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Guadalupe River Mercury Concentrations and Loads During the Large Rare January 2017 Storm

Prepared by

Lester McKee, San Francisco Estuary Institute

Alicia Gilbreath, San Francisco Estuary Institute

Sarah Pearce, San Francisco Estuary Institute

Ila Shimabuku, San Francisco Estuary Institute

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Regional Monitoring Program for Water Quality in San Francisco Bay (RMP)

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Executive Summary

Background

The Guadalupe River watershed has a long history of urbanization and is the location of a historic mining district that produced 40 million kg of mercury (Hg) during operation. The river system is listed as impaired and is a large pathway of Hg to San Francisco Bay. The TMDL calls for stakeholders to reduce load to an average of 9.4 kg per year over 20 years by removing Hg-laden wastes in the mining and urban areas and implementing other treatment practices. To demonstrate success, the stakeholders are documenting management efforts and have been conducting water sampling to show that average loads are decreasing or that Hg concentrations on suspended particles are trending towards the TMDL target of 0.2 mg/kg (dry wt., annual median). The Guadalupe River is capable of flows >10,000 cfs, and a flood flow of >6,000 cfs has a return interval of approximately 1:5 years yet most sampling has occurred at flows <4,000 cfs. Since most Hg is transported in the system during large storm events when Hg can be mobilized from the historic mining district, it is essential to measure the Hg load during these rare events. The main objective of this study was to sample and estimate loads during such a rare events.

Results and Discussion: January 7–13 Storm Series

During January 2017, forecast conditions were met for a “Hg mobilization event” and a field team was mobilized to the sampling site in San Jose, CA. The system was strategically sampled following a prepared but adaptive sampling strategy and 14 samples were captured over five days. Flow peaked three times (at 4,090, 3,970, and 5,490 cfs) in response to prolonged rainfall. Rainfall intensity in the historic mining district exceeded the hypothesized threshold for Hg mobilization (>2 inches in 6 hours) and Hg concentrations exceeded any measured since Water Year (WY) 2003. The field design was based on the use of turbidity as a surrogate to help estimate HgT concentrations between collected samples. Unfortunately, the USGS turbidity probe failed on January 8th at 4:30 am, necessitating the modification of sampling and interpretation techniques. Key findings from this field study are listed below.

- Total Hg concentrations ranged between 280-6,450 ng/L with a flow-weighted average of 2,500 ng/L, with just 1% transported in dissolved phase. The flow-weighted average for eight previously sampled years was 484 ng/L and the estimated long term mean for this system is about 1,700 ng/L (the TMDL load estimate 106.5 kg divided by the mean annual flow (63.3 Mm^3 equivalent to 51,318 acre foot).
- Particle concentrations ranged between 1.5-17 mg/kg, with a flow-weighted average of 6 mg/kg, exceeding the TMDL target (0.2 mg/kg (dry wt., annual median) by 30-fold.
- The ratio of flow in Alamitos Creek located near the historic mining district to flow at Hwy 101 explained about 88% of the variability in particle concentrations measured during the storm series providing further evidence of the importance of sources in and

near the historic mining district. Sources include bed, bank, and channel storage below the reservoirs, and tributaries that flow off mining contaminated areas downstream from the Almaden and Guadalupe Reservoirs.

- Based on USGS flow data, a volume of 35.41 Mm^3 (equivalent to 28,707 acre foot) flowed down the river during a seven-day period (Saturday January 7 to Friday January 13), equivalent to 56% of the average annual runoff (based on the period 1981-2010).
- Flow, during this one storm series, transported an estimated 70 kg of Hg. It is unknown what the total load might have been for the complete wet season since there was a larger and more significant storm in February. However, it is reasonable to suggest it may have been many 100s of kilograms and perhaps even close to 1000 kg given the total flow for the year was the second largest since WY 1932 when flow measurements in this system began.
- Based on comparisons between the January 2017 storm data and previous relevant data, the characteristics of Hg transport in the system were not different to those measured during December 2002 when a large and rare storm of similar size and intensity was last sampled. Aqueous concentrations, particle concentrations, the proportion of transport in dissolved phase, the relationship between instantaneous flow, suspended sediment loads and instantaneous Hg loads, and the mechanisms of transport (rainfall intensity and flow sources) appear to be unchanged over the 14 years.
- A correlation between particle concentration and the portion of flow coming from the area around the historic mining district was observed. This relationship could be used as a tool for loads computations and as a means for determining trends in Hg derived mainly from the lower urban part of the system (when flow from the mining areas is small) and from mining wastes (when the flow from the mining areas is large). This type of trend indicator is better than the use of any measure of central tendency (mean, median, or flow-weighted average) because it is less reliant on quasi-random sampling times and preserves the source-mobilization-transport process occurring during storms.

Sampling Recommendations

To measure particle concentrations or loads for the purposes of monitoring for trends associated with legacy mining wastes, a sampling program that focuses on large and rare storms is recommended. The program should be reactive to the mobilization criteria described in this report (or similar). Once those criteria are met, it is recommended that all remaining storms for the wet season be sampled. Since, on average, storms of this magnitude occur about every five years, a program like this should be about 1/5th of the cost of an annual sampling program. The cost during a mobilization year will be about $100-150k depending on how many storms occur after the initial Hg mobilization conditions have been met.

Introduction and Background

Mercury (Hg) is a toxic heavy metal that accumulates to concentrations of concern in the San Francisco Bay food web. Mercury exposure is one of the primary drivers behind the sport fish consumption advisory for San Francisco Bay (Office of Environmental Health Hazard Assessment, 2011). Mercury is also one of the primary pollutants causing both San Francisco Bay and the Guadalupe River to be added to the State of California 303(d) list of impaired water bodies in compliance with the Clean Water Act. Predatory fish, birds, and mammals (including humans that consume fish) at the top of the food web are most vulnerable to Hg exposure due to a process called biomagnification (Davis et al., 2012). Mercury is a neurotoxicant, and is particularly hazardous to nervous system development in unborn children and children under the age of 18. Mercury enters the Bay via multiple pathways but information presently available suggests that transport of Hg in stormwater from local watershed and atmospheric sources via small and large tributaries account for the majority of annual loads to the system.

The Guadalupe River Watershed at the southern end of San Francisco Bay provides the largest Hg load of any individual watershed draining from the nine counties of the Bay Area to the Bay. The lower portion of the watershed has been developed for urban land uses over the past 165 years (Figure 1) and is now home to more than 434,000 residents. The upper portion of the watershed is less developed and home to the historic New Almaden mercury mining district. After discovery that the “red rock” that the local Ohlone were using for pigments was cinnabar in 1845, the Mining District, which operated from 1850-1975, accounted for approximately 30% (40 million kilograms) of the North American mercury production and approximately 6% of global production during its operating lifetime (Cargill et al. 1980; Hylander and Meili 2003). Many of the former ore reduction and processing areas around the New Almaden mercury historic mining district were cleaned up by Santa Clara County in the 1980s and 1990s to concentrations suitable for reducing the risk of direct human exposure to mining wastes during use of the area for outdoor recreational pursuits (hiking, bicycling, equestrian). But mining residues in and adjacent to the historic mining areas remain a legacy Hg source that likely impacts water quality in the Almaden, Guadalupe, and Calero reservoirs, the river downstream, and ultimately San Francisco Bay. Elevated Hg concentrations associated with mining wastes are found in bed sediments in Guadalupe Creek and tributaries, Alamitos Creek and tributaries, Almaden lake, Canoas Creek, and the mainstem of the Guadalupe River all the way downstream to Hwy 237 (Austin et al., 2008). However, given the location in the on Alamitos Creek watershed of Mine Hill (the largest production area) and the Hacienda Furnace Yard (the largest processing area), Alamitos Creek is considered the major pathway for the historic mining wastes.

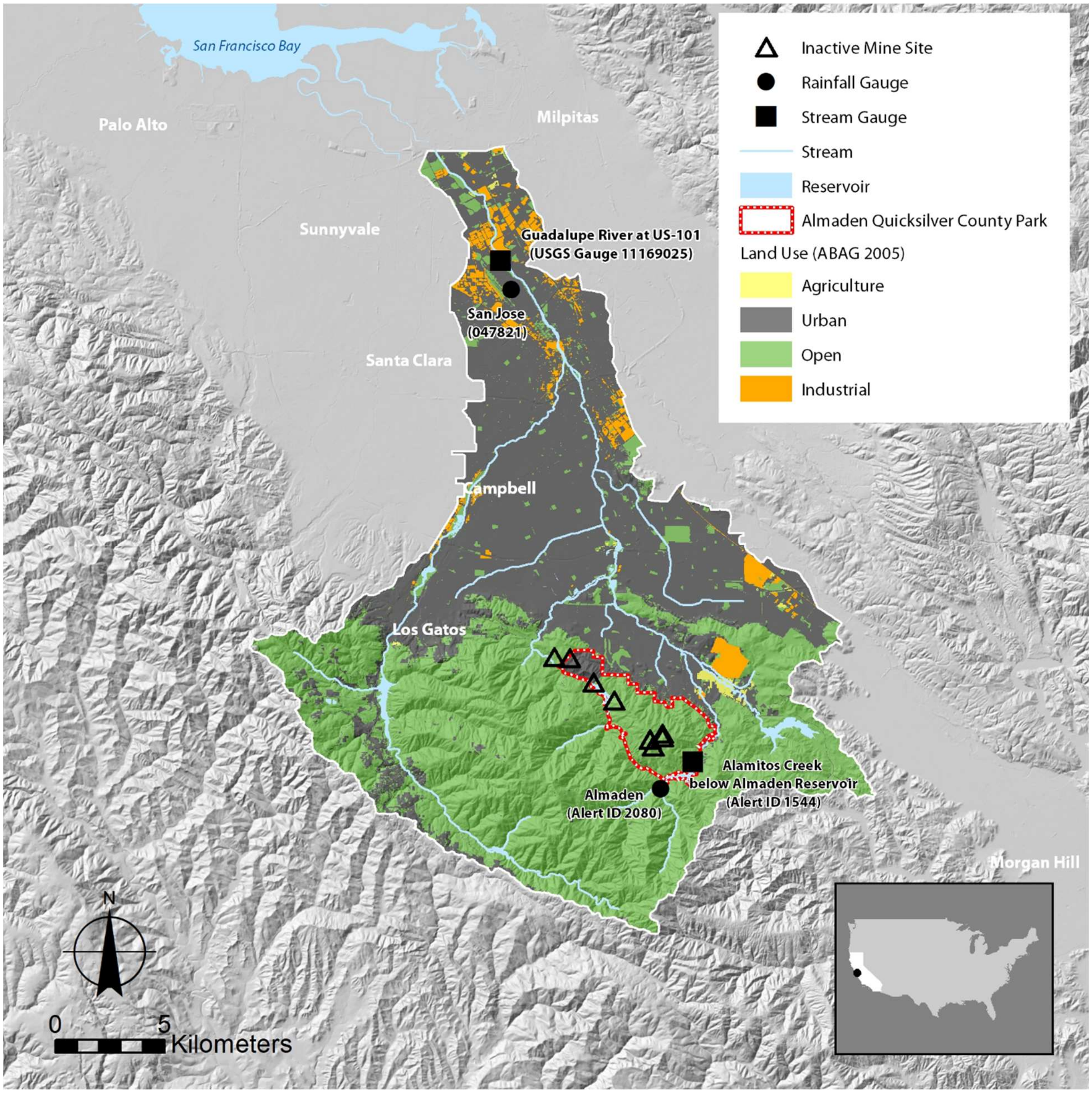


Figure 1. Map of the Guadalupe River watershed, main drainages, the Highway 101 (GR-101) sampling location and land-use/land cover. The Almaden Quicksilver County Park (outlined in red) is the location of a number of inactive mercury mine sites that operated from 1850-1975. Not shown are several inactive mines (Santa Teresa and Bernal) that were situated 3-4 miles northwest of the Calero Reservoir.

