

**Department of Energy, Office of Legacy Management
Monticello Mill Tailings Site Operable Unit III (MMTS OU III)**

Summary of Program Directive #: MNT-2010-03

Subject: Aquatic macroinvertebrate sampling and analysis for selenium at Monticello Wetland 3 and Sediment Pond, and background locations on Verdure Creek and Montezuma Creek.

Directive/Task Changes: Continue macroinvertebrate sampling and analysis for selenium in 2010 in accordance with the attached sampling and analysis plan. The scope of work and methodology described in the plan was originally developed in consultation with the Biological Technical Assistance Group (BTAG) for OU III biomonitoring in 2004. The 2010 plan was developed in consultation with BTAG after analysis of previous years' data. 2010 biomonitoring includes macroinvertebrate sampling at Wetland 3, the Sediment Pond, and background locations. At the request of the U.S. Environmental Protection Agency and the Utah Department of Environmental Quality, concurrent surface water samples will be collected. Sediment sampling within these wetlands will be discontinued.

Affected Program Documents: Monticello Mill Tailings Operable Unit III Post-Record of Decision Monitoring Plan

Justification: Collection of aquatic macroinvertebrates for selenium analysis is a component of the ongoing OU III biomonitoring program to evaluate potential selenium accumulation in the wetlands at OU III. Biomonitoring requirements are outlined in the MMTS OU III Post-Record of Decision Monitoring Plan (August 2004) and the MMTS OU III Record of Decision (June 2004).

Effective Date: June 1, 2010

Expiration Date: September 30, 2010

MMTS Operable Unit III Biomonitoring Macroinvertebrate Sampling and Analysis Plan 2010 Field Season

I. Introduction

The U.S. Department of Energy (DOE) has been conducting biomonitoring activities at the Monticello Mill Tailings Site (MMTS) since 2005 per requirements in the *MMTS Operable Unit III Post-Record of Decision Monitoring Plan* (DOE/LMGJ684-2004, U.S. Department of Energy, Office of Legacy Management, Grand Junction, Colorado, August 2004). This Sampling and Analysis Plan describes activities to be conducted in 2010, and it was developed in consultation with the Biological Technical Assistance Group (BTAG) after review of previous years' data.

Selenium has the ability to accumulate in the aquatic food chain and potentially harm organisms, particularly avian species during developmental stages. Following surface remediation at the MMTS, benchmark levels for selenium were exceeded in some surface water samples. This triggered biomonitoring in 2005, which included avian surveys and sediment, macroinvertebrate, and additional surface water sampling. In 2010, biomonitoring efforts will focus on macroinvertebrates in Wetland 3, the Sediment Pond, and at one or two background locations, as available, on Montezuma Creek upstream of the former millsite and at Verdure Creek. Verdure Creek is located approximately five miles south of MMTS and was used as a reference area for the baseline ecological risk assessment for OU III conducted in 1995 and 1996. Results from previous years' data have excluded Wetland 1 and Wetland 2 from further sampling. Also, no further sediment data are required at this time. The need for future avian monitoring will be assessed when 2010 macroinvertebrate data have been analyzed. At the request of EPA and UDEQ, surface water samples will be collected at the same time and locations as macroinvertebrate samples.

II. Scope

Field sampling will be performed by S.M. Stoller personnel and will consist of procuring necessary field equipment, planning field activities, traveling to the field site, and collecting macroinvertebrate samples. Dip net and surface water samples will be collected in late June or early July 2010 at five or six locations each at Wetland 3, the Sediment Pond, upstream of the former millsite, and Verdure Creek.

Sample identification and preparation will be performed by S.M. Stoller personnel and will consist of storing samples, cleaning, sorting and identifying macroinvertebrate taxa, weighing samples, and preparing samples for shipment to the laboratories. Surface water samples will be preserved in the field.

Macroinvertebrate sample analysis will be performed by the Battelle Marine Sciences Laboratory in Sequim, Washington according to protocols established in previous monitoring years. Surface water sample analysis will be performed by a contracted analytical laboratory. Results will be provided in an electronic data format.

A summary of the field activities and laboratory results will be prepared by S.M. Stoller personnel, and interpretation will consider results of past sampling efforts, background values, and current regulatory benchmarks. Finalization of the report will include incorporation of comments received from DOE and BTAG; the summary will be included in the 2010 Annual Groundwater Report (prepared in summer or fall annually).

III. Field Sampling Procedures

A. Macroinvertebrate Sample Collection

Wetland macroinvertebrates will be sampled using triangular-frame heavy duty dip nets with 500 micrometer mesh netting. Each dip net sample for selenium analysis will have a minimum mass of 3 grams (g) wet weight. A portable balance will be utilized to estimate the weight of each sample in the field, and this weight will be recorded in field notes. If the goal of collecting a mass of 3 g wet weight per sample cannot be achieved, then samples for a location will be composited prior to analysis.

