adjacent to the Quicksilver County Park, home of the historic New Almaden Mining District (Table 8). An alternative explanation is that the increased rainfall intensity in WY 2003 caused more mercury and suspended sediments to be washed from the watershed surfaces into drainage lines which then took a few years to pass out of the system. The relationship between six-hour rainfall intensity and particle concentration (Figure 24), although having plenty of scatter, provides evidence that rainfall appears to play a role in influencing sediment quality.

So while it is plausible that District efforts may be affecting the trends, data collected to-date are not sufficient to rule out climatic effects. To help evaluate the potential role for climactic variation on trends in loading, additional loads measurements would be most helpful for wet years, such as El Nino events or years with rainfall distribution and intensity at least of significant as WY 2003. In any event, these findings regarding total mercury do not correspond well to trends in total or dissolved methylmercury. Total methylmercury monthly load was not statistically different between WYs 2005, 2006, and 2010. Dissolved methylmercury exhibited no relationship to suspended sediments, and was similar across years sampled (WYs 2005, 2006, and 2010).

Table 8. Santa Clara Valley Water District removal of mercury from channels adjacent to the Quicksilver County Park. The large numbers for 2009-2010 are from the Jacques Gulch site. The variability is due to the range of analytical results multiplied by the large volume of sediment moved to the top of the mountain.

Year	Mercury Removed
2004-2005	390 kg
2005-2006	31 kg
2006-2007	43 kg
2007-2008	100 kg
2008-2009	46 kg
2009-2010	327 kg – 1632 kg*

*Assuming that 12,000 cubic yards of soil has been removed at 20mg/kg – 100mg/kg, the amount of mercury removed would be in the range of 327 kg Hg – 1632 kg Hg.

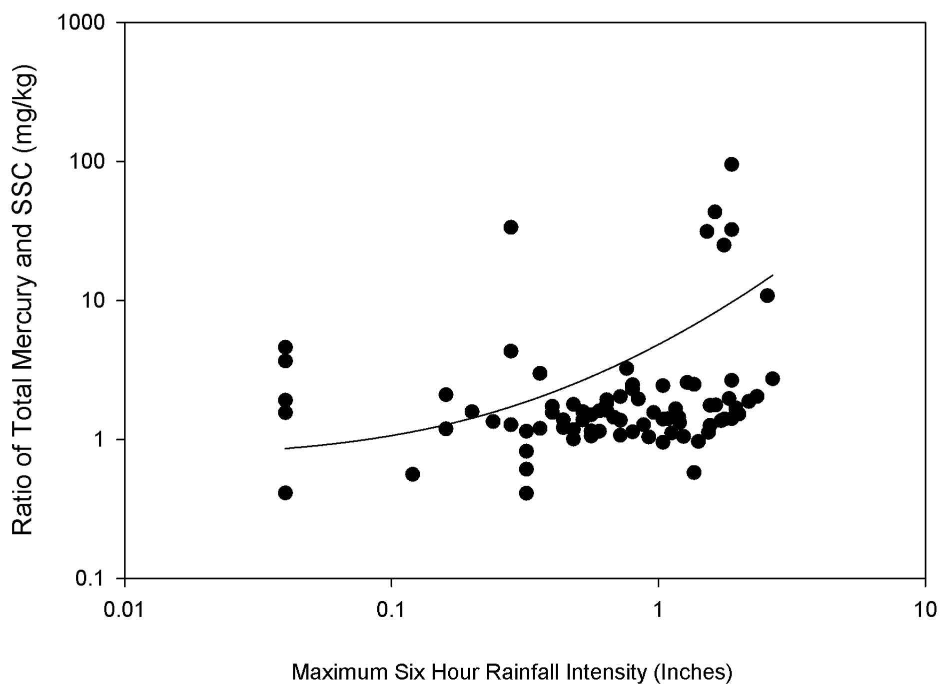

Figure 24. The relationship between particle concentration (the ratio of total mercury to SSC) and six-hour rainfall intensity recorded at the District gauge at Almaden.

TMDL targets

In terms of meeting the TMDL targets, the loads observed during WY 2010 at the Highway 101 gauge (14.8 kg) appear to be close to those prescribed by the TMDL (9.4

kg). WY 2010 had a discharge about 14% above the long term average. Given error bars about our loads estimates of about 30% it could be argued that the loads target was met in WY 2010. From the perspective of particle concentrations, the flow-weighted average particle concentration for WY 2010 was 2.2 mg/kg (Table 9) or about 10 fold greater than the TMDL target.

Table 9. Summary of suspended sediment and total mercury loads and the mean particulate mercury concentration (ratio of total mercury to SSC) for the water years of record.