Austin et al., (2008), summarizing all work completed to that time to support the Guadalupe River Watershed TMDL, reported that, on average, a baseline load of 106.5 kg per year of total Hg (HgT) was transported to San Francisco Bay from this watershed. The majority of HgT in the watershed (92 kg per year or about 86%) was estimated to emanate from the historic mining district via nonurban stormwater runoff that passes down the Guadalupe River system. These estimates were based on work mostly completed by Tetra Tech in support of the TMDL (see details below). The Guadalupe River Hg TMDL wasteload allocation is 9.4 kg per year, which translates to a required 91% reduction from the estimated baseline load and was based on achieving a median dry weight concentration of 0.2 mg Hg per kg of suspended sediment particles discharged from the watershed. The TMDL implementation plan calls for control measures in various areas of the watershed, including the historic mining district, reservoirs and lakes, and urban stormwater runoff (Austin et al., 2008). Control measures include implementation of urban best management practices (BMPs), methylmercury controls in the reservoirs, and erosion controls in and around the historic mining district. To demonstrate progress towards the wasteload allocations, the stakeholders can either:

- document the removed Hg mass associated with mining and urban wastes;
- measure Hg loads and show that a rolling five-year annual average Hg load is trending towards or is less than the allocation (9.4 kg); or
- quantitatively demonstrate that the Hg concentration on suspended sediment that best represents sediment discharged is below the suspended sediment target of 0.2 mg/kg (dry wt., annual median).

Stakeholder Efforts to Monitor and Remediate Watershed Mercury

The Guadalupe River Watershed Mercury TMDL, establishes contaminant allocations, implementation plans, and monitoring requirements for mine and reservoir owners in the watershed with the goal of reducing mercury in fish tissue to protect wildlife and human health. The landowners in the former mining district (Santa Clara Valley Water District, Santa Clara County, Midpeninsula Regional Open Space District, and Guadalupe Rubbish Disposal, Inc.) are encouraged to coordinate monitoring through a Coordinated Monitoring Program (CMP). The first phase cost share of the CMP begun on November 9, 2010 with a final report submitted to the Regional Board in March 2017 (AECOM, 2017). In June 2017 (before this current report was prepared), the SFBRWQB issued requirements for the next phase of monitoring (i.e. second phase) based on discussions with the CMP Partners and lessons learned.

The Santa Clara Valley Water District has voluntarily treated reservoirs to prevent methylation since 2007 (Kirsten Struve, personal communication, February 2018). Over the past five years, the District has operated hypolimnetic oxygenation systems in three reservoirs in the

Guadalupe River watershed (Almaden, Calero, and Guadalupe) and solar circulators in Almaden Lake to prevent anaerobic conditions that occur during spring and summer reservoir stratification. Stratification is the separation of the water column into two layers: the epilimnion (top layer) and the hypolimnion (bottom layer). Under low-oxygen conditions, mercury can be converted to methylmercury, a highly toxic compound that bioaccumulates in fish tissue and presents serious health risks to birds and people consuming fish. The District addressed previous operational challenges and achieved continuous operation during the summer months of 2016 and 2017 (Kirsten Struve, personal communication, February 2018).

The District conducted twice-monthly water quality monitoring in each reservoir during oxygenation system operation and monthly monitoring during the remainder of the year. Fish were sampled twice per year. The District reported to the San Francisco Bay Regional Water Quality Control Board on the findings of the studies that evaluate the effectiveness of hypolimnetic oxygenation in addressing mercury contamination in 2015 and 2017. By doing so, the District remains in compliance with the Guadalupe River Watershed Mercury Total Maximum Daily Load (TMDL) (Kirsten Struve, personal communication, February 2018).

Operation of the systems has resulted in a significant reduction in methylmercury in the hypoliminia of the reservoirs, rarely exceeding the water quality allocation of 1.5 ng/L. However, methylmercury concentrations in the upper water column either increased or were unchanged. Only Guadalupe Reservoir exhibited a significant declining trend in fish tissue mercury concentrations. Additional studies are needed to evaluate the factors that determine effectiveness of the systems (Kirsten Struve, personal communication, February 2018). In addition to these efforts in the reservoirs and lakes, the District has completed calcine removals on Alamitos Creek and Guadalupe River from 2007 to 2009, and restored portions of Lower Jacques Gulch by removing calcine deposits and restoring more than 2,000 linear feet of streambank in 2010 (AECOM, 2017).

The Santa Clara County Parks and Recreation Department has also been implementing source control projects for remnant mercury mine waste in the Guadalupe River watershed (AECOM, 2017). For example, the Senador Mine project was completed in Fall 2016 and restored a headcut and other erosional features in a tributary to McAbee creek and removed several small calcine piles to reduce erosion of mercury mining wastes. The Calcine Roads project, expected to go to construction in 2017, will remove calcine materials from approximately 4 miles of historic mine roads. Additional remedial work being conducted by Santa Clara County Parks includes removal of residual mine wastes at the Hacienda Furnace Yard (AECOM, 2017). Santa Clara County Parks will restore creeks adjacent to the Hacienda Furnace Yard, once the largest mercury ore processing facility at New Almaden. The project would remove calcines from about 500 feet of streambed and restore reaches along these creeks (AECOM, 2017). Some of these projects are still under discussion with SFBRWQCB and going through permitting so the details may change a little.

Other projects in the watershed include the remediation of an eroding slope of mercury mining waste at Hicks Flat by the Midpeninsula Regional Open Space District in 2014 and implementation of erosion control measures at Guadalupe mine by the Guadalupe Rubbish Disposal Company (AECOM, 2017). This brief summary highlights the considerable time and expense of the CMP partner stakeholders to monitor and remediate mercury in and near the historic mining areas of the Guadalupe River watershed.

Previous Loading Studies and Data Gaps

There have been a number of studies on Hg contamination in the Guadalupe River over the past 20 years. Abusaba and Tang (2000) published the first estimates of mercury loads from the Guadalupe River presented in a TMDL context. They proposed a load of 49 kg per year as the best estimate for average mercury loads discharged from the Guadalupe River into lower South Bay, with a likely range of 7 to 320 kg/yr. The mercury load estimates were based on published estimates of sediment generation rates from the watershed (7 to 32 million kg/year) and published measurements of mercury concentrations in suspended sediments and bedded sediments of the lower Guadalupe River (1 to 10 mg/kg). The authors noted that interannual variability was likely to be high and also that the mercury load estimates from the Guadalupe Watershed into Lower South Bay were much larger than the estimated mercury load discharged from the reservoirs in the upper watershed (0.4 to 4 kg/yr). That insight provided a clue early in the development of the TMDL that storage and remobilization within the watershed may be a significant ongoing mercury source to lower South Bay (Abusaba and Tang, 2000).

Thomas et al. (2002) reported on water column Hg concentrations measured throughout the watershed during October 2000, when flow conditions ranged between 15-150 cfs, and used these to estimate an annual HgT load between 4 and 30 kg by combining suspended particulate Hg concentrations (0.5 - 4 mg/kg) with the annual average sediment load (7,400 metric t). These estimates were smaller than those presented by Abusaba and Tang (2000) likely because of the relatively low flow conditions that were sampled. The Guadalupe River is known to be capable of flows >10,000 cfs, and a flood flow of >3000 cfs has a return interval of approximately 1:2 years. The Thomas et al. (2002) measurements were made under relatively low flow conditions during an October storm event; an antecedent condition we now know would not have resulted in a Hg mobilization event from the historic mining district.

Austin et al. (2008) summarized work completed by Tetra Tech to support the development of the Source Analysis, a component of the Guadalupe River Hg TMDL. Sampling occurred in the winter season of WY 2004 in the creeks surrounding the historic mining district. To estimate the mining waste load, data on total suspended solids and mercury in Los Capitancillos Creek collected on two dates (March 3 and 26, 2004) were combined with data from other mining impacted creeks sampled in the wet season to estimate an average particle concentration of 17.5 mg/kg. An uncalibrated SWAT model was used to estimate flow from Los Capitancillos Creek that was then compared to sampled suspended sediment concentrations to generate a regression equation. Suspended sediment loads were then generated from the modeled flow data and combined with the average particle ratio to estimate loads that were then normalized by the area of Los Capitancillos Creek watershed. This resulted in a unit area mining waste load of 54.5 µg/m^2 for total mercury for the 2003-2004 wet season. This was then scaled by area for the mining area as a whole. A similar method was followed for the urban loads estimates using measured flow and sampling conducted in Ross Creek, an area that is almost entirely urbanized and has no history of mining activities. This resulted in unit area urban stormwater runoff loads of 1.6 µg/m^2 for total mercury. Background loads were also estimated using similar methods and a small non-urban watershed near Lexington Reservoir and found to be about 75% of the urban unit area loads, the authors suggesting that perhaps the urban loads were underestimated. The authors recognized that the estimated loads and yields were highly uncertain even for WY 2004 (although was noted that their estimate of 10 kg at Hwy 101 was not too different to that reported by McKee et al. (2005) (14.8 kg), and did not reflect the average that might occur over the longer term. To rectify this, they used a Monte Carlo simulation to estimate the uncertainty and make a better estimate of the mean, the result being a new estimate of total Hg loads for the wet season of WY 2004 of 12 kg with a range of 8-20 kg. A similar method was then used to estimate multi-year uncertainties and a long-term average based on flows for the climatic period (WY 1960-2002). Based on these methods and an average particle concentration of 3.4 mg/kg, an average suspended sediment load of about 31,000 t, an average annual load of 106.5 kg with 86% derived from the mining areas was adopted in the TMDL (Austin et al., 2008).

McKee et al. (2010) reported on loads estimated from storm-focused sampling at two locations, the USGS gage at Hwy 101 (11169025) and an upstream gage on Guadalupe River at Almaden Expressway (11167800). Using the available data they were able to make an estimate of the Hg load that was generated from the urban portion of the watershed (17%) versus the upper area that was dominated by loads emanating from the legacy historic mining district (83%), which corroborated the area-associated contribution estimates listed in the TMDL (Austin et al., 2008). They also made arguments for focusing any future monitoring on high intensity storms when there is a greater likelihood of further Hg mobilization and transport from historic mining areas. They suggested that the largest remaining gap in relation to annual loads was for periods with rainfall intensities and runoff greater than or equal to that observed during Water Year (WY) 2003. They recommended that routine annual high effort monitoring of the Guadalupe River could therefore be discontinued and replaced with a response-based sampling design that would cost less in the long run and provide the needed data. They cited the Regional

Monitoring Program for Water Quality in San Francisco Bay (RMP) as a possible venue for providing a stable structure for budgeting and planning such a sampling program (McKee et al., 2010). These suggestions were not adopted at the time and annual wet season sampling continued in WY 2011 (Balance Hydrologics, Inc., 2011), WYs 2012-2014 (Gilbreath et al., 2015), and in WY 2015 (AECOM, 2015). Sampling during these years coincided with a severe drought. Rainfall intensities and annual flows and loads were lower than average during this period but small improvements were made in knowledge about loads coming from urban runoff that largely confirmed the estimate of urban loads reported in the TMDL.

