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FROM: Carrie M. Austin, P.E.
Project Manager, Guadalupe River Watershed Mercury TMDL
PLANNING/TMDL DIVISION

DATE: December 28, 2018

SUBJECT: Transmission of data from XRF Survey of Almaden Quicksilver County Park on August 14, 2018

Summary

This letter and associated data satisfy our access permits and communicate findings about mercury concentrations observed during the field study. The San Francisco Bay Regional Water Quality Control Board (Water Board) was interested in sampling certain locations in order to test a new sampling technology and to identify upland mining-affected features with elevated mercury concentrations. On August 14, 2018, Water Board staff undertook a one-day mercury survey in Almaden Quicksilver County Park (AQCP). Staff used a mobile x-ray fluorescence (XRF) metals detector (Niton XL3t GOLDD+ Analyzer) for *in situ* measurements of mercury concentrations in dry sediment and soil between different features such as non-mined tributary sediments and eroding mercury mining waste. The main reference for mining waste locations is the Almaden Quicksilver County Park and Santa Teresa County Park Mine Material Evaluation, Amended Final Report, by URS, May 16, 2011 ("URS 2011 Report").

August 2018 sampling indicates that the XRF instrument has utility to distinguish between non-mined and mining-affected features with elevated mercury concentrations.

Purpose

This one-day field effort was designed to test the utility of the Water Board-owned portable x-ray fluorescence (XRF) mobile metals detector (Niton XL3t GOLDD+ Analyzer) to distinguish mercury concentrations in dry sediment and soil between the following three types of different features, all on County Parks property:

- Non-mined tributary
- Mining waste piles along Enriquita trail – Table 5 & Figure 1 [Tile 4] in URS 2011 Report
    - URS features WS16 Yellow Kid Jr. Dumps Unknown Material Type;
    - WS15 Providencia Opencut, with waste piles downslope, Serpentine; and
    - WS14 Enriquita Mine Retort Calcines Pile
- Mined tributaries: creek sediments above the shoreline of Guadalupe Reservoir and downstream of mining waste piles:
    - Drainage Below WS-15 & WS-16
    - Drainage Below WS-14

Guadalupe Reservoir was selected for this test of the XRF instrument because the Santa Clara Valley Water District plans to completely dewater the reservoir in the near future for their dam seismic strengthening project, and because this reservoir consistently has the highest fish methylmercury levels of all California reservoirs. Dewatering may provide an opportunity for coordinated remediation of upland mining wastes and capping of areas of reservoir sediment with elevated mercury levels.

Field staff and access permits

- San Francisco Bay Regional Water Quality Control Board (Water Board) staff: Carrie Austin and Nicholas Piucci
- Santa Clara County Parks and Recreation (County Parks) staff: Mark Frederick

Access permit no. 9717 was obtained from Midpeninsula Regional Open Space District for access to the Rincon Creek sample location. Park permit no. 18526 was obtained from County Parks for access to and non-destructive sampling in Almaden Quicksilver County Park. Additionally, County Parks required that their staff drive and accompany Water Board staff in their park. Water Board staff gratefully acknowledge Mark Frederick's excellent advance planning for the field work and expert field assistance.

Previous data used to select sample locations:

The Guadalupe River Watershed mercury TMDL required mine site owners to evaluate and report on the potential for mining waste to erode from their properties. In 2011, URS prepared

this report for County Parks: Almaden Quicksilver County Park and Santa Teresa County Park Mine Material Evaluation, Amended Final Report, which is available here: URS 2011 Report.

Water Board staff planned a one-day field effort that included a range of site types in close proximity to one another and to Guadalupe Reservoir: non-mined tributary, mined tributary, mining waste piles, and creek sediments downstream of mining waste piles above the shoreline of Guadalupe Reservoir. Accordingly, Water Board staff selected the upstream portion of Guadalupe Reservoir for sampling because it contains the desired range of site types in close proximity to one another (see Table 5 and Figure 1 [Tile 4] in URS 2011 Report). Table 1 provides a summary of mercury information for the selected mining waste piles from URS 2011 Report. Importantly, this was not complete or comprehensive sampling of known mine features upstream of Guadalupe Reservoir. Many more upstream features were investigated by URS and are indicated on Figure 1 [e.g., Tiles 2 and 4] in the URS 2011 Report.