Water Year	Suspended sediment (metric t)	Total Mercury (kg)	Mean particulate mercury concentration (mg/kg)
2003	10,587	116	11
2004	8,485	15	1.7
2005	4,918	8.0	1.6
2006	11,768	22	1.9
2007	1,232	-	-
2008	4,699	-	-
2009	2,280	-	-
2010	6,829	14.8	2.2

Differences between upper and lower loads and speciation

During this observation season, since data on suspended sediments and mercury species were collected at two locations with quite differing land use patterns (Table 10), an estimate of load entering the channel from between the sites (a mainly urban area) can be made. This is done by simply subtracting the loads at the upper site from the loads at the lower site. Of note, the area draining to the upper gauge includes the former mining district area and Ross Creek. The lower gauge site include this and urban San Jose including Los Gatos Creek. Given the likely errors in our loads calculations for mercury species are about +/- 30% it is perhaps surprising that this style of mass balance has worked so well but it appears that land use and the sizable change in watershed area and land use styles between the two locations is large enough to override the error bounds around our calculations. We conclude that the difference method for estimating urban watershed load is valid.

Table 10. Land use characteristics of the two sampling locations excluding areas upstream of reservoirs. Source: Combination of ABAG 2000 and SCVWD's land use data sets.

	Upstream of Highway 101				Upstream of Almaden Expressway				Land between two gauges			
	Area				Area				Area			
Land use	km^2	mi^2	Acres	%	km^2	mi^2	Acres	%	km^2	mi^2	Acres	%
OPEN	30.0	11.6	7413	13%	20	7.8	4999	26%	9.8	3.8	2414	6.1%
RES-RURAL-LOW	22.1	8.5	5449	9.2%	14	5.2	3348	17%	8.5	3.3	2101	5.3%
RES-MED-HI	93.4	36.1	23077	39%	5.6	2.2	1385	7.1%	87.8	33.9	21693	55%
COMM-PUBLIC	37.9	14.6	9362	16%	2.9	1.1	706	3.6%	35.0	13.5	8656	22%
FOREST	36.2	14.0	8949	15%	32	12	7920	41%	4.2	1.6	1029	2.6%
AGRICULTURE	8.3	3.2	2050	3.5%	4.4	1.7	1078	5.5%	3.9	1.5	972	2.5%
INDUSTRIAL	10.6	4.1	2613	4.4%	0.06	0.024	15	0.079%	10.5	4.1	2597	6.6%
Total	238	92	58913	100%	79	30	19451	100%	160	62	39463	100.0%

It is estimated that 2.5 kg of total mercury and 5.4 g of total methylmercury was sourced from the land area (160 km^2) and channel systems between the two gauges (Table 11). Land use in this area is 89% urban with about 6.6% industrial. Normalizing the loads by area it is estimated that this represents about 15.6 µg of total mercury per m^2 of area and 0.034 µg of methylmercury per m^2 of area. These estimates appear to be reasonable and fall within the upper range observed in other watersheds with urban land use influences for total mercury and in the lower range for methylmercury (Table 11: Literature review by McKee et al., 2006). During the summer and fall of 2009, considerable work was done on the channel just downstream from the upper sampling site. A multi-stage channel was built and completed only days before the first rains of the year. However hydro-seeding and other vegetation cover techniques were not completed and bare soils remained exposed into the wet season. During the October 2009 and January 2010 storms, substantial sediment loss occurred from the upper Guadalupe channel project site. Unfortunately, although manual grab sampling proceeded per our sampling plan, automated turbidity measurements were not made at the lower site during the October 2009 storm and there was also missing data at the upper site during the January 2010 storm. As a result, sufficient data is lacking to determine if there were measurable, anomalous fluxes of sediment during either of these two storms in relation to the channel erosion problems.

At a given discharge, all mercury forms measured were higher at the upper site than the lower site. The elevated particulate mercury concentrations at the upper site may stem in part from elevated concentrations of particulate carbon and other suspended material. However, at a given mercury concentration, the total and dissolved methylmercury concentrations were also higher in the upper site. We conclude that the data clearly indicate that mercury concentrations passing through the upper gauge site are greater than those passing though the lower gauge. The difference appears to be associated with inputs of cleaner mainly urban stormwater and sediment in between the two gauge sites and perhaps partially due to erosion of cleaner sediment from the new multistage channel just downstream from the upper sampling site. We also conclude that the data clearly show area normalized total mercury loads

Table 11. Estimated loads associated with the land area between the gauge at Highway 101 and the gauge at Almaden Expressway excluding areas upstream of reservoirs.

	Area (km^2)	**SS (metric t)**	**SS (kg/ha)**	**HgT (kg)**	**HgT (µg/m2)**	**MeHgT (g)**	**MeHgT (µg/m2)**
Highway 101 gauge	238	6829	287	14.8	62.3	25.6	0.11
Almaden Expressway gauge	79	2563	324	12.34	156.3	20.1	0.25
Area in between the two gauges	159	4266	268	2.5	15.6	5.4	0.034
Cache Creek mercury mining watershed in Yolo county (Domagalski et al., 2004)	-	-	-	-	4.3	-	-
Other watersheds with urban dominated land use (Literature review by McKee et al., 2006)	-	-	-	-	0.26 - 24	-	0.03 - 0.16

passing through the upper gauge site (156 µg/m^2) were greater than those passing through the lower gauge site (62µg/m^2). If we assume that Ross Creek (20 km^2) has a normalized load that is similar to urban San Jose, the load of the rest of the watershed that is impacted by the historic mines for WY 2010 was about 12 kg over an area of 59 km^2 or about 201µg/m^2. During WY 2010, the urban area (including the eroded channel reach) only supplied about 19% of the load despite being 75% of the watershed area below reservoirs.