It should be noted that the realization that monitoring should focus on high intensity storms is not unique to the Guadalupe River watershed setting. The Contra Costa Clean Water Program (CCCWP) has been monitoring mercury in the Marsh Creek watershed with an interest in understanding mercury loads from the upper watershed that may originate from the historic Mount Diablo mercury mine. After several years of sampling low intensity storms conveying only lower watershed urban runoff, the CCCWP recommended shifting the sampling paradigm to focus on high intensity storms. From a practical standpoint, this meant only deploying monitoring crews during late season events when the primary spillway of the Marsh Creek reservoir conveyed flows from the upper watershed to the lower watershed (CCCWP, 2015). This new monitoring paradigm is currently being implemented, and upper watershed flows were sampled by CCCWP for the first time in Marsh Creek during the 2016 – 2017 storm season.

AECOM (2015) described storm sampling conducted during WY 2015 in accordance with a Coordinated Monitoring Plan prepared by County of Santa Clara, the Guadalupe Rubbish Disposal Company, Inc., the Midpeninsula Regional Open Space District, and the Santa Clara Valley Water District (Interested Parties) as directed and approved by the San Francisco Bay Regional Water Quality Control Board (SFBRWQCB). This report was written to support the final, 5-year monitoring report that was due to the SFBRWQCB on or before March 31, 2017 (AECOM, 2017). The report presented a load of 6.3 kg for WY 2015 based on 28 samples (an appropriate QA samples) collected during four storms with the maximum flow sampled in excess of 5000 cfs. Loads were determined by combining the results of estimating continuous total Hg concentrations for 15 minute time steps generated using a combination of a regression equation between SSC and 15 minute flow and SSC and total Hg (based on the 28 samples). The 2015 regression relationships were then used to recompute a load for WY 2010 of 12.3 kg, and based on comparison to previously reported loads of 14.8 kg for WY 2010 (McKee et al., 2010), imply there has a ~20% reduction in load and a reduction in the ratio between total mercury and SSC. Although this exercise in encouraging, WY 2015 was slightly drier than normal (89% mean annual precipitation for San Jose based on the period 1981-2010), and collectively, WYs 2012–2015 were the driest consecutive four years in the 142 year rainfall record for San Jose.

As such, 2015 was not likely representative of a year when mercury would be transported from source areas around the historic mining district. Thus, the trend, if real, more likely represents a trend mercury loads emanating from urban runoff since impervious surfaces tend to produce flow even during drier years and smaller storms. To determine a trend in mercury emanating from the historic mining areas, samples need to be collected during storm periods when there is significant runoff emanating from those areas. This was likely not the case in WY 2015; the authors of future reports need to make this justification to support claims of trends in mining related Hg loads.

Domagalski et al. (2016) collated data from technical reports by McKee and coauthors for WYs 2003-2006, and 2010, and estimated an average load for Guadalupe River at Hwy 101 of 35 kg based on the arithmetic average of the five years of data. This contrasts with the TMDL estimate of 106.5 kg that was based on limited wet season sampling completed by Tetra Tech but used a Monte Carlo technique to climatically extrapolate the small dataset to make reasonable estimates of long-term average annual loads. The Domagalski et al. arithmetic average estimate also contrasted with the climatically-adjusted average annual estimates made by McKee reported in the *Pulse of the Bay* each year (e.g., SFEI, 2013), which have been consistently >120 kg and generally consistent in magnitude to the TMDL estimate. The work by Domagalski et al., although valuable in other ways, further helped to highlight the need to formally publish estimated Guadalupe River loads and propose the standardization of more sophisticated averaging techniques in systems with highly variable climate and when data collection often fails to sample significant storms.

McKee et al. (2017) rectified this information weakness when they reported on the long-term data set for Guadalupe for a wide range of organic and inorganic pollutants including Hg. They presented a climatic adjustment technique and used it to make an updated estimate of long-term average annual loads of 10,627 t of suspended sediment and 139 kg/yr for Hg. They used this technique to adjust the load estimates for both the upper and lower gauging locations and estimated that, on average, the historic mining district contributes 88% of the annual load, the balance of 12% coming from the urban area downstream of the Almaden Expressway gage (McKee et al., 2017). This again independently corroborated the proportional load estimates for the mining and urban areas reported in the TMDL (Austin et al., 2008).

Based on all this work, the challenge with this watershed remains a lack of sampling during rare large events. During WY 2003 when concentrations and loads were the highest measured since sampling began, flow peaked at 6071 cfs (a 1:5 year return event) and rainfall intensity in the historic mining district exceeded 2 inches in a 6 hour period. At no time since then have such flows in relation to these rainfall intensities been sampled or even occurred. In order to assess whether management efforts are having an impact on legacy mining-related loads, storm conditions equaling or exceeding those conditions need to be sampled repeatedly over time.

Such data, once available, would also be useful for rechecking the current estimate of long-term average loads that are based on very limited data from WY 2003.

Conceptual Model of Hg Source-mobilization-transport Processes

Urban Hg

Mercury is transported in the Guadalupe River from three main sources (atmospheric deposition, local urban stormwater, and legacy mining runoff). The atmospheric and local urban sources are supplied, mobilized, and transported to the mainstem river via the urban drainage system that is designed to convey stormwater off roads and roofs and away from buildings during most rain events. Although there are differences in the amount of Hg mobilization from urban areas among storms associated with factors such as first flush, antecedent conditions (number of dry days between storms and rainfall season to date), and rainfall intensity, the transport of Hg from urban areas occurs during every storm that produces runoff from impervious areas (most rain storms). These storms produce loads that are well-correlated with flow volume, suggesting little residual storage in the urban drainage system between storms. However, the yield (the Hg mass produced per unit watershed area) from the urban area downstream from the Almaden Expressway (USGS gage number 1167800) (134 g/km^2/y) is at least 4-fold greater than the Hg yields from other urban areas in the world (McKee et al., 2017). Either this urban area is unusually high in Hg or there is mining debris stored in the lower channel system that are transported during smaller urban dominated storms and drier years when there isn’t significant runoff from the historic mining district. If there are residual contaminated mining debris stored in the lower urban portion of the Guadalupe River channel system, the use of the Hwy 101 location for monitoring change in relation to urban management effort could be confounded since only about 25% of the dry year signal may be truly urban in origin. Higher concentrations are seen in the system during earlier season urban runoff storms that might be associated with urban first flush or remobilization of Hg in the main stem channel or both but data don’t suggest that there is disproportionally higher loads during dry years that follow wet years.

Mining Hg

In contrast, the mobilization and transport of Hg from mining sources occurs periodically as “mobilization events” when conditions are suitable and is much more sporadic then conveyance of Hg from the urban areas of the watershed. The prevailing hypothesis for the system is that Hg mobilization events occur when soil moisture deficits are diminished to the point where sheet flow and shallow landslide erosion of legacy Hg deposits in and adjacent to the historic mining district are transported to tributary channels. This occurs when there has been a reasonable amount of rainfall for the season (estimated at a minimum of seven inches) and when rainfall intensity in the historic mining district exceeds about 2 inches in a 6 hour period during a storm. When these conditions are met, the system switches from supply-limited (very little Hg getting to the channels for transport) to transport-limited (lots of Hg is supplied to the channels). Even when these threshold conditions are met, the concentrations and loads in relation to flow are highly dependent on the character of the storm and will be unique for each storm or storm series in relation to factors that are not yet fully understood.

After an initial mobilization event, as the season continues, the amount of rainfall needed to trigger such Hg mobilization events appears to diminish based on data from WY 2003 (the only year with suitable data). Interpretation of the data collected to date does not support reservoir release or channel bed and bank erosion as being primary Hg sources in the Guadalupe River, although these sources probably do play some minor role (although it should be noted that shorter reaches in Alamitos Creek and McAbee Creek may be locally important). Elevated and sustained flow in Alamitos Creek from reservoir release or spill and flow from tributaries such as McAbee Creek and other creeks flowing off historic mining district into Alamitos Creek likely do help to transport any mobilized Hg downstream and through the main river system. This proposed dominant set of processes is consistent with the location of Mine Hill (the largest mine) and Hacienda Furnace Yard (once the largest mercury ore processing facility at New Almaden) in the Alamitos Creek watershed. The available data also suggests that once the initial mobilization is triggered within one storm, there is likely to be further mobilization during the next storm within the same wet season, but the nature of that process is not well understood due to too few observations during these conditions. Data do not suggest there is any residual mobilization during a dry or normal year that follows a wet year. The data do not appear to support the dominance of the alternative transport model of intermittent transport after Hg has accumulated in the streamed and transport downstream via a sequence of storms but these could be a minor processes.

Objectives

This study was designed to focus on the mining-related mobilization and transport processes that occur in this system during rare large events. Data collected on the transport of Hg associated with urban sources were ancillary. The objectives of the study were to:

1. safely sample rare high flow conditions on the Guadalupe River during the peak and falling stages and subsequent baseflow condition of a major storm or storm series to estimate Hg concentrations and loads for that storm;
2. compare the resulting data to relevant previously collected data, in particular data collected during key storms of WY 2003 when a 1:5 year (6,071 cfs peak flow) storm series caused the mobilization and transport of high mercury loads; and

3. discuss how the data relate to some of the key management questions for the system and make recommendations about how future sampling campaigns could be improved.

Methods

Decision to Mobilize

Waiting for and sampling a very large and rare storm event is challenging in any river system. In this study, the approach to meet that challenge involved the following four pre-storm planning elements:

1. A sampling and analysis plan (SAP) and budget was prepared and approved 18 months in advance that included justifications and general objectives, mobilization criteria, analytes, numbers of samples, quality assurance sample types and numbers, details of equipment, a general staffing plan, and a mock up sampling design in relation to a large storm scenario;
2. A governance structure that is nimble enough to make the high level mobilization decision in a 24-hour time frame in response to a request from RMP managers (Jay Davis, Phil Trowbridge), and the Lead Scientist (Lester McKee). The RMP has such a structure that was kept apprised of evolving environmental conditions in the months and weeks leading up to the decision request.
3. A final field design (expected time of first sample and subsequent samples) based on conditions presented in the forecasts (this was prepared five days in advance and adjusted each day as the forecast evolved and then modified using real time rainfall and flow data during the storm)
4. A senior team of decision makers (RMP managers) who were engaged with the Lead Scientist at critical moments to mobilize the field team and then make the final decision to call the field team home (“false start”) or to initiate and complete the sampling plan.

By the end of 2016, several base criteria had been met.

- The watershed had received greater than seven inches of rainfall at all gage locations, over 10 inches in the historic mining district, and over 20 inches on the Loma Prieta ridgeline;
- The Guadalupe and Almaden reservoirs were filling, indicating that the soil moisture conditions were becoming saturated. Despite the previous four dry years, all indications were that the Almaden Reservoir would be spilling in the next big storm event;
- Baseflow at the USGS Highway 101 gage (11169025) was elevated (35 cfs versus autumn base flow conditions of 26 cfs prior to the first storm). Storm hydrographs had become

more peaked and started to show double peaks or evident second rise components associated with flow from the upper watershed. The hydrographs were generally showing longer tails indicating greater influence of groundwater.

On January 4th 2017, a check on conditions and forecasts revealed the following.

- Rainfall for the season was well above average for January. There had already been 33 inches of rainfall on Mount Umunhum (SCVWD gage number 2081), 24 inches of rainfall at Loma Prieta (SCVWD gage number 2072) (both on the ridgeline in the headwaters of the Guadalupe River), and 16 inches of rainfall at the head of the Almaden Reservoir (SCVWD gage number 2080);
- A rain forecast of 9-12 inches in the Santa Cruz Mountains had been issued associated with an atmospheric river emanating from the tropics near Hawaii;
- The Almaden Reservoir was 82% capacity and was likely to fill completely with the rainstorm in the forecast.

This forecast and the watershed conditions at the time suggested that a Hg mobilization event was imminent. Emails and phone calls were initiated with Kirsten Struve, Chris Sommers, Brett Calhoun, Carrie Austin, and Tom Mumley to discuss the forecast and watershed conditions and to warn them that a request to release RMP funding was about to occur.