Sample locations

Figure 1 is a map of the six 2018 XRF sample locations, and Table 2 provides detailed descriptions and representative photos of each location.

The first location sampled was a non-mined tributary, Rincon Creek, which drains Mt. Umunhum. In this report "non-mined" means there is no record of mercury mining and no known mercury mining waste piles in the watershed. However, it is likely that the Rincon Creek watershed was contaminated from ore roasting at New Almaden and Guadalupe mines. Ore roasting emits mercury, some of which deposits locally on soil, vegetation, and the water surface.

The sample locations were the following:

- Non-mined tributary, Rincon Creek, which drains Mt. Umunhum
- Mining waste piles along Enriquita trail – Table 5 & Figure 1 [Tile 4] in URS 2011 Report
    - URS features WS16 Yellow Kid Jr. Dumps Unknown Material Type;
    - WS15 Providencia Opencut, with waste piles downslope, Serpentine; and
    - WS14 Enriquita Mine Retort Calcines Pile
- Mined tributaries: creek sediments above the shoreline of Guadalupe Reservoir and downstream of mining waste piles
    - Drainage Below WS-15 & WS-16
    - Drainage Below WS-14

Field x-ray fluorescence (XRF) mercury procedures

Soil metals concentrations were measured by XRF *in situ*. The XRF is a mobile metals detector (Niton XL3t GOLDD+ Analyzer). The standard instrument mercury detection limit is 10 mg/kg,

which is many orders of magnitude greater than laboratory detection limits (e.g., detection limit of 0.004 mg/kg for U.S. EPA method 7474). Quality control measurements of blanks and certified reference materials were taken before the first field measurement and after the last field measurement, and no quality control concerns were noted for mercury. Therefore, the detection limit for mercury in the samples was 10 mg/kg.

Field work was performed late in the dry season after grasses had died back, which allowed for visual assessment of erosion (see Table 2 for erosion notes). Where necessary, vegetation in about a 5-cm square area was cleared with the sampler's boot prior to taking an XRF measurement. The plan was to collect 10 XRF measurements at each sample location to accommodate the expected high degree of variability of mercury concentrations. However, in the field the decision was made to reduce the number of measurements to 6 at several locations, which allowed staff to sample all locations in one day.

XRF mercury results

Complete XRF results are provided in the accompanying spreadsheet, which indicates both mercury measurement results and the associated instrument error value for each measurement. For this data evaluation, mercury detections lower than 10 mg/kg were adjusted up to the detection limit of 10 mg/kg (work shown in Table 3 and "Hg Summary" tab of the spreadsheet).

Statistical evaluation

Table 4 provides the results of a non-parametric statistical analysis that was performed to determine if the mercury concentration at each location was significantly different from the detection limit. (It is preferable to perform a statistical analysis to determine if the mercury concentration is significantly different between locations, but the high number of non-detects prevents this analysis.) For the statistical analysis, non-detects were evaluated at the detection limit of 10 mg/kg. The results of one-sample Wilcoxon tests that compared mercury concentration data for each location to 10 mg/kg (the limit of detection). The hypothesis is that the median of data is less than or equal to 10 mg/kg, and the alternative hypothesis is that the median is greater than 10 mg/kg. Statistical test results are interpreted by p-values, where p-values less than 0.05 are significant [the chance of wrongly rejecting the null value are 5%]; p-values between 0.05 and 0.1 are evidence for significant difference; and p-values equal to or greater than 0.1 are not significant. The range of mercury concentrations by location are illustrated on Figure 2.

The analysis shows that mercury concentrations of the mining waste at WS-16 Yellow Kid Jr. Dumps is statistically significantly higher than 10 mg/kg, and there is evidence that mercury concentrations at both the Drainage Below WS-15 & WS-16 location and previously remediated WS-14 Enriquita Mine location are also higher than 10 mg/kg.

The statistical results show that it would be preferable to have 10 measurements if the mercury concentration exceeds 20 mg/kg in one of the first 6 measurements. Staff made the decision in the field to reduce the number of measurements from the planned 10 to 6 at several locations where there was a high proportion of non-detects or the highest concentration was less than 30 mg/kg. At both WS-14 Enriquita Mine ($p < 0.1$) and WS-15 Providencia Open Cut ($p > 0.1$), additional XRF mercury measurements may have resulted in greater statistical certainty.

