RESULTS OF JUNE/JULY 2016 ASSESSMENT of SOIL, SEDIMENT, and FISH

Huancavelica Heavy Metals Remediation Project
Huancavelica, Peru


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Introduction

From June 22 to July 1, 2016, The Environmental Health Council (EHC) conducted additional assessment of mercury and other heavy metals to address potential exposure to the people living in and near Huancavelica, Peru. The assessment consisted of the collection and analysis of soil samples from adobe homes and surface soil in Huancavelica, sediment samples from the Ichu River upstream, downstream, and within Huancavelica, and fish from several trout farms near Huancavelica. The assessment was conducted as a continuation of the work previously conducted by the EHC from 2009 to 2015 which is summarized in the Remedial Investigation (RI) dated July 2015 and in the Pilot Study Report dated October 2015. The results of the following assessment work will be incorporated into the RI and can be used to support remedial decisions at the site.

Background

The following presents a brief summary of the RI, the complete version of which is available upon request.

Mercury (Hg) contamination from historic mercury processing in and near Huancavelica, Peru is above health-based screening levels in the walls, floors, and indoor air in 75% of the earthen homes studied, with the potential of 19,000 people being at risk of mercury exposure and adverse health effects. Despite the end of mercury processing in the 1970s, Huancavelica remains among the most mercury-contaminated urban areas in the world (Hagan 2014). Several investigations from 2009 to 2014 have been conducted to characterize the extent and magnitude of mercury contamination. Project-specific published studies based on the investigations provide peer-reviewed documentation of significant contamination and risk to residential occupants.

Over 400 years of mercury processing associated with the Santa Bárbara mercury mine several kilometers south of Huancavelica has resulted in contamination of earthen homes, surface soil, sediment, and food in and near Huancavelica. Historic furnace exhaust from roasting cinnabar at several furnace locations in Huancavelica, resulting in atmospheric fallout of mercury, has contaminated local surface soil within the city. The majority of the homes in the city are constructed from contaminated earthen materials and often interior walls and floors in these homes are unsealed and uncovered. Consequently, the walls and dirt floors of homes are contaminated with a variety of mercury compounds, some of which are bioavailable. In addition, elemental mercury in the walls and floors has the potential to be released in the indoor environment as a vapor, resulting in elevated mercury vapor levels in indoor air. Tailings (processed rock) may have also been used for construction of roads, and contaminated aggregate dredged from the Rio Ichu continues to be routinely used in construction projects. Over 50% of the homes in Huancavelica are constructed of locally-derived adobe bricks or rammed earth materials, often contaminated.

There are two main exposure pathways for humans to be exposed to mercury in homes, incidental ingestion of soil particles, and inhalation of contaminated air. Site-specific risk-based screening levels were developed using site-specific exposure factors for the ingestion pathway and established reference concentrations (RfCs) were used to evaluate the inhalation pathway. The site-specific screening level for total mercury in walls and floors, based on risk to children, and using site-specific bioavailability analysis, was determined to be 75 milligrams per kilogram (mg/kg). The World Health Organization (WHO) screening level or RfC of 0.2 micrograms per meter cubed (ug/m^3) was used for inhalation of mercury in homes.

Extrapolating from results of residential sampling of 60 homes in the city, mercury in walls, floors, and indoor air of approximately 3700 homes is above exposure-specific screening values. About 20% of the homes may have mercury vapor above 1 ug/m^3, which is an action level for time-critical relocation of the residents, for several regional Removal Programs of the United States Environmental Protection Agency's USEPA.

Preliminary assessment of sediment in the Ichu River identified elevated levels of mercury.

Sediment may be a likely source of methyl mercury in local fish, and also the source of contamination in products utilizing aggregate drawn from the river. Other food stocks were assessed in a limited manner, additional assessment of those food stocks is warranted.

Based on the results of the investigations, the evaluation of site-specific risk, and the conclusions of the RI, the EHC recommended several remedial actions. Primarily, homes with mercury above site-specific screening levels should be remediated or replaced. In support of remediation, the EHC has conducted a pilot project to evaluate the feasibility of covering the interior walls and floors to reduce exposure to mercury through incidental ingestion as well as reduction of mercury vapor. Interior walls of several homes were covered in 2015, and 2016.