Once the preliminary discussion had occurred with key stakeholders, an email was sent to the RMP Technical Review Committee and the Steering Committee by lunchtime on January 4th. By January 6th the storm forecast had continued to solidify. Further event planning preparations were completed including a revised and “operational” sampling plan that used real forecast information, a staffing plan, a safety briefing, and a logistics plan (equipment, sample shipping, etc). On January 6th, the forecast for Saturday 4 pm through Sunday later in the day was for 9.5 inches in the higher elevations of the Santa Cruz Mountains (with as much as 12 inches in local spots) associated with an atmospheric river that was aimed directly at the Santa Cruz Mountains. In addition, the modeled estimated flood peak for Guadalupe River had been slightly increased to 7,000 cfs with the timing of the peak flow estimated to be on Sunday January 8th at about 8 am.

Additional sampling support had also been gained from the RMP for collecting a PCB flow composite sample and to collect a microplastic flow composite sample during the urban component of the hydrograph. PCB data will be reported in the annual Pollutants of Concern (POC) monitoring report that is planned for February 2018 (Gilbreath et al., 2018). The microplastics data will be reported through the Moore Foundation microplastics project being led by Meg Sedlak and Rebecca Sutton of SFEI.

Sampling Location and Design

Water samples were collected at the USGS gage station 1169025, Guadalupe River at Highway 101, hereafter referred to as “lower” or GR-101 (Figure 1). This gage is downstream from most of the urbanization in the watershed, including residential, commercial, and transportation land uses and historical industry, including railyards, waste and metals recycling, and manufacture of electric equipment. The sampling location is about 18 miles downstream from the town of New Almaden (the historic center of mining operations and the location of the Hacienda furnace yard where the majority of ore was processed). Estimated average annual flow for the period 1981-2010 for GR-101 is 63.3 million m^3 (Mm^3) (equivalent to 51,318 acre foot). Mirroring rainfall, 89% of flow occurs on average between October 1 and April 30. At this location, turbidity measurements are collected every 15 minutes using a Forest Technology Systems Limited (FTS) model DTS-12 turbidity sensor equipped installed in the central deepest position of the channel using a depth-proportional boom (Eads and Thomas 1983).

The field methods have been well documented in a series of technical reports (McKee et al., 2004; 2010; Gilbreath et al., 2015) and a journal article (McKee et al., 2017). Sampling was carried out using clean techniques, laboratory-prepared sampling equipment and storage containers, and a Teflon coated FISP D-95 depth-integrating sampler (utilizing laboratory TE cleaned Teflon bottle, cap, and nozzle) deployed from the bridge at the USGS gage location in a single vertical using a b-reel attached to a four-wheel-boom-truck and crane assembly (Figure 2). During this event, field staff were on site (or resting periodically in a nearby hotel room) for six days. All samples were kept cool in the field on wet ice and driven to the lab during the field deployment to ensure that samples for analysis of dissolved Hg (HgD, operationally defined as <0.45µm) were filtered at the laboratory within 48 hours.

Based on the conceptual model of the Hg source-mobilization-transport process described above, the sampling plan was designed to focus on runoff from the historic mining district. Since the transport time for runoff from the historic mining district and the upper watershed to GR-101 is about six to seven hours, all water in the rising stage of a large flood flow when there has been rainfall in the urban portions of the watershed will be associated with urban runoff and have relatively low Hg concentrations. This part of the process was not targeted. The arrival of “mining debris contaminated water”, about 5-6 hours after rainfall begins in the upper watershed, can be subtly observed in changes to the rise of the hydrograph and to the turbidity record during the flood event. A general sampling plan was prepared that included sampling at a higher rate (1-2 hour intervals) just before, during, and just after the peak in the hydrograph with an increase in the time between samples (1, 2, 4, 8, 16, 32 hours) leaving one sample for a base flow condition approximately 40-60 hours after the flood event had passed. Based on budget and logistics, a total of 14 samples were planned. The actual sampling program implemented was more complex due to three storm peaks.

Figure 2. Field equipment and field conditions.

Laboratory Methods and Quality Assurance

Water samples were analyzed for Total mercury (HgT), total dissolved mercury (HgD) and suspended sediment concentration (SSC) by Moss Landing Marine Laboratory (MLML), Moss Landing, California. This is the same lab that supported the project in WY 2003. Particulate Hg (HgP) was calculated by difference (HgT – HgD = HgP). Upon receipt at the lab (within 48 hours), water samples were preserved with a final concentration of 0.5% v/v bromine monochloride (BrCl). Prior to preservation, each water sample was loaded with a trace metal cleaned Teflon stir bar and placed on a magnetic stir plate. Aliquots were pipetted out of the homogenous sample. The dissolved samples were filtered using acid-cleaned Nalgene 0.45 micron filter units. Samples were then analyzed following U.S. EPA method 1631e, modified, using cold-vapor atomic fluorescence spectrometer (CVAFS) detection. A sample size of 25 mL was used and complete digestion of the Hg associated with sediment particles was ensured by colorimetric addition of BrCl. Since the sample concentrations were so high, many had to be diluted, and dilution factors for each sample can be found in the metadata. Therefore, 25 mL was the volume used in the analysis for all samples, diluted or undiluted.

Samples were analyzed for SSC using the laboratory’s method MPSL-108, a filtration and drying method similar to Standard Methods 2540 D for total suspended solids (TSS), except avoiding potential subsampling variability errors by filtering the entire sample volume.

All data were subjected to a rigorous quality assurance/quality control (QA/QC) procedures prescribed by the RMP (Yee et al. 2017). Quality control was assessed across all analytes by the percentage of non-detected samples, detections in blanks, blank spike recoveries, the use of standard reference materials, and field replicates.

Load Computations

The original field design was based on the assumption that turbidity would be used as a surrogate to help estimate HgT concentrations between samples collected during the storm series. Unfortunately, the USGS turbidity probe failed January 8th, 4:30 am. Therefore, the interpretation methods to estimate loads were modified to include two methods:

1) linear interpolation of concentration between all samples; and
2) flow-weighted average concentration based on 14 instantaneous Hg measurements multiplied by total storm series flow

To apply these methods, the following assumptions were made.

- The HgT concentration at time zero (Saturday January 7 at midnight) was 157 ng/L.
- Concentration at the end of day 6 (January 13 at 23:45) was 314 ng/L.

The HgT assumptions were based on a linear regression between instantaneous 15 minute flow (cfs) and measured HgT (Equation 1) generated from measurements made in WYs 2004, 2005, 2006, 2010, 2012, 2013, and 2014.

HgT (ng/L) = 0.2506*flow (cfs) + 73.812 (Equation 1)

Results: January 7–13 Storm Series

Rainfall and Flow

By January 1, 2017, rainfall accumulation since the beginning of the water year (October 1, 2016) was 12.99 inches at the Almaden Reservoir (SCVWD gage number 2080). On January 2, a series of storms began to converge on the watershed. It rained lightly on January 2, 3, 4, and 5 with accumulations of 0.16, 1.6, 1.5, and 0.12 inches, respectively, bringing rainfall for the season up to 16.34 inches with a maximum rainfall intensity of 1.06 inches in 6 hours.

After just a two day reprieve, rainfall began again in earnest on January 7 and did not completely stop until 1:30 pm on January 13, by which time a further 11.10 inches had fallen for a total season to-date accumulation of 27.44 inches. During that period, a rainfall intensity of >2 inches in a 6-hour period was exceeded from 1:15 pm to 5:45 pm on January 8 (Figure 3), coinciding with, if not leading to, the mobilization of Hg into the river system (Figure 4). The flow that resulted from this storm series had three main peaks. The first double-peaked storm peak reached 4,090 cfs at 6:45 pm on January 8 in response to rainfall in the urban portions of the watershed and 3,970 cfs at 2 am on January 9 in response to rainfall from the historic mining district and the ridge line. The second flow hydrograph peaked 5,490 cfs at 2:15 am on January 11. Maximum 6-hour rainfall intensity in the historic mining district for this second storm was less than the first (1.69 inches, Figure 3) yet due to saturated soils, flow peaked at 5,490 cfs and Hg mobilization continued (Figure 4). Over the seven day period from Saturday January 7 to Friday January 13, a total discharge of 35.41 million m^3 (equivalent to 28,707 acre foot) flowed down the Guadalupe River past the sampling location at the USGS gage at Hwy

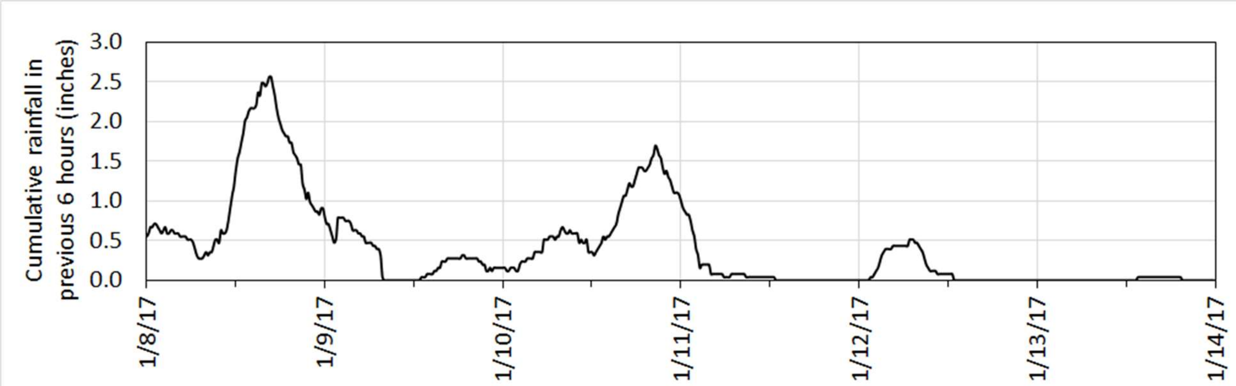


Figure 3. Rainfall intensity measured at Almaden Reservoir (SCVWD gage number 2080) during the January 2017 mercury mobilization event (Provisional data subject to change).

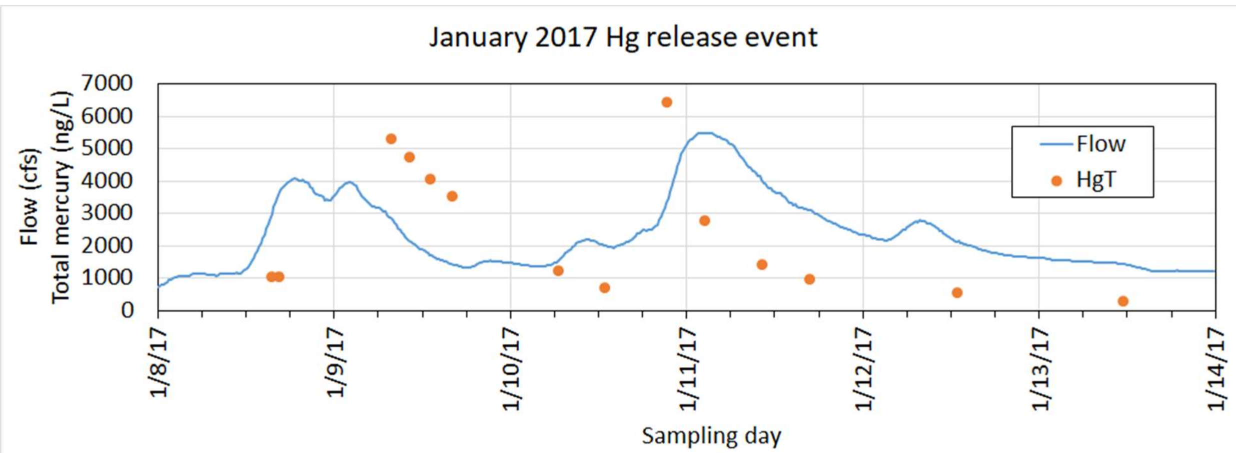


Figure 4. January 2017 Mercury Concentrations and Flow. The graph illustrated a double peak for the January 8/9 hydrograph, a larger single peak for the January 10/11 hydrograph and a very long recession period after the event had passed. Note the timing of samples relative to the total mercury concentrations.