Although the downstream normalized loads are clearly diluted by urban runoff load, no matter how we manipulate the data, these normalized loads are extremely elevated relative to typical urban areas and are more akin to loads associated with mining. We have no reason to suspect District facilities between the two gauging locations are impacting loads either positively or negatively (although the erosion associated with the partial washout of the upper Guadalupe channel just below the upper sampling location certainly had some impact, given turbidity probe malfunction, we are not able to determine impact from the data collected during this study).

Organic carbon measurements

Collection of dissolved and particulate organic carbon in 2010 was recommended in 2010 because of the role organic carbon can play in regulating the dissolved mercury fraction. Literature indicates that sediment to water partitioning (i.e., K_d) of mercury and methylmercury are related to organic carbon content in freshwater and marine systems (Hammerschmidt and Fitzgerald, 2004; Marvin-DiPasquale et al., 2009). Additionally, organic carbon is related to mercury and methylmercury in San Francisco Bay sediments, and is believed to be implicated in methylmercury production (Conaway et al., 2003). The present study indicated that DOC was moderately related to dissolved mercury and weakly related to dissolved methylmercury. Although these results suggest an association between DOC and dissolved mercury species in the Guadalupe River, continued data on DOC are not needed as the relationships are not sufficient to make strongly predictive regression correlations to replace mercury measurements. Similarly, as POC is strongly associated with turbidity and suspended sediments, continued measurement of POC is not warranted.

Water Quality Parameters

The water quality parameters (DO, conductivity, temperature, pH) measured during storm events were inconclusive or redundant as to their utility in understanding mercury or suspended sediment transport and loading. There was minimal variability in the parameters measured both within a sampling event and over the sampling season. None of the water quality parameters measured were used in any of the load calculations. These data measured a snapshot of ambient conditions at the water surface during storm events and some dry flow conditions and are generally not useful in understanding the larger processes that are occurring within the system. We recommend discontinuing the collection of these water quality parameters in future monitoring activities if the objective is to understand mercury transport and loads.

Monitoring Design

In May 2008, the Sources Pathways and Loading Workgroup (SPLWG) of the Regional monitoring program for Water Quality in San Francisco Bay (RMP) recommended the development of a “Small Tributaries Loading Strategy” (STLS). In this context, a small tributary is defined as any river, creek, or storm drain that enter the Bay downstream of the confluence of the Sacramento and San Joaquin rivers. The Guadalupe River is a small tributary within this definition. The intent of the STLS was to ensure that the RMP is providing the information most urgently needed by managers to reduce loads and impacts of pollutants of concern entering the Bay from small tributaries. In this context, a pollutant of concern is any pollutant listed in provision C.8.f of the Municipal Regional Stormwater Permit (MRP) Order No. R2-2009-0074 with the caveat that more effort and budget would likely be applied to higher ranked pollutants of concern. The STLS is a planning framework for small tributary loads monitoring within the RMP that is consistent with and complemented by monitoring that will be completed in compliance with the MRP. During 2009, the RMP provided funds to address several pressing questions in relation to completing a multi-year sampling plan, the anticipated blue print for tributary monitoring over the first and perhaps subsequent MRP permit terms:

a) Develop Criteria and Rank Watersheds
b) Optimize Sampling Methods for Loading and Trends

The ranking process was intended to provide a classification scheme for small tributaries in the Bay Area as part of a framework for selection for monitoring. Input data for the ordination and cluster analysis included GIS data on 185 watersheds, % Industrial, % Residential, % Commercial, % Agriculture, % Open, 1954 % Industrial, % Impervious, Current and historic railroads (RR), Watershed area, Population/area, PG&E facilities/area, Pump stations/area, Auto dismantlers/area, Annual precipitation average, and UTM spatial coordinates. Note that mining was not uses as a category. A total of eight watershed clusters were generated using Bray-Curtis distance with Ward's linkage method (For details the reader is referred to the RMP report (Greenfield et al., 2010).

The Guadalupe River fell into cluster number 6. There were 22 watersheds in this cluster, examples included Coyote Creek, Alameda Creek, and San Lorenzo Creek (Greenfield et al., 2010). So although the Guadalupe River is somewhat unique with respect to it's known historic of mining and associated downstream transport of mercury, it is likely similar to many other watersheds with respect to other pollutants of concern.

