Cordero Mercury Mine Removal Assessment
McDermitt and Fort McDermitt, Nevada

Bioaccessibility, Sequential Extraction, and Spectroscopic Speciation Sampling and Analysis

Data Quality Objectives (DQO) Process Document
Objective Outputs

Contract: EP-S5-08-01
TDD No.: TO2-09-10-06-0002
Job No.: 002693.2094.01RA

This DQO documentation version reflects the project objectives as of April 5, 2011.

1. THE PROBLEM

Background

During September and October 2010, the United States Environmental Protection Agency (USEPA) conducted a removal assessment at the *Cordero Mercury Mine Site* in response to regulatory concern over the potential adverse impacts to human health or the environment from dispersion of mine waste that may have been used for development of roadways located on the Paiute Shoshone Indian Reservation and within the town of McDermitt, Nevada, and also potentially used for property development at the McDermitt Combined School in McDermitt, Nevada. Results from the 2010 removal assessment indicate that:

- Mercury exceeds the USEPA Region 9 Regional Screening Level (RSL) for residential soil (23 (milligrams per kilogram (mg/kg)) in surface samples collected at the Paiute Shoshone Indian Reservation North Road and South Road study areas; the McDermitt Combined School property study area; and the McDermitt, Nevada roadway study area. Mercury exceeds the USEPA RSL for industrial soil (310 mg/kg) in surface samples collected at the McDermitt, Nevada roadway study area and the former Cordero Mine.

- Arsenic exceeds the USEPA RSL range for residential soil (0.39 mg/kg to 39 mg/kg) in surface soil samples collected at the Paiute Shoshone Indian Reservation North Road and South Road study areas; the McDermitt Combined School property study area; and the McDermitt, Nevada roadway study area. Arsenic exceeds the USEPA RSL range for industrial soil (1.6 mg/kg to 160 mg/kg) in surface samples collected at the former Cordero Mine.

Based on these results, the USEPA determined that additional sampling and analysis is required at the site in order to characterize the physical and chemical properties of mercury and arsenic compounds and determine the degree to which mercury in residential soils is available for uptake in potentially exposed persons.

The objectives discussed herein are for the sample collection and analysis necessary to evaluate the bioavailability and speciation of mercury compounds, and to evaluate the speciation of arsenic compounds at areas of concern (AOCs) at the *Cordero Mercury Mine Site.*

Conceptual Site Model

- The medium of concern is soil; specifically, calcine mine waste.
- The principal contaminants of primary concern (COPCs) are (1) inorganic mercury above the current USEPA RSL for residential soil, November 2010; and, (2) arsenic above the current USEPA RSL for residential soil, November 2010.
- The soil medium was contaminated due to the deposition of point-source mercury and arsenic contaminated calcines, which originated at the Cordero Mine and have been historically used for roadway and land development at the site.
- The USEPA is interested in further evaluation of the specific mercury and arsenic species, within the medium of concern that may be ingested by humans from the environment and become available for absorption into the human body. Data from this assessment will be utilized to make decisions regarding the risk of exposure to mercury and arsenic contaminated calcines and to determine an appropriate site action level for potential removal actions.

Exposure Scenario

- Concerns based on current conditions include: (1) direct exposure of human and/or environmental receptors to contaminants in calcine material; and (2) exposure to contaminants in calcine material through ingestion by inhalation of particulate matter (dust). The residential roadways and public use areas (i.e., school) are susceptible to direct exposure to human receptors.
- Conditions at the site may pose an additional threat to human health during and/or after potential future construction activities that require grading or excavation in the area. Direct and airborne exposure of human and/or environmental receptors to mercury-contaminated calcines and calcine-derived particulates are of concern during potential future construction.
- The excess soil generated during potential future site construction may pose a threat to human health during transportation and disposal.

Available Resources

The current START budget for planning, field work, and reporting for the *Cordero Mercury Mine Site* removal assessment activities is approximately $52,700. Other budget constraints on USEPA resources for this project have not been specified. The primary decision-maker for the project is Federal On-Scene Coordinator (FOSC) Tom Dunkelman.