101. This flow is equivalent to 56% of the average annual discharge for the system based on the period 1981-2010, further illustrating the significance of this event.

Mercury Concentrations During the January 7–13 Storm Series

Total Hg concentrations analyzed in water samples collected during the event ranged between 280-6,450 ng/L and averaged over 2,000 ng/L (Table 1). Concentrations of this magnitude have not been measured at this sampling location since WY 2003 (McKee et al., 2004; McKee et al., 2017). As is typical of Hg transport during high flow conditions, the majority of HgT was in particulate form. Suspended sediment concentrations (SSC) were typical and as a result, particle concentrations (estimated as the ratio of HgT:SSC) were also the greatest measured since the storm series of WY 2003. These are similar to those measured near the historic mining district during the development of the TMDL, when the average particulate mercury concentration in creeks in the historic mining district during the 2003-2004 wet season was 17.5 mg/kg (Austin et al., 2008). Particle concentrations of this magnitude exceed the TMDL target of 0.2 mg/kg (dry wt., annual median) for the system by up to 85-fold and on average about 30-fold. These data all provide further evidence of the special nature of the conditions that caused this runoff event.

Table 1. Mercury concentrations measured in 14 water samples collected during the January 7-13 storm series period.

	HgT (ng/L)	HgD (ng/L)	SSC (mg/L)	HgT:SSC (mg/kg)	HgD:HgT (%)
Minimum	280	4.7	150	1.5	0.24%
Maximum	6,450	37	714	17	3.3%
Arithmetic average[1]	2,440	19	399	6.3	1.2%
Flow-weighted average based on discrete samples[2]	2,500	18	453	6.0	1.0%
Flow-weighted average based on dividing the total estimates load by the total flow[3]	1,980	16	-	-	0.81%

[1]Note, given the sampling design and the log-normal distribution of this data, the median is not a useful measure of central tendency.
[2]Computed by weighting the concentrations based on the flow rate during collection of each discrete sample.
[3]Computed by dividing the estimated load for the event (70 kg, derived by estimating concentrations using linear interpolation - see later section on loads) by the total event flow (35.41 Mm^3 equivalent to 27,540 acre-foot).

Mercury Loads During the January 2017 Event

As described in the methods section above, loads were estimated during the event using two methods. The first method (using linear interpolation between concentration samples to estimate concentration at 15 minute intervals that were multiplied with instantaneous 15 minute flow data) was used to generate a load estimate for every 15 minute interval for the 7 day period. The estimated peak load (0.62 kg/15 minutes) occurred on January 10 at 11:00 pm when discharge was 4,660 cfs. The estimated peak daily load (21 kg) occurred on Monday January 9 (Table 2). A total event load of 70 kg was estimated using the linear interpolation method. The second method of combining flow-weighted average concentration with total event flow generated a load estimate of 89 kg (Table 2). Less than 1% of the loads transported during this flood were in dissolved phase although there was a systematic increase in the portion in dissolved phase beginning at 9:15 pm on January 10. So is there some potential for a high or low bias with either of these methods? The main data weakness occurred between 1/8/2017 16:30 and 1/9/2017 7:45. If concentrations peaked higher during that data gap than the concentration observed at 7:45 am then the loads would be potentially bias low. However, since the turbidity probe malfunctioned it is hard to predict what the concentrations might have been. Since the method that combined the flow-weighted average of all the samples with the event flow is likely bias a little high due to the sampling bias towards the flow peaks, the best estimate of load is likely somewhere in between 70 and 89 kg. Note that a third method is discussed later that yielded a load estimate of 84 kg.

So, although the conservative estimate of 70 kg is preferred because it preserves the time varying relationship between concentration and flow within the computation, no matter which estimation method is used, a load equivalent to more than half of the previously estimated typical average annual baseline load for the Guadalupe River system was transported during this one storm. This further illustrates the very episodic nature of loads in this system and the need for a reactive sampling design to measure them. The loads during this storm series alone exceeded the TMDL wasteload allocation for this system (9.4 kg/year) by at least 7.3-fold (although note the load allocation is based on a different methodology that incorporated estimated average suspended sediment loads and a particle concentration of 0.2 mg/kg).

Discussion

Concentration Comparisons Between the December 2002 and January 2017 Storms

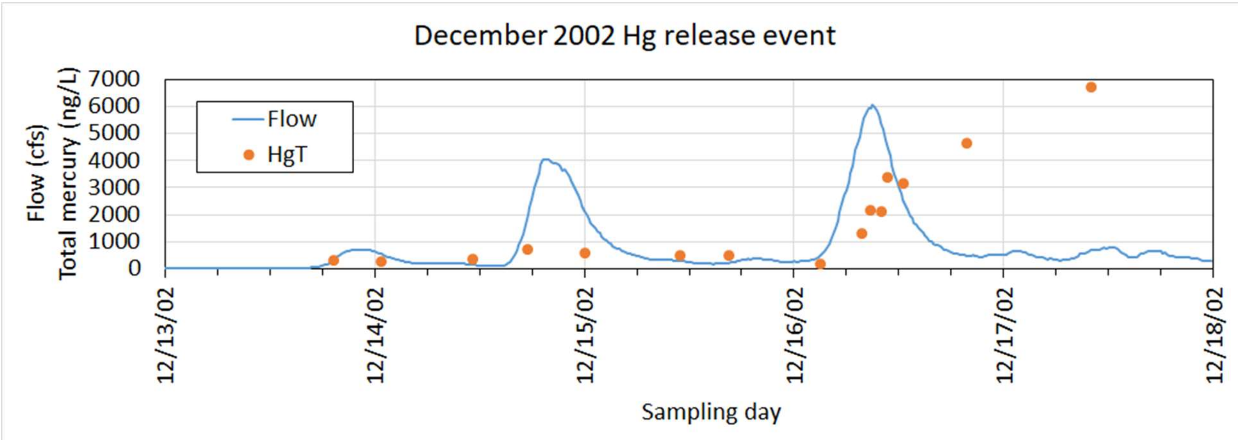
Although no two storms are identical, the storm series of December 2002 and January 2017 were very similar in many ways (Table 3). The patterns of flow and HgT concentrations during these storm series were different, however the concentrations measured were quite similar (Figure 5). During the December 2002 storm, the 6-hour rainfall intensity in the historic mining district was just 1.85 inches and concentrations remained <1,000 ng/L during and after the initial flow peak of 4,042 cfs. However, just 36 hours later, a second more intense storm hit the area with 6-hour rainfall intensity of 2.56 inches in the historic mining district and as that flow began to arrive at the sampling location at Hwy 101, concentrations progressively rose with every additional sample, reaching 6,699 ng/L on December 17th, 2002.

Table 2. Daily and event loads of mercury transported during the January 2017 event.

	Linear Interpolation Load estimation method: Estimate instantaneous concentration using linear interpolation between samples and multiply by the measured instantaneous flow			Flow-weighted Average Load estimation method: Multiply the flow-weighted average of the discrete samples by measured total storm series flow		
	HgT	HgD		HgT	HgD	
	(kg)		(%)	(kg)		(%)
Saturday, January 07, 2017	0.45	0.0018	0.40			
Sunday, January 08, 2017	7.58	0.046	0.57			
Monday, January 09, 2017	20.93	0.16	0.78			
Tuesday, January 10, 2017	16.45	0.094	0.54			
Wednesday, January 11, 2017	19.28	0.15	0.79			
Thursday, January 12, 2017	3.04	0.065	2.0			
Friday, January 13, 2017	0.97	0.037	3.1			
Total	70	0.57	0.81	89	0.64	0.72

Table 3. Rainfall and runoff characteristics of the large storm series of December 2002 and January 2017.

	December 2002 storm	January 2017 storm	Difference (%)
Rainfall season to date (in)	14.7	16.34	+11
Peak rainfall intensity (in/6 hr)	2.48	2.56	+3
Peak flow (cfs)	6,071	5,490	-10



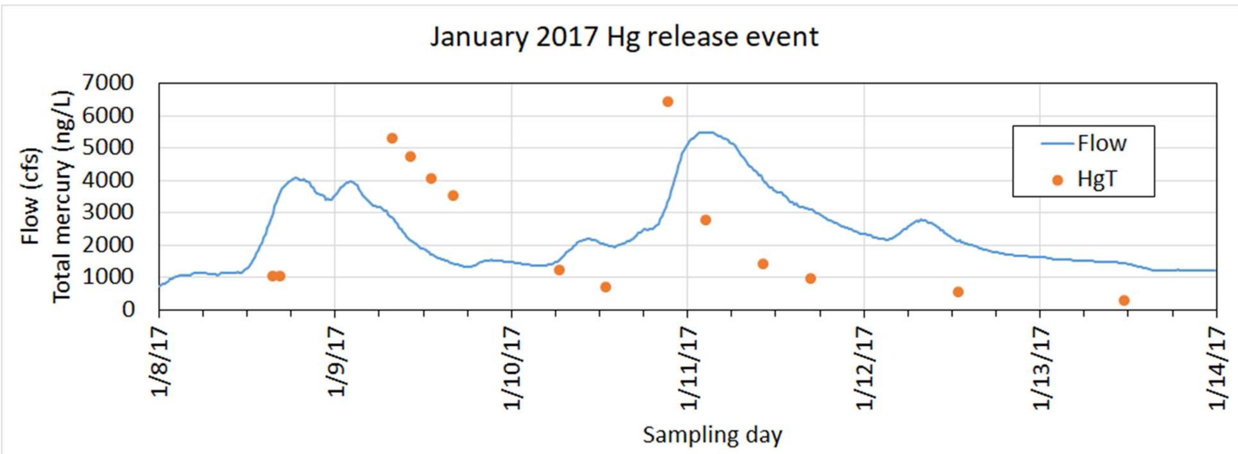


Figure 5. Comparison of flow and total mercury concentrations between the December 2002 and the January 2017 storm series.

In the case of the January 2017 event, despite the smaller initial peak, sufficient rainfall intensity and perhaps other moisture factors were achieved during the first peak such that, even with lesser rainfall intensity during the second phase of the storm that led to the larger flow peak on January 11, Hg mobilization continued. This further supports the conceptual model of transport outlined in the methods section of this report. A similar phenomenon occurred during subsequent storms in December in 2002 when, despite lower rainfall intensity in the historic mining district on December 19 (1.7 inches in six hours) and December 28 (1.6 inches in six hours), higher Hg concentrations were measured (Figure 6) (McKee et al., 2004; 2005). This is thought to have occurred in relation to soil saturation. Once a rainfall/saturation threshold was reached, mobilization of Hg appeared to continue even with relatively small additional storm rainfall. This appears to result in relatively large and continued mobilization and transport of Hg.