To support recommendations for future sampling design in relation to determining annual loads and to trends in small tributaries, a statistical resampling of existing empirical data was completed using three years of data from Zone 4 Line A (a 4.5 km^2 urban tributary in Hayward) and Guadalupe River (Melwani et al., 2010). A range of within-storm and among-storm designs were tested along with a variety of turbidity-surrogate regression designs. Power analysis to detect temporal trends in SSC: Hg and SSC: PCBs were examined for declining trends in 5 year increments from 5 - 50 years and for declining trends in 10% increments from 10 – 100%. We did not test how the power to detect trends would change with differing inter-annual sampling designs (e.g. sampling every 2nd, 5th, or 10th year) since for determining average annual loads it is most important to sample a large range of climatic variation (i.e. some drier years and in particular some of the very wettest years). In addition, costs were estimated for each of the designs so that accuracy, precision, and the power to detect trends could be compared to cost. Weighing all these factors, the turbidity surrogate regression estimator using 16 samples collected over 4 storms was recommended as the most cost effective method for loads and trends. It had similar costs to other modes of collection such as composite sampling but have much greater accuracy, precision, and power to detect tends. For the best accuracy, precision and power, it was recommended that sampling should occur during a large early season storm, a large mid-season (December or January) storm, and several later season storms (Melwani et al., 2010).

Given the evidence that higher particle concentration and loads in the Guadalupe River occur during years of high rainfall intensity and soil moisture levels (generally wetter years), the recommended methods for continued sampling should focus on those kinds of years. Practically this is difficult given it is near impossible to predict seasonal rainfall in advance. NOAA issues a winter outlook in the later summer and continues to update it roughly monthly throughout the wet season (http://www.noaanews.noaa.gov/stories2010/20101021_winteroutlook.html). The current outlook for the winter of 2010/11 is for La Niña conditions which are generally associated with below normal precipitation for California. However, it should be noted that El Niño only accounts for about 20% of our weather signal. Some stronger El Niño years have produced average rainfall conditions over California. "With the exception of the strongly positive rainfall anomaly in Southern California during strong El Niños the presence of either El Niño or La Niña is not a guarantee of either a significantly wet or dry year in California." Jan Null Golden Gate Weather Services Personal Communication. Given these uncertainties, a sampling design that includes contingency funds for sampling surprise wet conditions remains the recommendation of the SPLWG. In addition, given there is considerable effort to remove mass and implement urban best management practices, timing sampling during years after milestones of management effort has merit.

Given the existing information from moderate rainfall events and seasons and the dominance of high flow events on loads, for improving estimates of annual loading in the Guadalupe River, we see no argument for continuing to monitor every year. As mentioned above, we see no evidence in the data that the District facilities between Highway 101 and Foxworthy Bridge are having any impact on mercury loads and speciation. During WY 2010, 83% of the total mercury loads and 79% of the total methylmercury loads emanated from upstream of the Almaden Expressway gauge site. In terms of selection of a monitoring station, both stations have merit for providing data for trend analysis in relation to management to reduce loads of mercury, with the upper station having slightly more merit given its proximity to the historic mercury mining are. For other pollutants of concern such as PCBs and copper (dominantly urban derived pollutants), the Highway 101 monitoring station has the most merit, and base line data already exists for PCBs and other MRP pollutants of concern for WYs 2003-2006, and 2010, and for dioxins (WY 2010 only).

Summary and Recommendations

Data quality

Future sampling design should include the use of continuous turbidity measurement using the same time interval as discharge measurement (15 minutes). Turbidity is a demonstrated surrogate to estimating suspended sediment and POC concentrations during periods when there are no real water samples collected and analyzed. Probe calibration and firmware updates should only occur in the event of a malfunction – otherwise wiper replacement and external cleaning of the optical window are all that is necessary to ensure high quality data return.

Future sampling design should incorporate duplicate field samples captured under a variety of climatic conditions, field blanks, laboratory duplicates, certified reference material comparisons, and matrix spikes to provide high confidence in the data quality. Total mercury and total dissolved mercury should be analyzed using US EPA Method 1631 Revision E and total and dissolved methylmercury were analyzed using Modified US EPA Method 1630 if there remains an interest in concentrations during smaller floods and low flow conditions with low concentrations. Collecting all four mercury species provides an additional level of quality assurance.

Given greater than 96% of the mercury transported in the Guadalupe River is particulate, the ratio of total mercury concentration to suspended sediment concentration is a reasonable surrogate for particulate mercury concentrations (4% over protective).

Comparisons to previous years of data and trend evaluation

To help evaluate the potential role for climactic variation on trends in loading and tease out trends that are indeed related to considerable management effort in the watershed, additional sampling and related loads calculations would be most helpful for wet years, such as El Nino years or years with rainfall distribution and intensity at least as significant as WY 2003.

While loads vary from year to year in relation to climate, as do particle concentrations, particle concentrations present a more stable measure of trends in relation to TMDL targets. This conclusion is made because it appears that average particle concentrations in the Guadalupe River remained reasonably stable varying by only 1.4 fold during the last 4 years of observation (WYs 2004, 2005, 2006, and 2010) despite runoff and suspended sediment loads varying by between 2- and 3-fold. Particulate mercury concentrations remain 10 fold greater than the TMDL target of 0.2 mg/kg.