2016 Sample Collection and Analysis Procedures

Soil

Thirty soil samples were collected from roads, adobe brick borrow piles, public space and park surfaces in Huancavelica and nearby Sacsamarca on June 26 through June 30, 2016. Samples were collected using a gloved hand (new glove per sample), grabbing from about 1 cm below the soil surface. Particles greater than approximately 1 cm in size were removed from the sample material before placing in a new zip-able plastic bag. Approximately 5 to 10 sample aliquots were collected from the sample area consisting of about 1.5 square meters at each sample location. Approximately 500 grams of soil was placed in the sample bag and homogenized by turning the bag end over end several times and by massaging the soil to break up larger particles.

Sample bags were labeled with the sample ID (example S1 through S30), date and time of collection and placed in a second larger bag and bucket for storage and transport and kept at room temperature. Notes for the sample ID, such as general soil type, land use, latitude/longitude, and other specific indicators of the area were documented in the project field notebook or on the field sheets.

Samples were retained for analysis of 31 metals by field portable x-ray fluorescence (XRF) at Reflex in Lima using the Reflex Innov-X Delta handheld XRF analyzer. Arsenic (As), mercury (Hg), and lead (Pb) were the metals of focus for this assessment. Detailed information about the XRF analyzer is presented in Appendix B. The sample analyzer table and PC attachment was used for analysis. Table 1 presents the sample IDs, sample types, date and time of collection, sample description, and results which are further explained in the Results Section below. USEPA Method 6200 was generally followed for collection, homogenization, and analysis of soil and sediment samples using field portable XRF.

House (Adobe) Samples

Seventeen samples were collected from walls and floors of adobe or earthen homes in Huancavelica on June 25, June 27, and June 28, 2016. Samples were collected using a gloved hand (new glove per sample) to grab small loose fragments of walls from either the inside or the outside of the home, depending on access to the house. Floor samples were collected by scraping compact surface soil into a small pile of loose fine-grained soil using a clean steel

garden adze and then transferring to a clean plastic sample bag using a gloved hand. All houses were sampled per consent of the property owners.

Particles greater than approximately 1 cm in size were removed from the sample material before placing in a new zip-able plastic bag. Approximately 5 to 10 sample aliquots were collected for each sample from random locations of either the walls or the floor throughout the home. Wall and floor aliquots were not mixed. Approximately 500 grams of soil was placed in the sample bag and homogenized by turning the bag end over end several times and by massaging the soil in massaging the soil to break up larger particles.

Sample bags were labeled with the sample ID (example H1 through H17), date and time of collection and placed in a second larger bag and bucket for storage and transport and kept at room temperature. Notes for the sample ID, such as interior or exterior wall, room of the house, latitude/longitude, owner name, and other specific indicators of the sample were documented in the project field notebook or on the field sheets.

Samples were retained for analysis by field portable x-ray fluorescence (XRF) at Reflex in Lima using the Reflex Innov-X Delta handheld XRF analyzer. Table 2 presents the sample IDs, sample types, date and time of collection, sample description, and results which are further explained in the Results Section below. USEPA Method 6200 was generally followed for collection, homogenization, and analysis of soil and sediment samples using field portable XRF. Sample results were later correlated to the blind codes with the district abbreviations (ie YA-32, SC-4,…) following nomenclature from previous assessments.

Sediment

Fifteen sediment samples were collected from the depositional areas of the Ichu River downstream, upstream, and within Huancavelica, on June 26 through June 30, 2016. Fine-grained sediment was difficult to find in the Ichu River due to the inherent energy of the river, and possibly due to removal of fine-grained material for adobe-brick use. Quarry operations were evident in many locations of the Ichu River in Huancavelica during sampling.