<u>Other resources available include:</u>

- USEPA Region 9 Laboratory in Richmond, California
- United States Geological Survey (USGS) Laboratory in Menlo Park, California
- Rick Wilkin, USEPA Office of Research and Development Laboratory in Ada, Oklahoma
- Aaron Slowey, Stanford University, Synchrotron Research Lightsource
- START subcontracted laboratory

Planning Team

Mr. Tom Dunkelman, USEPA Region 9 FOSC
Mr. Stan Smucker, USEPA Region 9 Toxicologist
Mr. Richard Bauer, USEPA Region 9 Laboratory
Mr. David Neil Ellis, E & E – USEPA Region 9 START
Mr. Howard Edwards, E & E – USEPA Region 9 START
Mr. Charles Alpers, USGS
Mr. Mark Marvin-DiPasquale, USGS

Roles and Responsibilities

- Tom Dunkelman, the USEPA Region 9 FOSC, will be the primary decision-maker and will direct the project, specify tasks, and ensure that the project is proceeding on schedule and within budget. Additional duties include coordination of all preliminary and final reporting and communication with the START Project Manager and USEPA Quality Assurance (QA) Office.
- Stan Smucker, the USEPA Region 9 Toxicologist, will provide guidelines related to human-health exposure risks and coordinate with the planning team to develop project objectives.
- Neil Ellis, the START Project Manager, will coordinate with the planning team to develop project objectives and complete an approved Sampling and Analysis Plan (SAP).
- Howard Edwards, the START QA Officer, will oversee development and preparation of the SAP and other START deliverables. Mr. Edwards will provide overall project quality assurance and, if necessary, audit functions.
- Charles Alpers, with the USGS, will provide expert technical support to the planning team during development of project objectives.
- Mark Marvin-DiPasquale, with the USGS, will provide expert technical support to the planning team during development of project objectives and will provide laboratory support at the USGS Laboratory in Menlo Park, California.
- The START has arranged for the USEPA Region 9 Laboratory in Richmond, California to perform bioaccessibility sample analysis.
- START will be responsible for implementation of the SAP, coordination of project tasks, coordination of field sampling, project management, and completion of all preliminary and final reporting.
- START or a START contractor will be responsible for data validation.

Other Considerations and Constraints Related to Problem and Resources

- Laboratory analyses available for assessment are not always useful for determining disposal and remediation requirements and costs. Additional waste testing of excavated soil is usually necessary to determine disposal requirements.
- Contamination not found during this investigation may be revealed during excavation activities.

2. THE DECISION

Principal Study Questions

Previous assessments at the *Cordero Mercury Mine Site* indicate that surface calcine materials located at two roadway areas on the Paiute Shoshone Indian Reservation in Fort McDermitt, Nevada; at roadway areas in the town of McDermitt, Nevada; at the playground and access roadway areas on the McDerrmitt Combined School property in McDermitt, Nevada; and at the Cordero Mine approximately 11 miles west-southwest McDermitt, Nevada, are contaminated with elevated concentrations of mercury and arsenic.

<u>Study Question #1:</u>

What are the total mercury and arsenic concentrations in the calcine material samples collected?

- What are the range, mean, and standard deviation of total mercury and arsenic concentrations?

- Are the total mercury and arsenic concentrations distributed uniformly throughout site study areas or do certain study areas have higher concentrations?

Study Question #2:
What is the inorganic mercury species present in calcines and are they available for absorption in the human gastrointestinal (GI) tract?

- What mercury species predominate in calcines as indicated by X-ray Absorption Fine Structure (XAFS) Spectroscopy?

- What are the proportions of various mercury species (or fractions) indicated using Sequential Chemical Extraction (SCE)?

- What is the proportion of total mercury that is soluble and potentially available for absorption in the human GI tract (i.e., bioaccessible) in laboratory-replicated human gastric and intestinal solutions?

Study Question #3:
What is the arsenic species present in calcines and does this information support a less than 100% bioavailability assumption, such as the 50% bioavailability default recommended by the USEPA Region 8?

- What arsenic species predominate in calcines as indicated by XAFS Spectroscopy?

Actions that could result from the resolution of study questions

If it is determined that mercury and/or arsenic species in calcines are available for absorption in the human GI tract:

- o A remedial action at the site may be considered.
- o Further study to determine the human intake rates of contaminated calcines may be warranted.
- o Further study to determine the exact mercury and arsenic concentrations within human populations (e.g., biological sampling) at the site may be warranted.
- o A study to determine the cost effectiveness of potential removal actions or treatment remedies may be conducted.

If it is determined that mercury and/or arsenic species in calcines are not available for absorption in the human GI tract:

- o A remedial action may not be considered for the site.
- o Further study or testing at the site may be required.

Decision Statement(s)

Determine whether the specific mercury and arsenic species in calcines are available for human uptake (i.e., bioavailable) and if the mercury species are available for absorption into the human GI tract (i.e., bioaccessible) in order to evaluate human-health risks and determine whether the site needs remediation/removal, additional study, or no further action.