Differences between upper and lower loads and speciation

If there is a desire to continue to estimate loads derived from the urban portion of the watershed, continued monitoring of both sampling locations (Highway 101 and Almaden Expressway) appears to provide robust data for determination by subtraction. During very wet years when urban runoff would be expected to comprise a much smaller portion of the over all load, this method would be less robust; during drier years it would be more robust. It has logistical advantages over making measurements at multiple urban outfalls to the Guadalupe mainstem under any climatic condition and using these point loads to estimate total loads from the urban area as a whole.

Organic carbon measurements

For the purposes of monitoring for loads and trends of mercury species, it is recommended that organic carbon monitoring be discontinued. Although our results suggest an association between DOC and dissolved mercury species in the Guadalupe River, continued data on DOC are not needed since these relationships are now established, are not likely to change significantly, and do not provide much advantage in analytical cost or sampling frequency over direct measurement of mercury species. A similar conclusion was made for particulate organic carbon.

Water Quality Parameters

For the purposes of monitoring for loads and trends of mercury species, it is recommended that measurement of water quality parameters (DO, conductivity, temperature, pH) be discontinued. These water parameters did not exhibit sufficient variation in 2010 to provide a basis for assuming strong influence on mercury loading or trends not already accounted for by other measures (e.g. flow estimates). None of these water quality parameters were used in any of the load calculations.

Monitoring Design

For loads and trends analysis, a turbidity surrogate regression estimator using 16 samples collected over 4 storms appears to be cost effective. Sampling should occur during a large early season storm, a large mid-season (December or January) storm, and several later season storms to get a representation of a whole winter season.

Given climatic uncertainties and the difficulty for predicting winter weather conditions far enough in advance to prepare for a monitoring season, a sampling design that includes contingency funds for sampling surprise wet conditions remains the recommendation of the SPLWG. The RMP appears to be most well suited for this kind of sampling design given long term annual stable funding and ease of contracting. In addition, given there is considerable effort to remove mass and implement urban best management practices, timing sampling in relation to management effort should be considered.

For improving estimates of annual loading in the Guadalupe River, we see no argument for continuing to monitor every year. We see no evidence in the data that the District facilities between Highway 101 and Foxworthy Bridge are having any impact on mercury loads and speciation.

For measuring trends in relation to management in and adjacent to the historic mining area, the upper station has slightly more merit given its proximity. For other pollutants of concern such as PCBs and copper (dominantly urban derived pollutants), the Highway 101 monitoring station has the most merit, and base line data already exists for PCBs and other MRP POCs for WYs 2003 to 2006, and 2010, and for dioxins (WY 2010 only). Overall, we recommend the Highway 101 location for continued monitoring to address a greater number of questions.