Samples were collected using a small shovel and a gloved hand (new glove per sample) from about 2 to 3 cm's below the surface. Particles greater than approximately 1 cm in size were removed from the sample material before placing in a new zip-able plastic bag. Approximately 5 to 10 sample aliquots were collected from the sample area consisting of about 10 square ft at each sample location. Approximately 500 grams of sediment were placed in the sample bag and homogenized by turning the bag end over end several times and by massaging the soil in massaging the soil to break up larger particles.

Sample bags were labeled with the sample ID (example SD1 through S15), date and time of collection and placed in a second larger bag and bucket for storage and transport and kept at room temperature. Notes for the sample ID, such as general sediment type, land use, latitude/longitude, and other specific indicators of the river were documented in the project field notebook.

Sediment samples were then spread out on a new aluminum foil dish and set on a heater to dry the sample material prior to XRF analysis. Temperature of the heaters were not quantitatively assessed, but were estimated to be between 90 and 130° F based on knowledge of standard oil-filled electric radiator heater[i]. Sample material was shifted and broken apart using a dedicated clean tongue depressor, as it dried. Sample material was then placed in a new zip-able bag and homogenized in the fashion as the soil samples.

Samples were retained for analysis by field portable x-ray fluorescence (XRF) at Reflex in Lima. Table 3 presents the sample IDs, collection information, and analysis type. USEPA Method 6200 was generally followed for collection, homogenization, and analysis of soil and sediment samples using field portable XRF.

Fish

Thirty-five rainbow trout were collected from three trout farms located near Huancavelica. Several market-sized fish of approximately nine months of age were collected from the following six trout farms:

- Palca is a small trout farm located in a small river valley approximately 14 kilometers north of Huancavelica at an elevation of 12200 ft amsl. The water supply comes directly from the river (name) and is directed into approximately 2 feet deep unlined ponds with bottoms of gravel and sand. Fish are segregated by size. Fish are fed with Nicovita brand trout food made in Lima. There are no indications that significant methylation takes places in the river or in the ponds. Ponds have a flow rate that appears to similar to the flow rate of the river. Dissolved oxygen (DO) was not assessed, but because of the good health of the trout, the dissolved oxygen was likely at or near saturation. Samples were labeled PALCA1 through PALCA11.

- Pultocc is a lagoon trout farm located approximately 38 km southwest of Huancavelica at an elevation of approximately 15,400 ft amsl. Fish are raised in screened pens within the lagoon. DO and temperature were not assessed, but due to the elevation, and apparent volume of wind, the two parameters are likely very adequate for trout health. As with many lakes and reservoirs the potential for anoxic zones to exist at depth is possible which could support methylation. However, there were no visible signs of a reducing, low oxygen environment. Fish are fed Nicovita brand trout food. Samples were labeled PULTOCC1 through PULTOCC12.

- Acoria is a fish farm located in Acoria in the Ichu River Valley, approximately 19 km to the northeast of Huancavelica at an elevation of approximately 10500 ft amsl. The water supply comes directly from the Ichu river and is directed into approximately 3 feet deep concrete lined (bottom and sides). Fish are segregated by size. Fish are fed with Nicovita brand trout food made in Lima. There are no indications of methylation in the river or in the ponds. Ponds have a flow rate that appears to similar to the flow rate of the

river. Farm operators indicate that there is a confluence in the Ichu River just upstream of the farm that brings in a large volume of water from a drainage not impacted by Huancavelica's mercury impacts. Dissolved oxygen (DO) was not assessed, but because of the good health of the trout, the dissolved oxygen was likely at or near saturation. Samples were labeled ACORIA1 to ACORIA12.

Fish farm locations are presented in Figure 6.

Each fish was washed, gutted, and filleted. The fillets were washed with distilled water and then minced to about 0.5 cm cubes before placing in a new clean zip-able plastic bag. A stainless steel knife and plastic cutting board were used for processing and were cleaned with distilled water between each fish. Eviscera was carefully removed and washed from the cutting board before fillets were minced. Minced fillet samples were mixed prior to placing in the sample bag. Approximately 500 grams of minced tissue were placed in a new clean plastic zippable baggie for each sample. Samples were labeled and placed in an iced cooler and kept cool until analysis at CETOX. Samples were processed on site at each fish farm and later analyzed for total mercury using CVAA at CETOX in Lima.