3. DECISION INPUTS

New environmental data required to resolve the decision statements

- definitive analytical laboratory data for total mercury and arsenic concentrations in calcines collected between 0 and 6 inches below ground surface (bgs) at site study areas
- analytical X-ray fluorescence (XRF) data for total mercury and arsenic in calcines collected between 0 and 6 inches bgs at site study areas

- analytical data for mercury and arsenic species in calcines collected between 0 and 6 inches bgs at site study areas
- analytical data for bioaccessibility of mercury species in calcines collected between 0 and 6 inches bgs at site study areas
- physical site data such as observations of soil types at site study areas
- sampling location data

Sources of information available to resolve the decision-statement
- sources of site background information currently available
- analytical data from the October and September 2010 site assessment
- physical site data will be supplied by visual survey data, global positioning system (GPS) surveys, and site photographs
- laboratory analysis of all collected samples (~40) for total mercury, total arsenic, organic matter (OM) content by loss on ignition (LOI), and granular size distribution.
- laboratory analysis of 25% of the collected samples for SCE for inorganic mercury (5-step extraction method), *in vitro* bioaccessibility assay for mercury, and XAFS Spectroscopy for mercury and arsenic
- risk-based action levels for mercury and mercury bioavailability
- risk-based action levels for arsenic and arsenic bioavailability

Information Needed to Establish Action Level
- Information on what species of inorganic mercury is present at site study areas.
- Information on what species of arsenic is present at site study areas.
- Information on expected and actual duration of potential exposures at site study areas.

Collection methods
Soil samples can be collected using a stainless-steel trowel or stainless-steel hand auger.

Measurement methods
Collected samples can be field analyzed to determine COPC concentrations using the following non-definitive methods:
- EPA Method 6200 using a Portable Field X-Ray Fluorescence (XRF) Spectrometer for analysis of mercury and arsenic.

Collected samples can be analyzed to determine COPC concentrations using the following definitive SW-846 methods:
- total arsenic (EPA Method 6010B)
- total mercury (EPA Method 7471A)
- pH (EPA Method 9045D)

The following analytical methods can be used to evaluate calcine and soil characteristics, which can help to determine potential human-health risks at the site:
- *in vitro* bioaccessibility assay (following EPA Region 9 Laboratory SOP, EPA OSWER 9200.3-51)
- SCE (5-step extraction method, following USGS Laboratory SOP)
- XAFS Spectroscopy (mercury and arsenic speciation method)
- particle size distribution (to evaluate clay, sand, and silt content, ASTM 422)

- OM by LOI (following USGS Laboratory SOP)

Confirm that appropriate analytical methods exist to provide the necessary data
The definitive and non-definitive USEPA and USGS laboratory methods have sufficient sensitivity, accuracy, precision, and other quality parameters to generate necessary data, provided the data are not needed within a critical timeframe.

4. STUDY BOUNDARIES

Define the Population Being Studied
Calcine material within the site boundary that have mercury concentrations greater than 23 mg/kg and arsenic concentrations greater than 39 mg/kg is the population being studied.

- A sample decision unit from the target population will consist of two 4-ounce jars, approximately 450 grams each (900 grams total).

Spatial Boundary of Investigation
The site boundary includes two roadways on the Paiute Shoshone Indian Reservation in Fort McDermitt, Nevada; public roadway areas in the town of McDermitt, Nevada; playground and access roadway areas on the McDermitt Combined School property in McDermitt, Nevada; and mine waste at the Cordero Mine located approximately 11 miles west-southwest McDermitt, Nevada, which were previously sampled in September and October 2010. New sample locations for this investigation will be selected from areas where elevated levels of COPCs were previously detected. Samples will have a depth of 0 to 6 inches bgs.

Temporal Boundary of Investigation
The decisions will apply to determinations of risk associated with long-term direct exposure to contaminated surface calcines. However, decisions may also apply to direct short-term (acute) exposure to contaminated calcines due to future development activities.

Inorganic mercury and arsenic in soil media are environmentally persistent and migrate slowly; therefore, the concentrations of mercury and arsenic in calcines will not generally vary greatly over time. However, the migration of airborne particulate matter (dust) containing inorganic mercury and/or arsenic is dependent upon weather conditions and area use. Increased roadway or human activity use would be expected to increase the potential for exposure to mercury and/or arsenic-laden dust.

Thus, the following assessment time-frame has been proposed:

- The SAP will be submitted to USEPA FOSC by April 15, 2011 and should be reviewed and revised prior to the first day of proposed work.
- Sample collection will take place following SAP approval by the USEPA.
- Preliminary data should be available approximately 4 weeks from the date of sample delivery to the laboratory.
- Data packages and final data should be reported to project management approximately 6 weeks after sample delivery to the laboratory.
- Laboratory data generated using USEPA definitive analytical methods should be evaluated following USEPA Region 9 Tier 2 guidance. Evaluated data should be reported to project management approximately 6-7 weeks after sample delivery to the laboratory.
- Decision statement resolutions are expected to occur approximately 7-8 weeks after sampling and should take place prior to development decisions.