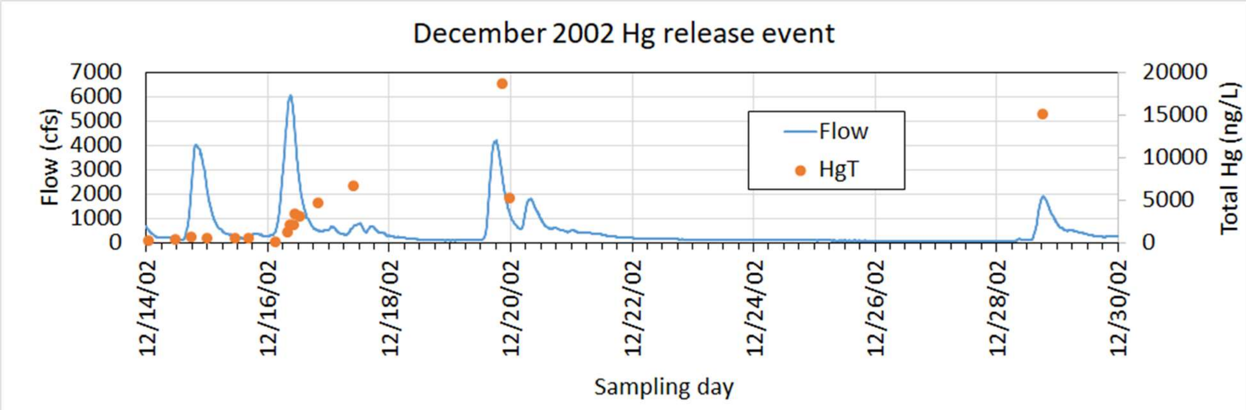


Figure 6. Flow conditions and total mercury concentrations during the subsequent smaller storms in December of 2012 that occurred after the initial Hg mobilization event on December 16th 2002.

Particle Concentration Comparisons Between the Storms of 2002 and January 2017

Mercury concentrations on suspended sediment particles in 2017 remained well above the TMDL target (0.2 mg/kg dry wt., annual median) and were as high, or higher, than those observed in WY 2002 (Figure 7). Note that dissolved phase Hg was not measured in 2002, therefore in order to make comparisons, the convention of estimating particle concentrations as the ratio of HgT to SSC was used here. During the December 2002 event, particle concentrations varied in relation to storm conditions with an initial brief increase in the third sample but then decreasing again and remaining relatively low until the 15th sample when again the ratio increased. During the January 2017 event, the pattern followed two hysteresis loops; the first counterclockwise loop indicates higher particle ratios on the falling stage of the first peak, and then a clockwise loop was measured on the second larger peak. Overall, the particle ratios measured were similar or perhaps even more elevated during the January 2017 event (Table 4) and also quite similar to the range and average particulate mercury concentrations in creeks in the historic mining district measured by Tetra Tech in the winter of WY 2004 (Austin et al., 2008). The arithmetic averages of the particle concentrations in the two events were nearly identical. The flow-weighted average of the January 2017 event was greater, although comparing the data in this manner is influenced by the happenstance nature of sample capture by the field teams during each of the storm series; it is better to compare the data in relation to another common variable such as flow (discussed more below).

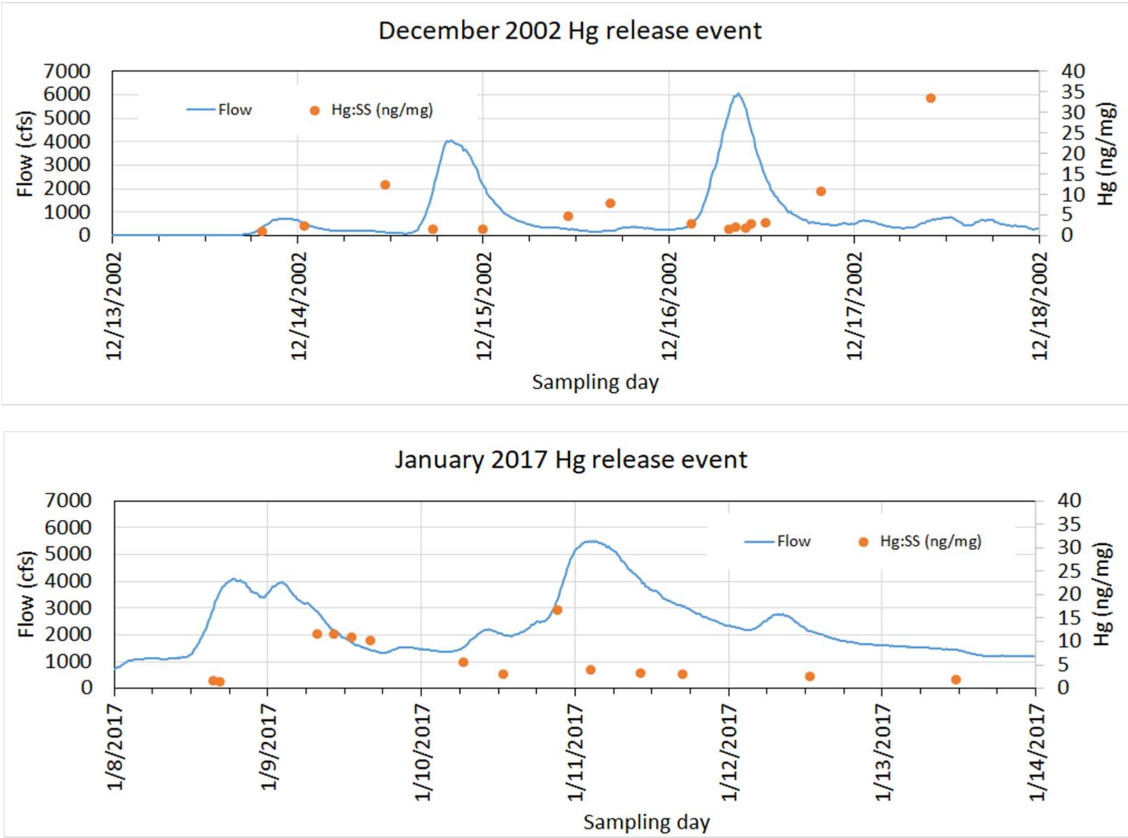


Figure 7. Particle ratios (ratio of total mercury to suspended sediment concentration) in relation to flow during the December 2002 and January 2017 mercury mobilization events.

Table 4. Summary of aqueous concentrations and particle concentrations that occurred during the December 2002 and the January 2017 mercury mobilization events.

	December 2002 Hg mobilization event			January 2017 Hg mobilization event		
	SSC (mg/L)	HgT (ng/L)	Particle concentration HgT:SSC) (ng/mg)	SSC (mg/L)	HgT (ng/L)	Particle concentration (HgT:SSC (ng/mg)
Minimum	29	178	1.0	150	283	1.5
Maximum	1,148	6,699	33	714	6,446	17
Arithmetic average	480	1,795	6.1	399	2,437	6.3
Flow-weighted average	850	2,088	3.1	453	2,503	6.0

Load Calculation Methods

The sampling design and loads computation methods were planned to incorporate continuous 15-minute turbidity measurement. Unfortunately, the USGS turbidity probe failed on January 8th at 4:30 am. As such, two other methods were selected that, while reasonably compatible with the data and producing reasonable accurate and precise estimates of loads, were not as robust as loads estimates that would have been made with the assistance of a continuous turbidity record. The DTS 12 turbidity probe in use at this location is a very reliable unit and has been in continuous service at this site since November 2002. It survived all previous storms and over that period has resulted in a 99.99% data capture only failing once before because of a bed lag deposit that caused the probe to be elevated above water level late of the recession limb of the storm. On January 8, 2017, bed scour caused damage to the way the anchoring mechanism holds the boom and probe in place in the water column. As a result, the wiring that is used to communicate between the data logger and the probe was disconnected causing loss of power to the probe. However, the probe was retrieved after the storm and is in good condition. Given this service record, the use of turbidity as a surrogate measure for this site in recommended as a component of any future storm sampling efforts.

Load Comparisons Between the Storm Series of December 2002 and January 2017

Despite well planned sampling designs, the unpredictable and unknown nature of rainfall-runoff generation processes leads to a somewhat happenstance nature of time gaps in the sample capture by the field teams during the storm series in relation to the Hg mobilization processes. Therefore, as mentioned above, simple comparisons of concentration between storm series, while informative, do not necessarily lead to a full understanding of the causative mechanisms behind the observations. For example, concentration is not independent of flow; the aqueous concentration of HgT (ng/L) can be diluted or concentrated depending on how much flow there is and where it is coming from relative to Hg source areas. To explore this a little more, instantaneous Hg mass transport was compared to instantaneous flow for the samples that were collected during December 2002 storm series during WY 2003 and the WY 2017 January storm series (Figure 8). There appears to have been no change in loads in relation to flow over the 14 year period between the rare storm series Hg measurements, or putting it a different way, the slopes of the two data sets (which represent the mean concentration in relation to magnitude of flow) have not changed through time.

In the same manner that concentration is not independent of flow, particle concentration is not independent of sediment mass transport. The amount of soil erosion and sediment transport among storm series and among years is influenced by soil moisture conditions, rainfall intensity, and variation in vegetation cover. In the same way that flow can dilute Hg mass mobilization in relation to sources, sediment erosion and transport from less polluted areas can also influence particle concentrations. To explore this process a little more, instantaneous Hg mass transport

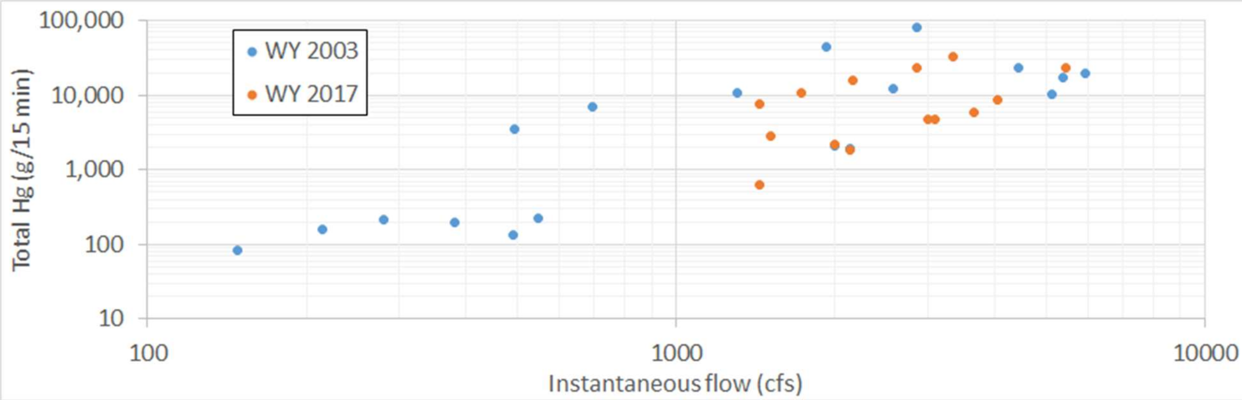


Figure 8. Comparison of the instantaneous total mercury mass transport to instantaneous flow between the events of Water Year 2003 and the Water Year 2017. In this case, all the data from WY 2003 December storm series were included (December 13-17, December 19, December 28).

was compared to instantaneous suspended sediment mass transport for the samples that were collected during December 2002 storm series and the WY 2017 January storm series (Figure 9). In a similar manner to flow, there appears to have been no change in loads in relation to suspended sediment transport over the 14 year period between observations, or putting it a different way, the slopes of the two data sets (which represent mean particle concentration in relation to a given magnitude of suspended sediment load) have not changed through time.