Mercury transport to Guadalupe Reservoir from locations sampled

Mercury transport is a combination of erosion potential and mercury concentration. Table 2 describes the visual assessment of erosion potential of the sample locations and Table 4 provides a summary of the mercury concentrations. WS-16 Yellow Kid Jr. Dumps has the greatest risk of mercury discharge to Guadalupe Reservoir of the locations sampled. This risk is due to both high erosion potential and elevated mercury concentrations. Moreover, as shown on Figure 1, WS-16 Yellow Kid Jr. Dumps is located upstream of the only mercury hot spot identified in Guadalupe Reservoir in 2005. However, at an intermediate location along the drainage (Drainage Below WS-14) mercury was not statistically significantly different from 10 mg/kg.

Conclusions

The XRF was a rapid and useful means to identify elevated mercury levels. The XRF instrument has utility to distinguish between non-mined and mining-affected features. WS-16 Yellow Kid Jr. Dumps has the greatest risk of mercury discharge to Guadalupe Reservoir of the locations sampled; many more known mine features are located upstream of this reservoir. Field staff should aim to collect at least 10 measurements at each location if at least one of the first 6 measurements exceeds 20 mg/kg. A feasible number of XRF field measurements is approximately 40 per day, but this will depend on drive time between sites and the office.

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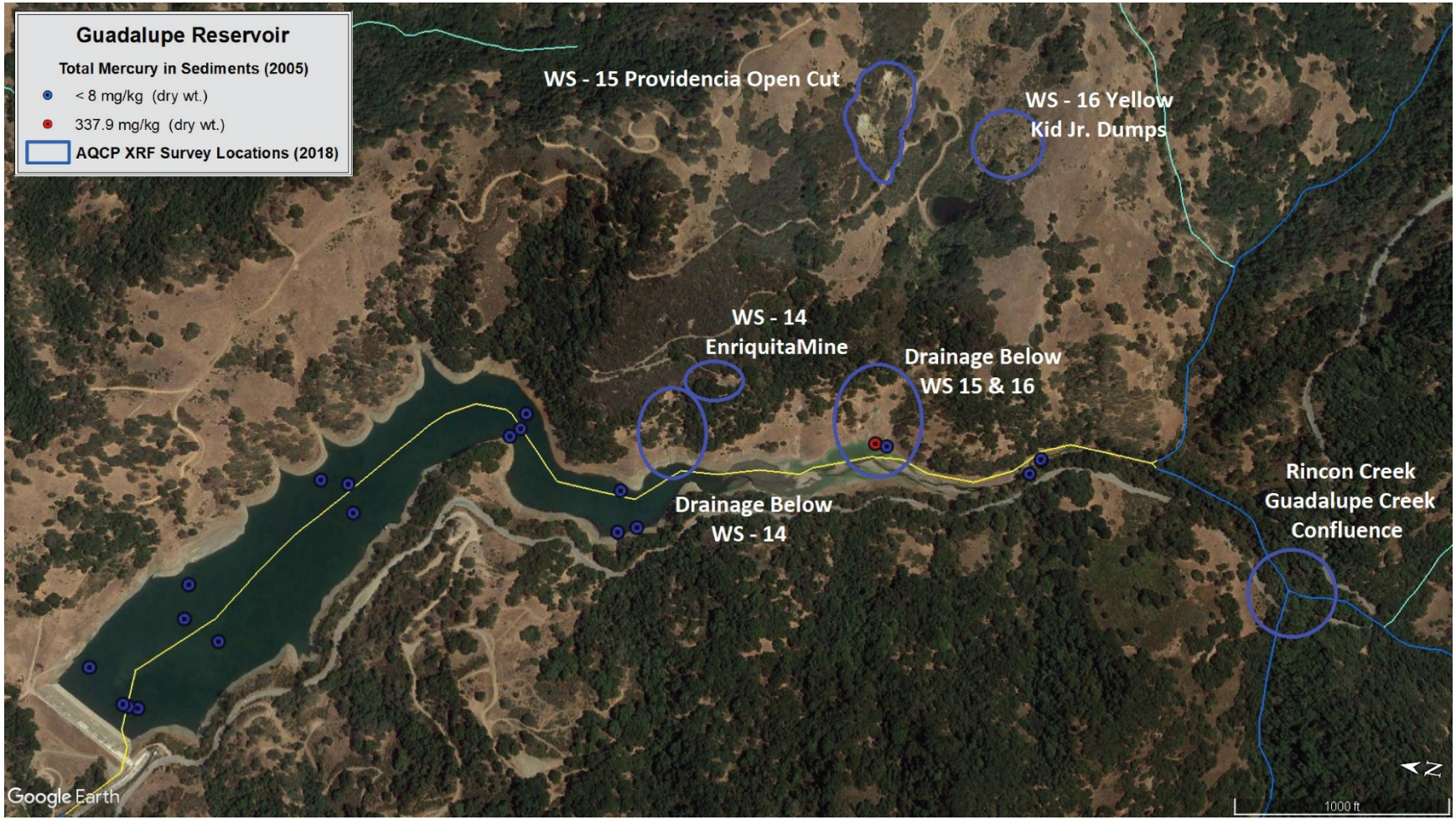