Sample Results

Soil, sediment, and house sample analysis took place on July 1, 2016 at Reflex in Lima. Prior to analyzing soil, sediment, and house samples, several reference standards prepared by OREAS were analyzed as a means of potentially correcting XRF results, if need be. OREAS supplies certified reference materials (CRMs) predominantly for the mineral exploration industry. Reference materials were low in As, Hg, and Pb concentrations. Additional information about reference materials and quality assurance is presented in the Quality Assurance section below.

Samples were transferred into new unused XRF cups with mylar covers. Sample material within the plastic baggies were mixed end over end within the baggie prior to transferring to the mylar cups. XRF analysis consisted of 3 x 30 second XRF shots that were averaged within the InnovX software. Each sample ID was attached to the analysis prior to analyzing so that the final table of analytical results had sample IDs and no additional correlation of sample IDs was necessary after downloading the table. The raw analytical table for all results is presented in Appendix C.

<u>Soil</u>

Soil sample results are presented in Table 1. Duplicate or triplicate analyses are presented as averages of those duplicates or in some cases, triplicates in the results table. Arsenic concentrations ranged from 5.8 to 2268 parts per million (ppm) with 24 out of 30 sample results being above the local background of 16 ppm. Additional information on the development of local background concentrations is presented in the risk screening section below. Mercury concentrations ranged from below the level of detection to 543 ppm with 10 out of 30 sample results being above the site screening level of 75 ppm, which was developed in the RI (July 2015). Background Hg concentrations range from not detected to 11 ppm. Five out of the seven

background samples had no detection of Hg at or above the detection limit which could be between 1 and 10 ppm. Generally speaking, any result than 10 ppm for Hg is likely an un-impacted background concentration. Lead concentrations ranged from 12 to 6138 ppm with 10 out of the 30 sample results being above the USEPA regional screening level (RSL) of 400 ppm for residential exposures. The local background lead concentration was determined to be 22 ppm. Additional information on lead and screening values is presented in the risk screening section below.

Generally, samples that appeared to be tailings or impacted by tailings (reddish/pinkish in color) had elevated metals concentrations. Also, generally all three metals were elevated in samples that had at least one elevated metal, also indicating the presence of tailings, or ore. Samples collected from areas believed to be un-impacted by tailings or historic emissions, had low concentrations of each of the metals.

Samples collected from Sacsamarca were markedly elevated in comparison to samples collected in Huancavelica. Although there were several borrow piles in Huancavelica that had concentrations similar to samples collected from Sacsamarca.

House (Adobe) Samples

House sample results are presented in Table 2. Duplicate or triplicate analyses are presented as averages of those duplicates or in some cases, triplicates in the results table. Arsenic concentrations ranged from 51 to 1611 ppm with all sample results exceeding the local background of 16 ppm. Mercury concentrations ranged from below 9 to 926 ppm with 13 out of 17 results being above the site screening level of 75 ppm, which was developed in the RI (July 2015). Lead concentrations ranged from 159 to 5282 ppm with 11 out of the 17 sample results being above the USEPA regional screening level (RSL) of 400 ppm for residential exposures.

Sixteen of the 17 samples appear to be impacted by tailings or historic emissions, or potentially from ore exposed in surface soil in Huancavelica. Sample H4 is the only sample that has relatively low concentrations of the three metals. Three of the 17 samples were collected from floors. There was no significant difference in concentrations between wall samples and floor samples.

