QUALITY ASSURANCE REVIEW

Integral conducted a quality assurance review of laboratory data from chemical analyses of dust, soil, and drinking water samples from the communities near La Oroya, Peru, located in close proximity to the Doe Run Peru Metallurgical Smelter Complex. These samples were collected during the June 2005 sampling event.

The following samples were collected in the communities of Chucchis, La Oroya Antigua, La Oroya Nueva, Marcavalle, and Tupac Amaru and submitted to EnviroLab, Lima, Peru, for metals analysis:

- 20 community dust samples plus 1 duplicate sample
- 37 community soil samples plus 4 duplicate samples
- 18 residential dust samples plus 2 duplicate samples
- 1 residential soil sample
- 10 drinking water samples plus 1 duplicate sample
- 2 equipment rinsate blanks
- 1 drinking water blank.

A quality assurance review was conducted to verify that the laboratory implemented the quality assurance and quality control procedures of the referenced methods (Table 1) and to evaluate the quality control results reported by the laboratory for the June 2005 sampling event. Quality assurance review of these data was performed using U.S. EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (EPA 2002), in the context of DQOs specified in the QAPP (Integral 2005). Data qualifiers defined in U.S. EPA Functional Guidelines were applied to the project data.

The following laboratory deliverables were reviewed during data validation:

- Method blank results.
- Results for laboratory quality control samples required by the referenced methods, including laboratory control sample/laboratory control sample duplicate (LCS/LCSD) analyses, and matrix spike/matrix spike duplicate (MS/MSD) analyses.
- Results for field quality control samples.
- Analytical results for analyses performed.
- Comparison of analytical results for standard reference materials from laboratory to certified values obtained from National Institute of Standards and Technology (NIST).

Data that did not meet the applicable laboratory or data validation quality control limits were qualified during the quality assurance review. The Doe Run Peru June 2005 data, with data qualifiers, are included in Table 2. A total of 885 results were reported by the laboratory for the June 2005 sampling event. Of these results, 535 (61%) were qualified as estimated (assigned a J qualifier), no results were restated as undetected (assigned a U qualifier), and no data were rejected (assigned an R qualifier). All data from the June 2005 sampling event, including the qualified data, are acceptable for the uses defined in the Human Health Risk Assessment Work Plan (HHWP, Integral 2005a).

Analytical Methods

Drinking water samples were analyzed for arsenic, cadmium, copper, lead, and zinc. Drinking water samples analyzed for arsenic were prepared by digestion with nitric and sulfuric acids, reduced to trivalent arsenic using tin chloride, and converted to a volatile hydride using hydrogen produced from a zinc/hydrochloric acid reaction; samples were analyzed by atomic absorption-gaseous hydride (AA-GH) according to EPA method 7061A (EPA 1997). Drinking water samples analyzed for cadmium, copper, lead, and zinc were prepared by digestion with nitric acid and analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) according to EPA method 200.8 (EPA 1994b) (Table 1).

Dust and soil samples were analyzed for antimony, arsenic, cadmium, copper, lead, mercury, selenium, silver, thallium, and zinc. Samples analyzed for arsenic and selenium were prepared by digestion with nitric and sulfuric acids, reduced to their respective trivalent forms using tin chloride, and converted to volatile hydrides using hydrogen produced from a zinc/hydrochloric acid reaction; samples were analyzed by AA-GH according to EPA methods 7061A and 7741A (EPA 1997), respectively. Samples analyzed for antimony were prepared by digestion with nitric acid, reduced to trivalent antimony using potassium iodide, and converted to a volatile hydride using hydrogen produced from the acidified sample with sodium borohydride; samples were analyzed by AA-GH according to EPA method 7062 (EPA 1997). Samples analyzed for silver were prepared by digestion with nitric acid and analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) according to EPA method 200.7 (EPA 1994a). Samples analyzed for cadmium, copper, lead, thallium, and zinc were prepared by digestion with nitric acid and analyzed by ICP-MS according to EPA method 200.8. Mercury was analyzed by cold vapor atomic absorption spectroscopy (CVAAS) according to EPA method 7471A (EPA 1997) (Table 1).

Drinking Water Results

A total of 55 drinking water results were reported by the laboratory for the June 2005 sampling event. Of these results, 22 (40%) were qualified as estimated (assigned a J qualifier), no results were restated as undetected (assigned a U qualifier), and no data were rejected (assigned an R qualifier).