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APPENDIX A

APPENDIX B

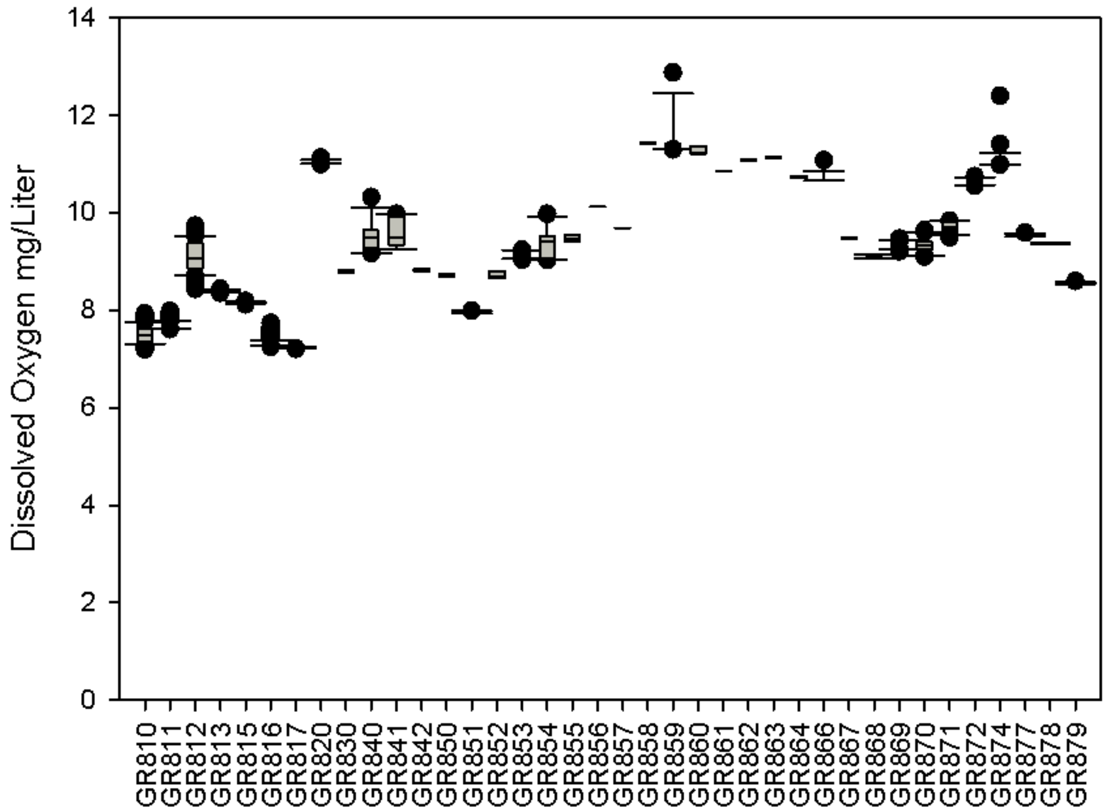

Figure B1. Dissolved oxygen concentrations (mg/L) for each stormwater sampling event from October 2009 (GR810) to April 2010 (GR 879).

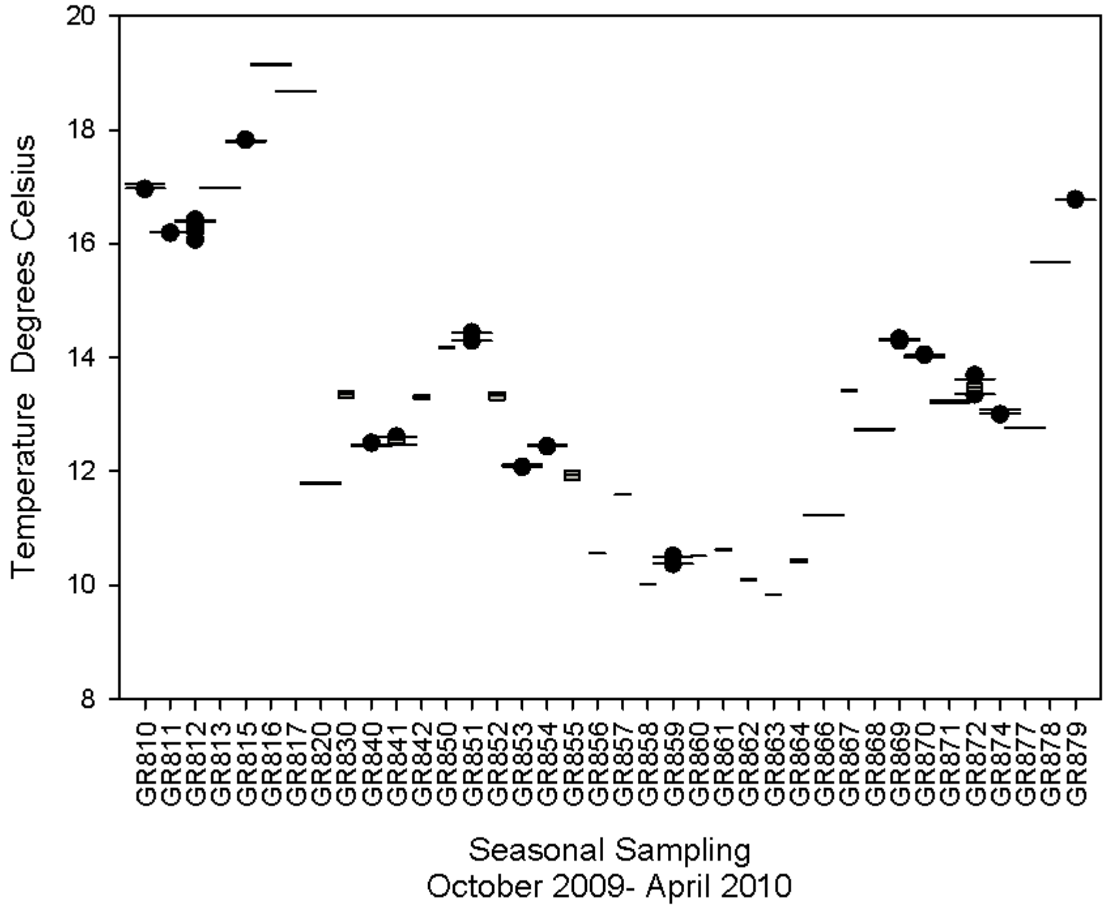

Figure B2. Temperature (°C) for each stormwater sampling event from October 2009 (GR810) to April 2010 (GR 879).