Figure 1. XRF sample locations August 14, 2018 and Guadalupe Reservoir 2005 bottom sediment mercury

Sample locations were selected to represent a range of historical mining influence that could be sampled in a single day. Therefore, locations were selected at the upstream portion of Guadalupe Reservoir. In 2005, mercury concentrations (mg/kg dry wt) in Guadalupe Reservoir bottom sediment generally ranged between 0.42 to 7.29 (blue dots), with one extreme value of 337.9 (red dot at sample location GR-6-A). The reservoir extreme value is located downstream of sample locations Drainage Below WS-15 & WS-16, and WS-16 Yellow Kid Jr. Dumps.

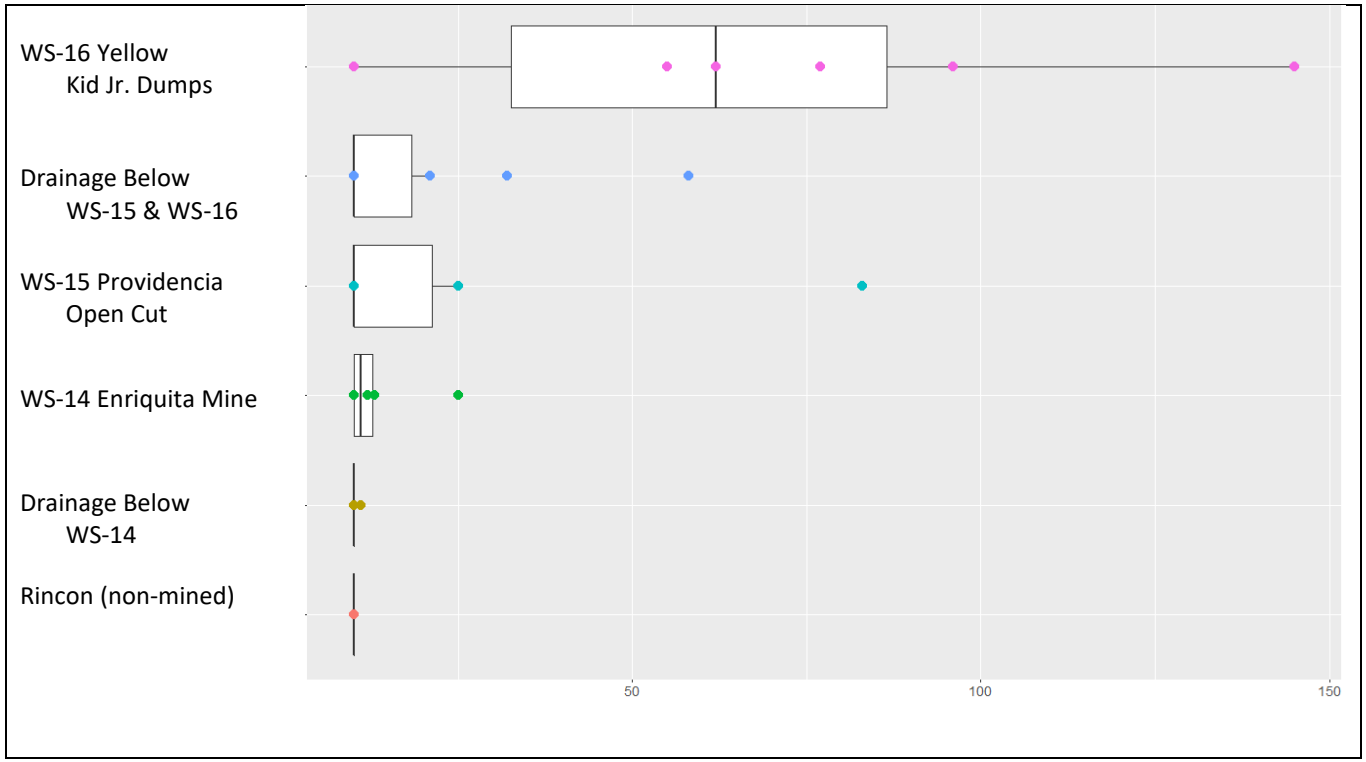

Figure 2. XRF mercury results (mg/kg) by location
WS-16 Yellow Kid Jr. Dumps has the highest mercury concentrations and they are statistically significantly higher than the XRF detection limit of 10 mg/kg. Enriquita Mine was previously remediated. The mercury concentration downstream of these two mine features (Drainage Below WS-15 & WS-16) is not significantly different from 10 mg/kg.

Table 1. Mercury information from URS 2011 Report		
Site Name and Description	**Table 1 URS 2011 Report Final Waste Site Importance 5 = highest score**	**Table 5 URS 2011 Report Waste Type**
WS16 Yellow Kid Jr. Dumps	2.47	Unknown Material Type
WS15 Providencia Open Cut, with waste piles downslope	3.41	Serpentine
WS14 Enriquita Mine Retort Calcines Pile	2.83	Calcines

Table 2. Description of sample locations and photo illustrations
Locations correspond to background/Rincon site at lower right in map (above) and then from right to left and upstream to downstream