One field duplicate sample was collected from a school drinking fountain located in La Oroya Antigua (DRP2-WOA-01 and DRP2-WOA-01D). The relative percent difference between the field duplicate sample and its parent sample exceeded the target control limit of 35 RPD (EPA 2002) for lead and zinc. All detected concentrations of lead and zinc in the drinking water samples were qualified as estimated (J qualified) based on the precision of the duplicate results.

Dust and Soil Results

A total of 830 dust and soil results were reported by the laboratory for the June 2005 sampling event. Of these results, 513 (62%) were qualified as estimated (assigned a J qualifier), no results were restated as undetected (assigned a U qualifier), and no data were rejected (assigned an R qualifier).

Laboratory blanks were analyzed with each analytical batch. Target analytes were not detected in the method blanks at concentrations above the method detection limit. Arsenic, copper, lead, and zinc were detected in both of the deionized water equipment blanks collected as field quality control samples; concentrations are listed in the table below:

Sample ID	As (mg/L)	Cd (mg/L)	Cu (mg/L)	Pb (mg/L)	Zn (mg/L)
DRP2-DEB-01	0.0237	ND	0.013	0.035	0.030
DRP2-SEB	0.0079	ND	0.010	0.029	0.027

The concentrations of the analytes detected in the equipment rinsate blanks listed above did not affect the qualification of the samples because the arsenic, cadmium, copper, lead, and zinc concentrations in the associated samples were greater than 5x the concentrations found in the blanks.

A matrix spike (MS; muestra adicionada) and matrix spike duplicate (MSD) sample was analyzed with each analytical batch. The percent recoveries (%R) and relative percent differences (%RPDs) for the MS/MSD samples were acceptable and fell within the laboratory's quality control limits.

A laboratory control sample (LCS; muestra de control numero) was analyzed with each analytical batch for each target analyte. The percent recoveries for the LCS sample were acceptable and were within the laboratory's quality control limits.

Five field duplicate samples were collected as described in the following table:

Matrix	Community	Location	Sample ID
Community Soil	Chucchis	Playfield	DRP2-CSCH-39(0-2) & DRP2-CSCH-39(0-2)D
	Chucchis	Playfield	DRP2-CSCH-39(2-10) & DRP2-CSCH-39(2-10)D
	La Oroya Antigua	Empty lot	DRP2-CSOA-101(0-2) & DRP2-CSOA-101(0-2)D
	La Oroya Antigua	Courtyard	DRP2-CSOA-102(0-2) & DRP2-CSOA-102(0-2)D
Residential Dust	Chucchis	Private residence	DRP2-RDCH-19 & DRP2-RDCH-19D
	La Oroya Antigua	Private residence	DRP2-RDOA-104 & DRP2-RDOA-104D
Community Dust	La Oroya Antigua	Basketball/Soccer Court	DRP2-CDOA-05 & DRP2-CDOA-05D

The relative percent differences highlighted in Table 3 between the field duplicate samples exceeded the target acceptable control limit of 35 RPD (EPA 2002). Selected results for antimony, arsenic, cadmium, copper, tellurium, zinc, silver, and mercury (51% of the data) were qualified as estimated (J qualified) due to the precision of the field duplicate results.

Subsamples of two standard reference materials obtained from the National Institute of Standards and Technology (NIST) were submitted to EnviroLab to assess accuracy of results. Table 4 provides a comparison of results obtained from EnviroLab to the NIST certified values for each SRM. Comparibility between the analytical results and certified values were acceptable for all analytes of interest except antimony, selenium, and mercury. Dust and soil sample results were qualified as estimated (J qualified) for antimony and selenium due to the low recoveries of these metals in the NIST SRM. Sample results were qualified as estimated (J qualified) for mercury due to all analytical concentrations of mercury being approximately 50% lower in SRM 2711 (moderately elevated trace element concentrations) than the NIST certified values; two of the three mercury recoveries were acceptable in SRM 2710 (highly elevated trace element concentration).

Revised QA/QC data and analytical results for sample DRP2-RDOA-06 were received from EnviroLab on July 25, 2005. The revised information is provided in this report and accompanying tables.

Conclusion

The precision, accuracy, representativeness, and comparability of the data were assessed during data validation. Completeness was calculated by comparing the total number of acceptable data (non-rejected data) to the total number of data points generated. Completeness for the Doe Run June 2005 data was 100 percent, which exceeded the completeness goal of 90 percent in the QAPP (Integral 2005). The Doe Run June 2005 data met the project data quality objectives (DQOs) and are usable for all project purposes.

References

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