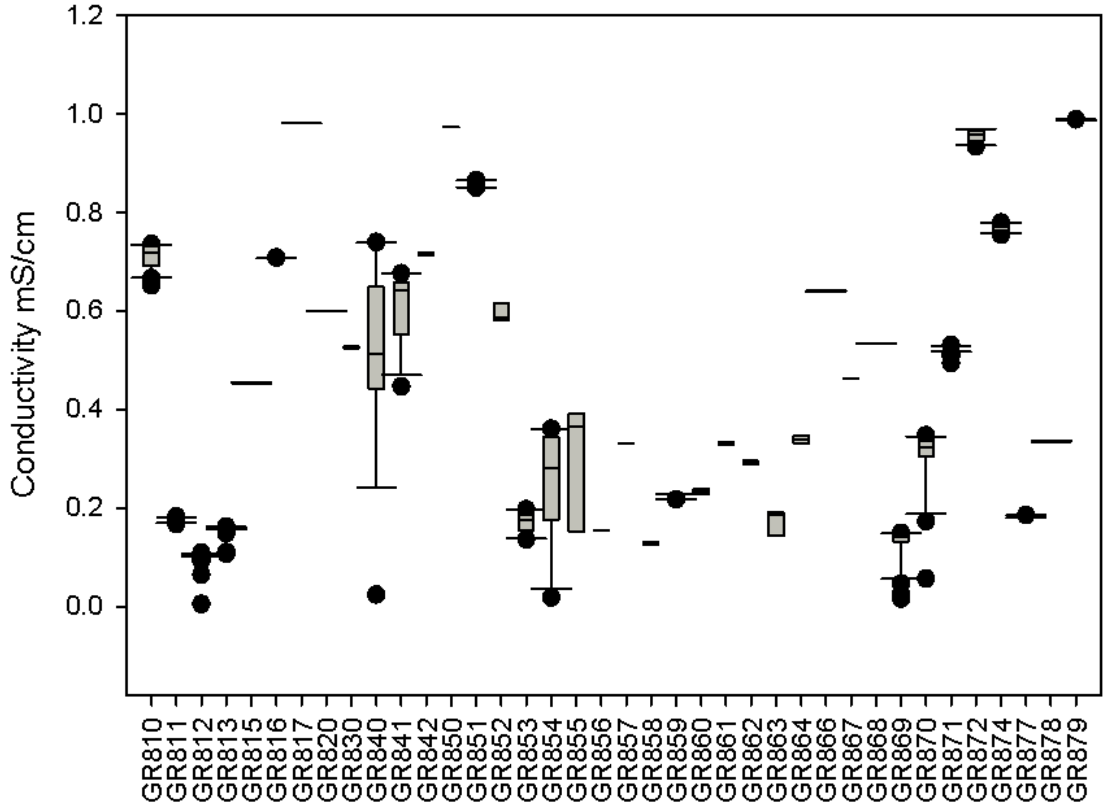

Figure B3. Conductivity (mS/cm) for each stormwater sampling event from October 2009 (GR810) to April 2010 (GR 879).

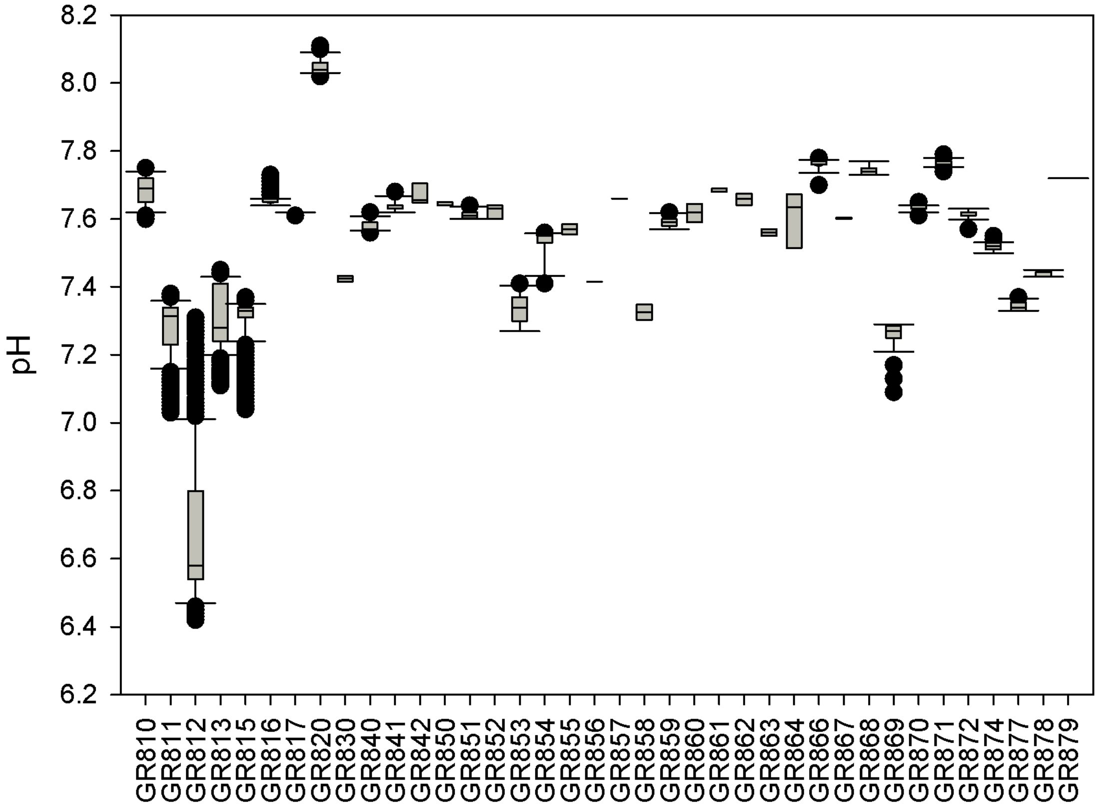

Figure B4. pH for each stormwater sampling event from October 2009 (GR810) to April 2010 (GR 879).