Scale of decision-making
A decision/resolution of the study questions will be based on calcine materials collected between 0 to 6 inches bgs and their analytical results. The calcine materials collected from a site study area are considered representative of conditions at that site study.

If mercury and/or arsenic in specific locations and samples are found at concentrations significantly less than other sample locations, those locations and the corresponding soil may be considered separate decision units.

Constraints on Data Collection

- The turnaround times on data are always estimated and cannot be assured. Sample and system problems may indiscriminately increase data turnaround times.
- Definitive data will undergo a USEPA Region 9 Tier 2 validation review prior to final reporting. Problems identified during this review may initiate additional data reviews, which will increase the time needed before data are finalized.
- Specific data may be qualified or rejected based on the results of the data review process.
- Civil constraints such as site access agreements, tribal requirements, and permit requirements may exist and, if so, will need to be addressed prior to sampling.

5. DECISION RULE

Statistical Parameter
The range of total mercury and arsenic concentrations and the average of each identified mercury and arsenic species define the statistical population of interest.

Action Level
The site-specific action level will be based, in part, on the species of mercury and arsenic present in calcines, which has not yet been established.

Decision Rules
If the data indicate that a sample at a specific location has mercury and/or arsenic concentration(s) above the established site-specific action level, then it will be assumed that there is a potential human-health risk, and that decision unit, and the associated area will be considered in need of remediation or additional study/assessment.

If the data indicate that a sample at a specific location has mercury and/or arsenic concentrations below the established site-specific action level, then it will be assumed that there is not a potential human-health risk, and the associated area will not be considered as in need of remediation or additional study.

6. LIMITS ON DECISION ERRORS

Range of the parameter(s) of interest
Mercury and arsenic concentrations that exceed the current USEPA RSLs, respectively, and the speciation and bioaccessibility data associated with these concentrations are the parameters of interest for this assessment.

Baseline Condition ***(the Null Hypothesis)***
The COPC concentrations in calcines exceed the site-specific action levels.

Alternative Condition ***(the Alternative Hypothesis)***
The COPC concentrations in calcines do not exceed the site-specific action levels.

Decision Errors

Table 1. Decision Errors
Cordero Mercury Mine Site
McDermitt and Fort McDermitt, Nevada
E & E Project No.: 002693.2094.01RA TDD No.: TO2-09-10-06-0002

Decision Error	Deciding that the sample concentration exceeds the action level when it does not.	Deciding that the sample concentration does not exceed the action level when it does.
True Nature of Decision Error	The sample concentrations are either not representative or are biased high.	The sample concentrations are either not representative or are biased low.
The Consequence of Error	Areas of calcines represented by the sample will undergo additional investigation or may be immediately excavated or treated. Each situation would cost the EPA, Region 9, additional resources of time, money, and manpower.	The community could be directly exposed to COPCs in areas of contaminated calcines. Exposure would be an imminent threat to human health and the environment.
Which Decision Error Has More Severe Consequences near the Action Level?	**LESS SEVERE** to human health, but with appreciable economic consequences	**MORE SEVERE** because the contaminated calcines may pose risks to human health and/or the environment.
Error Type Based on Consequences	**False Acceptance Decision** A decision that the calcine contaminant concentrations are greater than the action level when they actually are not.	**False Rejection Decision** A decision that the calcine contaminant concentrations are less than the action level when they actually are greater.

Definitions
False Acceptance Decision = A false acceptance decision error occurs when the null hypothesis is not rejected when it is false.
False Rejection Decision = A false rejection decision error occurs when the null hypothesis is rejected when it is true.
See the EPA document titled, *Guidance for the Data Quality Objective Process*, Chapter 6, (EPA QA/G-4) for additional guidance regarding decision errors

Decision Error Limits Goals
For calculation of the decision error limit goals, the standard deviation between samples was assumed to be within 30%. The decision error limit goals for the site are presented in Table 2.