Dissolved Phase Transport

Prior to this study, dissolved phase Hg had not been analyzed during a large Hg mobilization event (no samples were analyzed for HgD during WY 2003). Yet high total Hg concentrations were measured in the spring of WY 2003 during relatively low flow and low SSC conditions, suggesting that much of the flux at that time could have been in the dissolved phase. It was unknown if this was indicative of a mobilization process or a transport process. The mobilization processes considered were 1. preferential weathering of ultrafine Hg and increased leaching associated with metacinnibar and soot fragments and 2. acid mine drainage associated with pyrite deposits near the Senador Mine in the McAbee Creek area at the northern end of the historic mining district). One open question is what impact does a lack of suspended sediment relative to HgT concentrations in the water column have on transport? Would there be a lack of sufficient binding surfaces for particulate transport (McKee et al., 2017)? As shown in Figure 10, the data collected during the WY 2017 January storm series falls within the typical patterns of dissolved phase transport measured for this system in previous years (data from WYs 2005, 2006, and 2010 were easily compiled and used for comparison). The data collected during this study do not indicate elevated mobilization of dissolved phase is associated Hg mobilization events from the historic mining district. Given that the dissolved

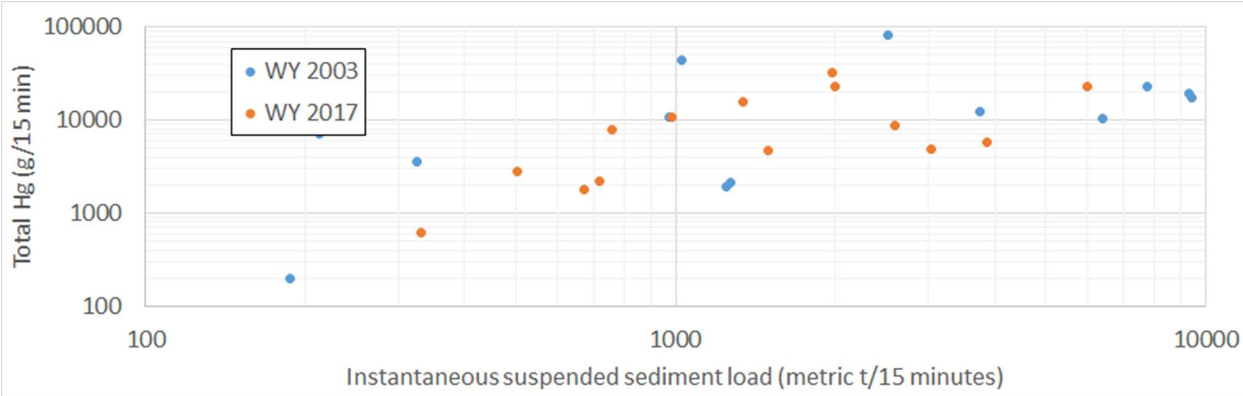


Figure 9. Comparison of the instantaneous total mercury mass transport to instantaneous suspended sediment mass transport between the events of Water Year 2003 and 2017. In this case, all the data from WY 2003 was included (storm on November 7-9, December 13-17, December 19, December 28, March 15, and April 12, and the baseflow sample on May 29).

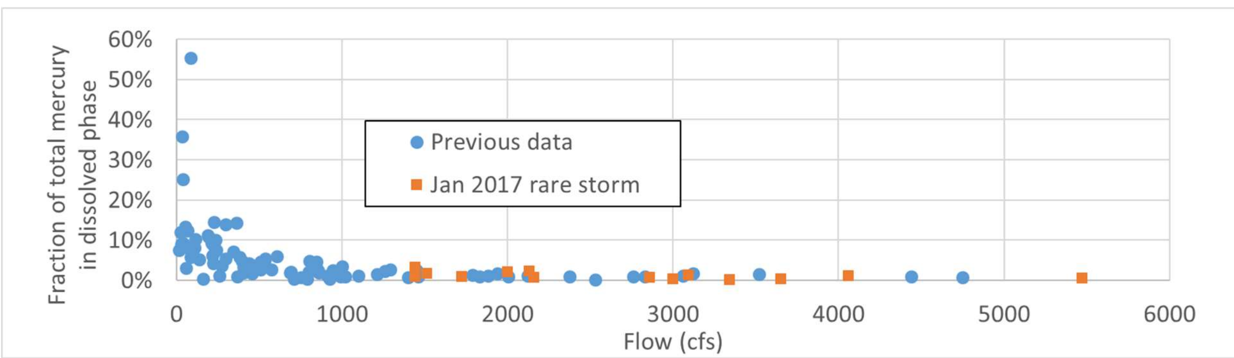


Figure 10. Comparison of dissolved phase mercury transport during the WY 2017 January storm series to previous data (WYs 2005, 2006, and 2010).

phase Hg transported during this event amounted to 0.57 kg (well less than the TMDL waste load allocation for the system) and contributed just 0.81% of the HgT transported, gaining an even better understanding of the dissolved phase transport for this system would not help with directing management actions. Therefore, it is suggested that no further dissolved phase data be collected for this system.

Modified Conceptual Model for Historic Mining District Mercury Mobilization Processes

As discussed throughout the report so far, the data collected during the large January 2017 storm series conform well to the hypothesis that large amounts of Hg can be mobilized during large storms. Specifically, periods when antecedent moisture conditions are elevated, when rainfall intensity in the historic mining district[1] exceeds a threshold of around 2 inches in 6 hours, and when there is sufficient flow in the tributaries in the vicinity of the historic mining district to transport the Hg mobilized downstream. But as described previously, since Hg mass transport is not independent of flow or sediment transport, an important question is, can we derive a more robust indicator that could explain the aqueous and particle concentrations that are observed at Hwy 101 in addition to rainfall intensity? It appears that flow in Alamitos Creek as indicated by the gage just downstream from the Almaden Reservoir has some potential (Figure 11). Given that Alamitos Creek is a primary pathway for runoff from the mining areas (although it is noted that Guadalupe Creek is also a source), and rainfall falling on the historic mining district likely causes flow in most of the creeks at about the same time, it makes sense that flow in this creek may be a good indicator of Hg transport down the whole system. Normalizing the particle concentration data in this manner may offer a mechanistic way of comparing trends over time. A future straightening and lowering of the curve at higher % of total flow at this from Alamitos Creek (the right side of the graph) would indicate reduction of mining related debris and management success. In contrast, a lowering of the y intercept on left side of the graph (when flow in dominantly from other tributaries and the urban area) would indicate management success for urban Hg sources.

Several other representations of flow were evaluated including flow in Guadalupe Creek below Guadalupe Reservoir, a summation of both Guadalupe Creek and Alamitos Creek, flow in Guadalupe River at Almaden Expressway, and combinations of longer and shorter lag times. But the ratio of flow at Alamitos Creek below Almaden Reservoir (SCVWD gage number 1544) lagged by 1.5 hours (an adjustment for travel time down the system) and flow at Hwy 101 was the best of those explored. This indicator explained 82% of the variability in particle concentration observed at GR-101. Replicating this analysis for the December 2002 storm series did not show such a pattern - there was little to no release of water from the Almaden Reservoir during December 2002 because the reservoir capacity was not exceeded. Ideally, the analysis would be carried out using a gage further downstream (below the confluence of Guadalupe Creek and Alamitos Creek to capture all flow that is potentially contaminated with mining debris) but no such gage exists. The data for Alamitos Creek at Greystone Lane for WY 2003 were explored but these data appear to be of poor quality and the gage has since been discontinued (or at least there are no data from this gage available from valleywater.org via their data download portal).

[1] As indicated by data collected at Almaden Reservoir (SCVWD gage number 2080).

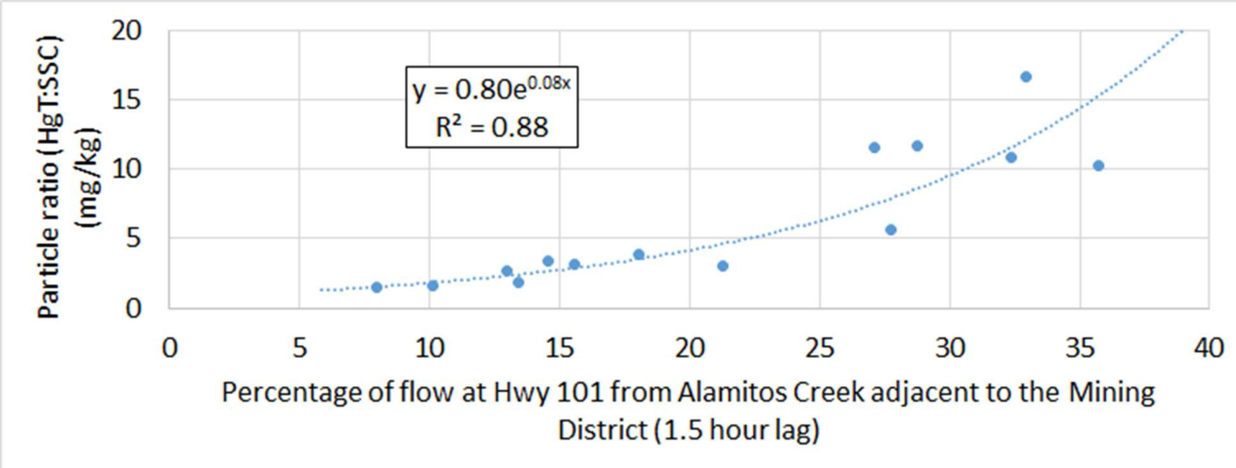


Figure 11. Correlation between the proportion of flow emanating from around the historic mining district (as indicated by flow in Alamitos Creek [lagged by 1.5 hours to account for routing time]) and the particle concentration measured at the sampling site on Guadalupe River at Hwy 101 (USGS gage 11169025) based on the January 2017 storm series data.

Mercury Mobilization During Other Storm Series in WY 2017

There was not one but a number of storms that occurred in the latter half of January and February 2017 that may have also transported Hg mining debris down the system and out in to South San Francisco Bay. This hypothesis seems reasonable given that in WY 2003, after the triggering event that caused the initial Hg mobilization conditions, all subsequent storm series that were sampled showed high Hg concentrations (>5,155 ng/L) and particle ratios (>10.9 mg/kg). This occurred despite 6-hour rainfall intensities at the Almaden rain gage on December 19, 2002 (1.73 inches), December 28, 2002 (1.57 inches), March 15, 2003 (1.30 inches), and April 13, 2003 (0.98 inches) being lower than occurring during the initial triggering storm series.

These previous measurements suggest that the rest of the storms in WY 2017 may also have transported anomalously large Hg loads. Another large storm occurred on February 21, 2017 with 15% higher flows (6,340 cfs) than observed on January 11 (5,490 cfs) that caused extensive flooding in the neighboring watershed to the east along Coyote Creek. There were also a series of smaller events in later January and early February (Figure 12). Based on provisional SCVWD data, maximum 6-hour rainfall intensities for subsequent flow peaks in WY 2017 were January 19 (1.7 inches), January 20 (1.1 inches), January 22 (1.4 inches), February 7 (1.6 inches), February 10 (1.4 inches), February 17 (1.4 inches), and February 21 (1.7 inches). Flow peaked in the last storm of this series at 6,340 cfs (the largest storm peak since January 3, 1998). Total rainfall for the WY 2017 season at the Almaden Reservoir (SCVWD gage number 2080) was

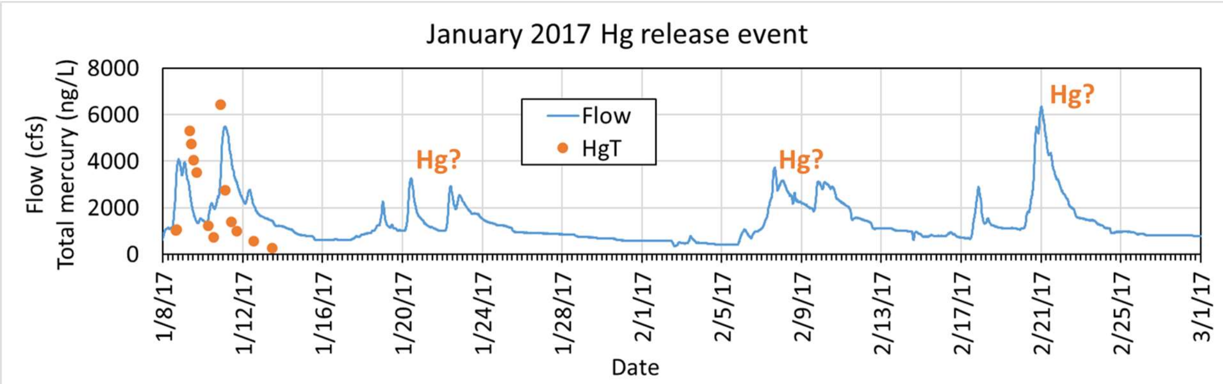


Figure 12. A comparison of flow and Hg concentrations during the early January 2017 storm series to flow during subsequent storm series in January and February 2017. Without sampling, concentrations during these latter storms would be possible yet it is quite likely they also transported large Hg loads.