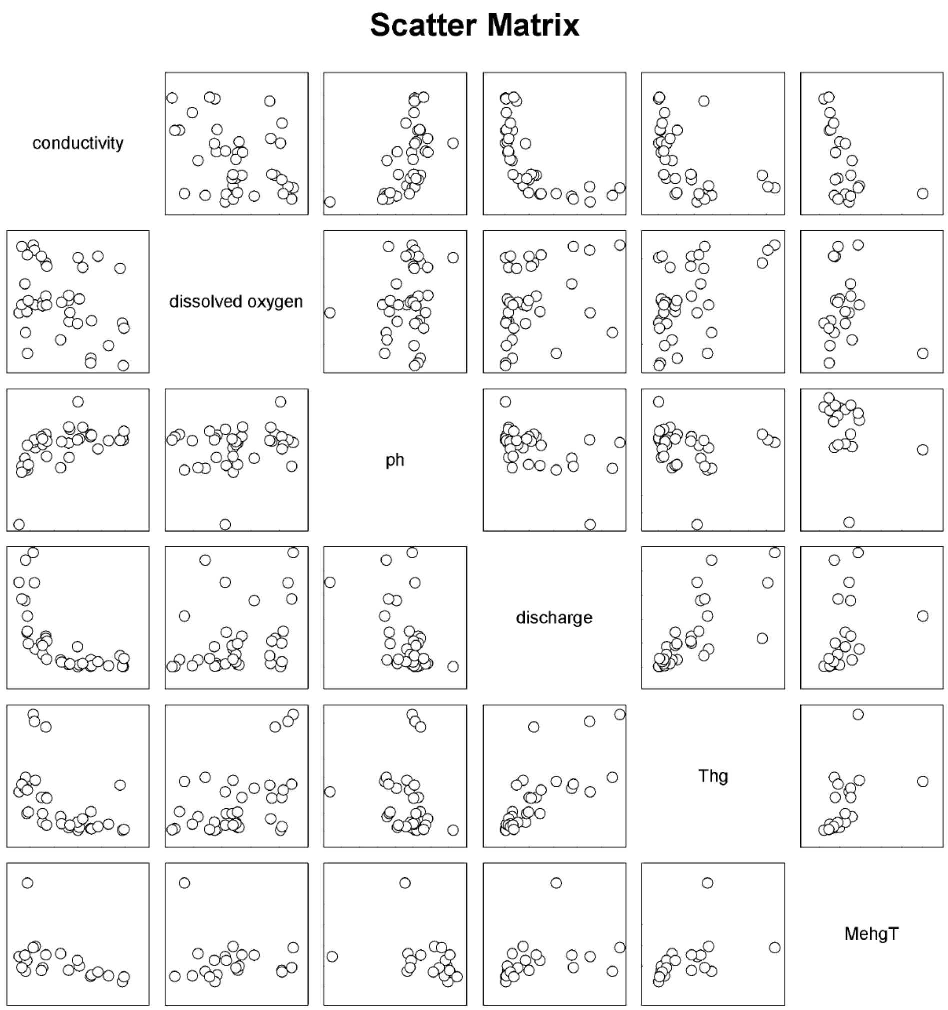

Figure B5. Scatterplot matrix illustrating relationships among flow (i.e., discharge), total mercury, methylmercury, conductivity, pH, and dissolved oxygen.

Table B1. Pearson's correlation matrix for water quality parameters showing the correlation coefficient (positive or negative), the P value, and the sample number.

	Dissolved Oxygen	pH	Discharge	Total Mercury	Total Methylmercury
Conductivity					
Correlation Coefficient	-0.339	0.531	-0.673	-0.53	-0.512
P value	0.0375	0.00061	0.00000676	0.000894	0.0177
Sample Number	38	38	36	36	21
Dissolved Oxygen					
Correlation Coefficient		0.174	0.31	0.488	-0.133
P value		0.296	0.0654	0.00254	0.566
Sample Number		38	36	36	21
Ph					
Correlation Coefficient			-0.504	-0.159	-0.343
P value			0.00172	0.354	0.128
Sample Number			36	36	21
Discharge					
Correlation Coefficient				0.771	0.328
P value				3.81E-08	0.146
Sample Number				36	21
Total Mercury					
Correlation Coefficient					0.476
P value					0.0291
Sample Number					21
Total Methylmercury					