"Rincon": Confluence of Rincon and Guadalupe Creeks; southeast side of culvert/bridge on Hicks Road This first site was chosen to represent mercury concentrations from the non-mined portion of watershed draining to Guadalupe Reservoir. These creeks drain Mt. Umunhum from an area that was not mined nor used as a staging area for mining activities. Soils could potentially be elevated in mercury from deposition of mercury vapors from ore processing at Guadalupe Mine located nearby (downstream of Guadalupe Reservoir). Foreground is Rincon Creek; samples were taken from both banks of Rincon Creek just above the confluence with Guadalupe Creek, so these sample locations are likely flooded by both creeks during high flows.	
Yellow Kid Jr. Dumps WS16 This site was chosen to represent mercury concentrations in erodible fines at a mine site upslope from Guadalupe Reservoir. It appears that a stream bisects a potential calcine pile, and that the stream has already eroded the middle portion of the pile.	 

<u>Providencia Open Cut, Pond, and Waste Piles Downstream WS15</u> This site was chosen to represent mercury concentrations in erodible fines at a mine site upslope from Guadalupe Reservoir.	 
<u>Drainage Below WS-15 & WS-16</u> This site was chosen to represent mercury concentrations in erodible fines below an identified mine feature and above reservoir high water mark. URS 2011 Report, Table 1, describes WS15 as having waste piles downstream. This sample location is downstream of waste piles and above reservoir.	 

Enriquita Mine WS14 This site was chosen to represent mercury concentrations in erodible fines at a mine site upslope from Guadalupe Reservoir. The Enriquita mine site was remediated previously.	
Drainage below WS14 This site was chosen to represent mercury concentrations in erodible fines below an identified mine feature and above reservoir high water mark. (Enriquita mine site was remediated previously.)	 