58.62 inches (SCVWD provisional data), about 184% of normal based on the period 1972-1999 (31.9 inches). Since no subsequent storm events in WY 2017 were sampled, only a rough estimate of the total loads for the season could be made. However, based on the characteristics of the season and the patterns of Hg mobilization observed in the December 2002 event, it seems reasonable to hypothesize that Hg mobilization from the watershed in later January and February 2017 may have been very high with Hg concentrations equal to and perhaps higher than measured in January 7–13 storm series. Given the total flow volume for WY 2017 was 239.6 Mm^3 (equivalent to 194,247 acre foot) (Note data are provisional from August 3 – September 30 and subject to slight change), it is possible that loads were well in excess of 500 kg, and perhaps 1,000 kg or more. A flow of this magnitude has not been observed since WY 1983 when the flow was only marginally larger (241.1 Mm^3) (equivalent to 195,463 acre foot). Once the USGS publishes the WY 2017 suspended sediment record for the system in early 2018, an estimate of total Hg load for the year may be attempted and compared to these hypotheses.

Answers to Management Questions and Recommendations

MQ1: What is the trend in Hg on suspended sediment in Guadalupe River and is there a difference between Hg on suspended sediment derived from legacy mining sources and the urban area?

The sampling program and data presented here were focused on characterizing the concentration of Hg on particles in runoff derived from the upper watershed in relation to the legacy mining debris after transport down the river system to the monitoring site at the USGS gage at Hwy 101. The rising stage (and urban portion) of the first storm hydrograph was not sampled due to this focus. Based on this sampling, and each of the different ways of manipulating the data presented above, there is no evidence of an up- or downward trend in particle concentrations during this type of large and rare event. Had data been collected during subsequent storm series later in January and in February, further insights may have been possible; it is always very hard to observe a trend with small data sets. In order to assess whether management efforts are having an impact on legacy mining-related loads, storm conditions equaling or exceeding conditions that occurred during WY 2003 and WY 2017 need to be sampled repeatedly over time. Such data, once available, would also be useful for trends evaluation and rechecking the current estimate of long-term average loads that are strongly influenced by data collected in WY 2003.

Measures of central tendency such as mean, median or flow-weighted average may not be very sensitive as trend indicators because they are highly influenced by random artifacts of imperfect field sampling programs and the lack of any possibility of relating the central tendency of data to the trends in source-mobilization-transport processes that are time varying and that are of importance. However, there was a good correlation between particle concentration and the portion of flow coming from the area around the historic mining district as indicated by the ratio of flow in Alamitos Creek and flow at the USGS gage at Hwy 101 (Figure 11). This relationship could be further explored as a means for improving loads estimation and determining trends in Hg derived mainly from the lower urban part of the system (when the ratio is small) and mainly from mining wastes (when the ratio is large). Such a continuous model avoids to much averaging (obscuring the processes that are operating) and the challenge of classifying where flow has come from (in a binary manner), the method that was applied in the past to estimate loads (e.g., McKee et al., 2004, 2005, and 2010; Gilbreath et al., 2015; McKee et al., 2017). It allows for a more direct comparison between the particle concentration observed at any moment in time and the source-mobilization-transport processes that occurred hours earlier to cause it. As a preliminary experiment, this relationship was used as a third method for estimating a Hg load for the January 2017 storm series of 86 kg based on preliminary suspended sediment loads estimates. This estimate of 86 kg compared quite well to the other two estimates of 70 and 89 kg which are conceptually likely bias a little low and a little high.

Since the system is dominated by mining Hg loads, the relationship should be quite sensitive to changes in loads from this part of the system but how well would it work as a tool for evaluating trends in urban loads? Conceptually, as discussed above, a trend in urban-derived Hg will be harder to observe in the main river system since the urban load is small relative to the mining area-associated load. In addition, there is possibly some mining waste in the urban portions of the Guadalupe flood control channel (system memory from previous storms) that can mobilize and mix with urban stormwater during the rising stage of flood events. Both these issues will make observing a trend in urban Hg loads challenging. That said, a lowering of the y intercept could be explored as an indicator of trends associated with urban Hg management.

MQ2: What is the trend in Hg loads in the Guadalupe River system and is there a difference between loads derived from legacy mining sources and the urban area?

Although the data sets are still very small, this latest effort has helped to provide further insights into the Hg source-mobilization-transport processes in the system. The data appear to indicate no trend but a more definitive answer may have been possible had a larger data set been gathered during the other January and February storms. Since there seems to be an ongoing mobilization of Hg during subsequent storm series in a season once some threshold is exceeded and Hg mobilization begins, a single storm series measurement of load may not be the best indicator. Since there does not seem to be any indication of elevated loads during a drier year that follows a wet year, it appears that if loads were to be used as an indicator of trend, sampling all storms during wetter years would be more robust than sampling a single storm or storm series during a wetter year. There appears to be no strong reason to continue to sample drier years.

The sampling program and data presented here focused on characterizing the load of Hg that emanated from the mining sources for this large, rare storm series. The program was not aimed at comparing load estimates for urban areas versus legacy mining wastes. Given the complexity of the system, differentiating loads between the two sources is a challenging endeavor using a single sampling site. Estimates can be made with the data from Hwy 101 perhaps by relating particle concentrations to the source of flow as proposed. But it will never be fully known how much or if any of the mining wastes that could be stored in the lower channel system are obscuring the urban signal even during the earlier season or smaller storms when no flow is coming from upper watershed. But the proposed flow ratio method would seem to be more robust that the other alternatives.

MQ3: What are the ideal monitoring procedures going forward for evaluating trend in Hg load?

An alternative to the single-sampling location design is to use a nested sampling design with sampling locations strategically placed in representative tributaries of the urban area that are not influenced by mining wastes and separately in tributaries nearer the legacy mining area. Such a design would be more sensitive in detecting trends for each of the two major sources, however there are tradeoffs and practical challenges that would need to be considered. Monitoring at multiple locations has additional cost. It is likely that one field team would not be able to carry out sampling in tributaries around the historic mining district and in urban watersheds downstream; at least two field teams would be required adding to cost. In addition, smaller watersheds respond faster to rainfall. Monitoring closer to the mining area in smaller watersheds and in urban areas in smaller watersheds requires a faster response time to get field staff on site with the likelihood that they would miss parts of events. In contrast, monitoring at Hwy 101 in the lower watershed is logistically easier mainly because of the slower response time. Lastly, there is a massive data set at Hwy 101 that has a lot of value for comparing changes to baseline loads; only relatively limited data exist for the upstream areas. Part of this value is the existence of a long term flow and suspended sediment record at the USGS gauge (11169025) at Hwy 101. Choosing other locations for monitoring may have to include flow monitoring. Lastly, the magnitude of the load reduction requirements overall and the small magnitude of the baseline urban loads (12.5 kg) relative to the waste load allocation (9.4 kg) suggests the focus should be on measuring overall trends in the system rather than adding further sampling complexity. Therefore, we recommend the following:

1. Making trends observations during large, rare storm series should remain the focus of additional sampling efforts with the differentiation of trends from each source (urban versus legacy mining) being quantified more loosely using an understanding of the source of the water at any sampling moment.
2. To measure particle concentrations or loads for the purposes of monitoring for trends associated with legacy mining wastes and urban derived loads, it is recommended that once a large storm for a year that meets all the mercury release criteria has occurred, all subsequent storms for that season should be monitored. Based on a recurrence frequency of 2 inches of rainfall in a 6 hour period at New Almaden, these storm series are expected every five years on average. Therefore the cost of such a program should be on average about 1/5th that of an annual program. Water samples should be analyzed for HgT and SSC. There is no further need to analyze for dissolved phase Hg. The turbidity surrogate method should be continued using continuous measurements of turbidity at the same time step and flow measurements. Such data, if available, will increase the accuracy and precision of the loads estimates generated. The sampling program should be reactive to the antecedent conditions and the forecast mobilization triggers as described in this report, including:
    - cumulative season rainfall >7 inches everywhere but with a focus on the middle and upper watershed gages,
    - baseflow at the downstream USGS gage elevated above typical dry season conditions and hydrographs that result from storms are starting to elongate with longer recession limbs,
    - storm forecast of 6-12 inches in the upper watershed, estimated 6 hour rainfall depths of >2 inches in the historic mining district, and

- Almaden Reservoir is near capacity and expected to fill with the coming storm (a further indicator of antecedent moisture conditions that are conducive to a Hg mobilization event and once it begins to spill, there is additional energy to transport mining waste Hg down the valley).

A false start may be realized early in the effort (resulting in bringing staff home) if some of these conditions do not end up prevailing. In particular, if six-hour rainfall does not exceed two inches in the historic mining district, staff may be called home unless a previous storm of the season met all these conditions. When these conditions are met, all storms for the remaining portion of the wet season should be sampled to better understand the processes of sustained Hg mobilization and to quantify, with certainty, the average particle concentrations and loads of Hg for the season.

One year in every five does not mean that there is not a chance of two or even three years needing to be sampled in a given five year period but it does mean that on average over a 20 year period, one might expect about 4-5 sampling years in total. Given all the discussion above, for program efficiency, continuing to sample at Hwy 101 should be sufficient for estimating loads and trends associated with load from the whole system. Trends and loads estimated at this location will be more sensitive to changes in loads from the mining area (the largest source) but if a flow-ratio method as described above is employed, it may be possible to tease out trends associated with urban sources as well. An estimate cost for sampling the remainder of any wet season when conditions are met would be $100-150k depending on how many storms occur after the initial threshold conditions are met.

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Appendix A. Raw data.

Date	USGS 11169025 Flow (cfs)	SSC (mg/L)	HgT (ng/L)	HgD (ng/L)	HgT:SSC (mg/kg)	HgD:HgT
1/8/2017 15:30	3,000	660	1,044	4.7	1.6	0.45%
1/8/2017 16:30	3,650	693	1,053	5.0	1.5	0.47%
1/9/2017 7:45	2,860	457	5,294	37.3	11.6	0.70%
1/9/2017 10:15	2,160	406	4,756	36.5	11.7	0.77%
1/9/2017 13:00	1,720	374	4,054	36.2	10.8	0.89%
1/9/2017 16:00	1,440	345	3,525	34.5	10.2	0.98%
1/10/2017 6:30	1,510	218	1,220	20.3	5.6	1.7%
1/10/2017 12:45	2,000	235	722	15.0	3.1	2.1%
1/10/2017 21:15	3,340	387	6,446	15.5	16.7	0.24%
1/11/2017 2:30	5,470	714	2,772	16.7	3.9	0.60%
1/11/2017 10:15	4,060	417	1,408	15.3	3.4	1.1%
1/11/2017 16:45	3,090	316	985	14.2	3.1	1.4%
1/12/2017 12:45	2,130	207	557	12.5	2.7	2.2%
1/13/2017 11:30	1,440	150	283	9.2	1.9	3.3%