Table 2 - Decision Error Limits Goals Cordero Mercury Mine Site McDermitt and Fort McDermitt, Nevada E & E Project No.: 002693.2094.01RA TDD No.: TO2-09-10-06-0002			
True Average Concentration of Sample (% of Action Level)	**Decision Error**	**Typical Decision Error Probability Goals (Based on Professional Judgment)**	**Type of Decision Error**
< 75	A decision that COPCs in a decision unit area are bioavailable when they are not.	Less than 5%	false acceptance
75 to < 100	A decision that COPCs in a decision unit area are bioavailable when they are not.	Gray area[1]	false acceptance
100 to 125	A decision that COPCs in a decision unit area are not bioavailable when they are.	Less than 5%	false rejection
> 125	A decision that COPCs in a decision unit area are not bioavailable when they are.	Less than 1%	false rejection

Notes

[1]Gray Area is where relatively large decision errors are acceptable.

7. DESIGN FOR OBTAINING DATA

Design

Approximately 40 sample locations from the 2010 removal assessment representing a range of detected mercury and arsenic concentrations will be re-sampled as close to their original locations as possible and analyzed for specific COPC species content and bioaccessibility of mercury content. Sampling locations in these DQOs are identified by COPC concentration range, and specific locations within these concentration ranges will be selected in the field. Areas of exposed calcines, and specifically roadway areas, the McDermitt Combined School playground, and mine waste at the Cordero Mine will be sampled for this assessment.

Primary sample locations from the following total mercury concentration ranges of interest will be targeted during this assessment:

- 23 to 80 mg/kg (20 samples)
- > 80 mg/kg (20 samples)

Site study areas determined in the 2010 removal assessment to represent a location with a specific concentration of interest will be sampled. A GPS will be used to get as close as possible to the original sample location. A biased sample will be collected from that location. Because the species identification within samples target specific mercury and arsenic concentrations, an XRF (EPA Method 6200) will be utilized in the field or prior to laboratory submittal in order to verify that COPC concentrations in the proposed sample locations are near the appropriate concentration. If XRF results indicate the desired COPC concentration has been located, the upper 6 inches of soil/calcines will be collected from the decision unit area and prepared for laboratory analysis.

At each sampling decision unit area one 4-point composite sample will be collected. Surface composite samples will consist of four equally-sized aliquots, collected directly into a new plastic bag for homogenization. After homogenization, samples will be field sieved by using a stainless-steel 250 micron (#60) mesh sieve and transferred directly into two 4-ounce certified-clean glass jars for holding and target analysis. Approximately 350 to 400 grams of soil will be collected from 0 to 6 inches bgs at each decision unit sample location.

Analysis

The primary analytes of concern are mercury and arsenic. All samples collected will be field analyzed for mercury and arsenic using the XRF (EPA Method 6200). The following laboratory analytical methods can be used to evaluate calcine and soil characteristics, which can help to determine potential human-health risks at the site:

- total arsenic (EPA Method 6010B)
- total mercury (EPA Method 7471A)
- pH (EPA Method 9045D)
- *in vitro* bioaccessibility assay (following EPA Region 9 Laboratory SOP, EPA OSWER 9200.3-51)
- SCE (5-step extraction method, following USGS Laboratory SOP)
- XAFS Spectroscopy (mercury and arsenic speciation method)
- particle size distribution (to evaluate clay, sand, and silt content, ASTM 422)
- OM by LOI (following USGS Laboratory SOP)

Decision Error Minimization

In order to meet the decision limit error goal stated in step 6 of this DQO, all 4-point composite samples must have 10 % duplicate analysis and data should not be qualified.

Data from sample locations

The decision-maker should consider data uncertainty when making decisions using sampling data and associated estimated values from a single decision unit. An individual data value reported below the action level may be biased low, while a data value reported above the action level may be biased high. The probability of decision error increases when COPC concentrations are near the action level due to both data uncertainty and data bias. Data that exceeds the action level by several times will likely not be in error.

Contamination Distribution Map

Data from sampling locations can be used to create a contaminant distribution map. The mapped COPC concentrations within an area should generally be based on the sample data from that area and the sample data from adjacent locations. The generated map model could be used to estimate the concentration of contamination throughout the study area. The decision-maker should consider the data source and statistical sophistication of the distribution map prior to making decisions based on the map. The uncertainty for estimated data (data based on extrapolations and interpolations) is typically greater than for actual data. Therefore the probability of a decision error is greatly increased when extrapolated data are used.

General requirement for generating usable data

All activities and documentation related to the project should proceed under a Quality Management Plan (QMP). All sampling, analytical and quality assurance activities will proceed under a USEPA-approved SAP. A record of sampling activities and deviation from the SAP must be documented in a bound field log book. Prior to sample collection, all project sampling personnel will review relevant sampling procedures and relevant quality assurance and control requirements for selected analytical methods.

Background Sampling

Background reference samples will be collected from each site study area at biased locations that appear historically undisturbed from calcines. One 4-point composite sample will be collected at each background location by using the same methods as primary sample collection.