Table 3. XRF Survey of Almaden Quicksilver County Park on August 14, 2018

Quality Control or Sample Location	XRF Reading No.	Quality Control Type	Latitude	Longitude	Mercury (Hg) mg/kg	Hg Adjusted mg/kg	Notes	
Quality control							LOD = Limit of Detection	
	518	System Check					If < LOD reported, then < 10	
	519	Blank			< LOD	4	If reported at less than 10,	
	521	NIST			< LOD	5	adjusted to 10	
	522	USGS			< LOD	6	ND = Not Detected	
	523	RCRA			< LOD	6	Adj = adjusted	
Rincon	524				< LOD	< 10	Count all	10
(non-mined)	526				< LOD	< 10	Count NDs	8
	527				< LOD	< 10		
	528				< LOD	< 10		
	529				< LOD	< 10		
	530				< LOD	< 10		
	531				7	10		
	532				8	10		
	533				< LOD	< 10		
	534				< LOD	< 10		
WS-16	569		37.18755	-121.866257	96	96	Count all	6
Yellow Kid	570		37.187538	-121.866257	62	62	Count NDs	1
Jr. Dumps	572		37.187489	-121.866295	55	55	Mean Hg Adj	74
	574		37.187397	-121.866524	77	77	Median Hg Adj	69
	575		37.187447	-121.866425	145	145	Max	145
	576		37.187405	-121.866386	< LOD	< 10		
	577		37.187321	-121.866318	8	10		
WS-15	561		37.18943	-121.86657	< LOD	< 10	Count all	6
Providencia	562		37.189739	-121.866455	< LOD	< 10	Count NDs	4
Open Cut	563		37.190186	-121.866104	< LOD	< 10	Mean Hg Adj	54
	564		37.18998	-121.866325	83	83	Median Hg Adj	54
	565		37.190796	-121.865845	25	25	Max	83
	567		37.189377	-121.866638	< LOD	< 10		

Table 3. XRF Survey of Almaden Quicksilver County Park on August 14, 2018

Quality Control or Sample Location	XRF Reading No.	Quality Control Type	Latitude	Longitude	Mercury (Hg) mg/kg	Hg Adjusted mg/kg	Notes	
Drainage	535		37.18721	-121.871422	8	10	Count all	10
Below	536		37.187275	-121.871582	< LOD	< 10	Count NDs	3
WS-15 & WS-16	537		37.188721	-121.871429	58	58	Mean Hg Adj	22
	538		37.188709	-121.87159	< LOD	< 10	Median Hg Adj	10
	539		37.18882	-121.871384	< LOD	< 10	Max	58
	541		37.18898	-121.871193	32	32		
	542		37.189003	-121.871155	21	21		
	543		37.188885	-121.87162	8	10		
	544		37.188854	-121.871651	5	10		
	545		37.188881	-121.871658	9	10		
WS-14 Enriquita	547		37.191166	-121.87133	25	25	Count all	6
Mine	548		37.191101	-121.871384	13	13	Count NDs	2
	549		37.191151	-121.871407	12	12	Mean Hg Adj	15
	550		37.190937	-121.871643	< LOD	< 10	Median Hg Adj	13
	551		37.19088	-121.871819	10	10	Max	25
	552		37.191006	-121.87175	< LOD	< 10		
Drainage	553		37.191368	-121.871399	< LOD	< 10	Count all	6
Below	554		37.191456	-121.871414	< LOD	< 10	Count NDs	5
WS-14	555		37.191429	-121.871429	< LOD	< 10	Max	11
	556		37.191715	-121.872421	< LOD	< 10		
	557		37.191715	-121.872482	11	11		
	558		37.191689	-121.872383	< LOD	< 10		
Quality control								
	578	Final Blank			< LOD	5		
	579	Final NIST			< LOD	6		
	581	Final USGS			7	4		
	582	Final RCRA			< LOD	7		

Table 4. Summary of XRF Mercury Results (mg/kg)

Location description and approximate coordinates	Non-detects	Median	Max	p-Value	Comments on statistical significance
WS-16 Yellow Kid Jr. Dumps 37.18755, -121.866257	1 of 6	69	145	0.03	Significantly different from 10 mg/kg
WS-15 Providencia Open Cut 37.18943, -121.86657	4 of 6	54	83	0.19	Not significantly different from 10 mg/kg
WS-14 Enriquita Mine 37.191166, -121.87133	2 of 6	13	25	0.091	Evidence for significantly different from 10 mg/kg
Drainage Below WS-15 & WS-16 37.18721, -121.871422	3 of 10	10	58	0.091	Evidence for significantly different from 10 mg/kg
Rincon (non-mined) 37.182424, -121.873312	8 of 10	N/A	10	N/A	N/A
Drainage Below WS-14 37.191368, -121.871399	5 of 6	N/A	11	0.5	Not significantly different from 10 mg/kg

Notes:

At Rincon (non-mined), the XRF was unable to locate satellites; these coordinates were determined from Google Maps.

Regarding statistical analysis, both non-detects and values lower than the detection limit were evaluated at the detection limit of 10 mg/kg.