Sediment

Sediment sample results are presented in Table 3. Duplicate or triplicate analyses are presented as averages of those duplicates or in some cases, triplicates in the results table. Arsenic concentrations ranged from 13.9 to 207 ppm with 12 out of 19 sample results exceeding the local background of 39 ppm. Mercury concentrations ranged from below 3 to 19 ppm with 15 out of 19 results being above the local background of 4 ppm. Lead concentrations ranged from 17 to 486 ppm with 14 out of the 19 sample results being above the local background of 27 ppm. Background concentrations were calculated by averaging five sample results for sediment samples located upstream of the urbanized area (SD-8, 9, and 10 plus duplicates). Some historic air deposition of contaminants may have occurred in the area of the background sediment sample locations. However, background sediment sample locations are above impacts from stormwater

runoff from the Santa Barbara mine. In addition, generally, the lowest results for each of the contaminants are located in the three most upstream sample locations (SD-8, SD-9, and SD-10), suggesting that the background sediment sample locations are indeed in background or less impacted areas than the remainder of the sample set.

More discussion on background, Cetox comparison, results from 2015 sample collection.

Fish

Fish were only analyzed at Cetox using CVAA for mercury. XRF detection limits are generally too high to assess heavy metals in organic tissue samples and thus fish samples were not analyzed by XRF. Mercury results in all 35 fish samples were below the quantified laboratory detection limit of 0.02 mg/kg. This is not unexpected because trout habitat does not generally include a carnivorous or benthic diet, trout in fish farms have a consistent diet of Nocovita brand trout food, and the fish farms assessed appeared to be poor methylation environments.

Several screening levels for human exposure to MeHg from fish ingestion can be used for risk screening. Subsistence level ingestion of fish could generate a risk screening level at or just above the detection limit of 0.02 mg/kg. Additional discussion on fish screening levels is presented in the risk screening section below. Fish analytical results are presented in Appendix C.

Quality Assurance

Quality assurance (QA) samples were collected and analyzed throughout the project. Twenty-six QA samples consisting of certified reference materials (CRMs) and clean plastic baggies were analyzed at Reflex using the XRF. CRMs are analyzed using inductively coupled plasma mass spectrometry (ICPMS) with much lower detections than XRF as per the certification process.. CRMs were produced by OREAS, which produces reference materials for the mineral exploration industry. The CRMs are low in mercury, arsenic, and lead therefore correlations were not completed for this project. However, a correlation could be done if additional quality assurance is needed.

Average error was calculated for arsenic and lead. Error in mercury results was not calculated because the CRMs had no detections of mercury. Arsenic results of CRMs averaged 17% error and lead results of CRM averaged 70%. Lead concentrations in CRMs are below 31 ppm. With a detection limit for lead and many other metals, in the 5 to 15 ppm range, minor fluctuations in the XRF results, translates to large errors. Thus, error calculations for lead are not very useable. Arsenic CRMs on the other hand, have higher concentrations ranging from non-detect to 469 ppm and provide more valuable error calculations. In addition, soil, sediment, and house sample result that all have elevated arsenic, mercury, and lead suggest that the sample was indeed impacted by tailings and likely have concentrations of those metals above risk-based screening values.

Three empty new plastic baggie samples from the same box of baggies used for sample collection were analyzed by XRF to determine if the baggies were contaminated with heavy metals. One clean new XRF cup and mylar cover was analyzed also to determine if the cups and

mylar sheeting was contaminated. One plastic baggie sample had a detection of mercury at 49 ppm which is likely cross contamination. The XRF window was cleaned prior to analysis of site samples. None of the contaminants of concern were detected in the plastic baggie samples or empty XRF cups and mylar after the window was cleaned.

Sixteen duplicate (including triplicate) soil, sediment, and adobe house samples were analyzed by the XRF at Reflex. One soil sample, one sediment sample, and one house sample were analyzed for mercury by CVAA at Cetox in Lima. Duplicate sample results had very good agreement. Error was not calculated. However, duplicate results were averaged and presented as final results.

One soil sample (S24), one house sample (H17 or YA-11), and one sediment sample (SD5) were analyzed for mercury at CETOX in Lima using atomic absorption spectrophotometry. CETOX accidentally labeled SD5 "S5". The laboratory report shows samples at 20.5 Celsius on arrival. The USEPA method for mercury analysis for CVAA requires samples to be kept at 4^{o} Celsius from time of collection to analysis. It is unknown if any mercury was lost due to elevated temperature. However, the sample jar was closed during transport, and total analysis dissolves all mercury in the sample regardless of possible chemical transformations that may have occurred due to elevated temperatures during storage and transport. XRF results for mercury for the three CETOX samples were in good agreement with the CETOX results, providing additional confidence that the XRF analysis was reasonably accurate. Table 4 presents the results of the quality assurance analyses.

Risk Screening

Screening values are presented in the results tables for soil, sediment, and house results. Sample results that exceed a screening level are shaded in the tables. The following are the screening values for each metal for a residential exposure scenario and the appropriate reference:

- Arsenic – 0.39 mg/kg (USEPA default RSL), local background is 16 mg/kg
- Mercury – 75 mg/kg (Site-specific screening value developed in the RI (July 2015)
- Lead – 400 mg/kg (USEPA default RSL)

USEPA developed Regional Screening Values (RSL) using default exposure parameters and are generally conservative. Additional site-specific exposure parameters can be used to develop more appropriate site-specific screening values.

Arsenic is often naturally elevated in volcanogenic soils. Much of the western US has arsenic in soil two orders of magnitude above the RSL of 0.39 mg/kg. This is likely the case for much of the soil in the Andes. An estimated background concentration was developed for arsenic based on a general review of the XRF results considering the locations of the samples, whether all three heavy metals were elevated or not, and whether the soil appeared to be impacted by tailings. The background arsenic concentration was calculated to be 16 mg/kg. Following standard cleanup

actions, the appropriate site screening value for a contaminant that has a risk-screening level below the background, is to use the local background as the screening value.

As presented above in the Results section, As, Hg, and Pb are above screening values for the protection of human health for approximately one third to one half of the sample results for outdoor soil and home samples. However, 80% to 100% of the outdoor soil samples and home samples were above at least one of the three contaminant screening levels.

Analysis of total Hg in sediment, MeHg in sediment, methylation parameters (sulphate/sulphite, total organic carbon, dissolved organic carbon, dissolved oxygen, temperature,…), and total Hg in fish are needed to better understand the impacts of Hg in sediment of the Ichu River. Using generic screening values for total Hg in sediment that attempt to model trophic uptake, can be complicated and often warrant additional analysis and study. Because of this, screening values are not compared to in this report for sediment. Direct analysis of fish tissue is the primary method for assessing methylation in the river system and is warranted for future studies of the Ichu River system.

Trout collected from three local fish farms, which make up a portion of the diet of the people of Huancavelica were all below the level of detection for Hg (0.02 mg/kg). A commonly used Hg fish advisory level for subsistence populations in the US is 0.04 mg/kg. This correlates to fish ingestion rate of about 8 ounces per day for a 70 kg person. Additional assessment of common fish ingestion rates and the species of fish eaten in Huancavelica will help better understand the risks. However, based on the results of this initial assessment of Hg in trout, the risk from Hg exposure from ingestion of local farmed trout appears to be minimal. Further assessment of fish in the Ichu River system including human ingestion rates of those fish, is warranted.

Summary

The EHC conducted assessment of soil, sediment, house, and fish samples collected in and near Huancavelica, Peru in June and July 2016. The work was developed as a continuation of the Remedial Investigation/Feasibility Study to address mercury contamination in Huancavelica related to historic mercury processing in and near Huancavelica.

Results of soil and house samples indicates that much of the soil and house adobe materials in Huancavelica are contaminated with arsenic, mercury, and lead above risk-based screening levels and that much of the soil and house adobe materials present an unacceptable risk to the residents of Huancavelica. The results can be used for prioritization of homes for remedial action. The same methods applied in the 2015 treatment activities (stucco wall covering and concrete floor installation) can be applied to additional homes as a means of protecting residents from both mercury vapor and incidental ingestion of heavy metals in dust and particles generated from the walls and floors.

Fish assessment results indicate that rainbow trout in three local farms were not impacted with mercury above common screening levels for ingestion of fish. Farm-raised trout does not appear to be a risk to residents of Huancavelica.