Depending upon water levels in the wetlands, five to six dip net samples will be collected in June or early July, 2010. Sampling in this time frame will ensure that a variety of macroinvertebrate taxa are present and that those sampled are likely to have originated in that wetland's sediment and water. Field samplers will make qualitative notes (e.g., field conditions or locations of populations of macroinvertebrates), as practicable, during the collection of samples.

To represent potential avian doses from selenium in macroinvertebrates in the entire wetland, Wetland 3 will be visually divided into five or six regions. One sample will be collected near the outlet of Seep 2 (a known source of selenium to the wetland); one sample will be collected near the outlet of Wetland 3 near Montezuma Creek; one sample will be collected where water from Montezuma Creek enters the wetland through an underground infiltration gallery; and two or three mid-gradient samples will be taken between these points. Exact sampling locations will depend upon water levels and the location of vegetation in 2010. The Sediment Pond will be similarly divided into five or six sampling areas. One sample will be collected near the inlet, and one will be taken near the outlet. In addition, one or two samples along the north and one or two samples along the south shores of the pond will be collected.

Verdure Creek and Montezuma Creek upstream of the former millsite represent background locations. These areas were sampled by ORNL in the late 1990's. Sampling locations will be located as near as possible to the ORNL locations in reaches of stream with characteristics as close as possible to Wetland 3 and the Sediment Pond (e.g., slow moving reaches are more appropriate than fast moving reaches).

Dip nets will be worked around the perimeter of the wetlands and in areas where there is open water between the emergent vegetation. If macroinvertebrates are observed on the submerged vegetation, they will be collected. Because they may bias samples, exceptionally large macroinvertebrates, such as large crayfish and snails, will not be included.

Field personnel will wear Nitrile gloves during sample collection. Macroinvertebrates will be removed from the kick nets with pre-cleaned forceps and placed in sterile high-density polyethylene collection bottles. Every attempt will be made to minimize detritus and other plant materials in the samples. To minimize potential predation between macroinvertebrate groups, water will not be added to the sample containers.

As soon as possible after collection, samples will be chilled and transported to the Monticello Field Office, where organisms will be identified to the lowest taxon possible, rinsed with deionized water on filter paper, weighed, and transferred to sterile pre-weighed standard plastic collection bottles. One sample will be split for quality control prior to shipping; samples will be shipped to Battelle Marine Sciences Laboratory for selenium analysis. If samples are less than 1 g wet weight, they will be composited for a particular wetland. Samples will be kept at or below 4°C during storage and shipping. Standard chain of custody methods and labels will be used for all collected samples.

To assess the quality of the field sampling technique, two types of quality control samples will be collected, field duplicates and equipment blanks. One field duplicate will be collected in the field. A second field duplicate will be a split of a sample prepared after identification and sorting. Care will be taken to make field duplicates indistinguishable to the lab so that personnel performing analyses cannot determine which samples are duplicates.

Equipment blanks are used to verify that selenium-contaminated equipment does not affect the quality of the samples. One field blank (deionized water rinse water that has rinsed all pre-cleaned field equipment to be used) will be prepared prior to sampling and submitted to the laboratory for analysis.

B. Surface Water Sample Collection

Applicable field practices or details not specifically addressed in this sampling plan, such as equipment decontamination, sample management, and field documentation will conform to the specifications in the *Sampling and Analysis Plan for U.S. Department of Energy Legacy Management Sites* (LM Sampling Plan [DOE 2010]).

Surface water samples will be collected at a given location before macroinvertebrate samples are collected to minimize turbidity. One sample will be collected at each macroinvertebrate sample location (i.e. five or six locations at each wetland) in a new and certified pre-cleaned high-density polyethylene bottle. The sample will be obtained by directly immersing the bottle near the center of the water column. An unfiltered sample will be taken because it best represents exposure to macroinvertebrates. The sample volume will be a minimum of 500 milliliters. Field parameters of temperature, pH, electrical conductivity and alkalinity will be determined at each sampling location. Field personnel will also record the approximate water depth and the general hydrological condition of the wetland or pond in the field logbook.

Surface water samples will be preserved in the field by adding nitric acid to reduce the pH of the sample to less than 2 standard pH units.

IV. Laboratory Test Analyses - Macroinvertebrates

The goal of the macroinvertebrate field sampling effort is to provide the following samples to the laboratory for selenium analysis:

- five or six samples collected with dip nets from Wetland 3
- five or six samples collected with dip nets from the Sediment Pond
- one field duplicate (collected in the field)
- one split sample (prepared in the Field Office)
- one equipment blank

The samples will be analyzed by Battelle Marine Sciences Laboratory according to the guidelines included in a separate Statement of Work. These guidelines are summarized below:

A. Percent Moisture Determination

The samples collected will arrive at the laboratory "as collected" and require that the percent moisture be determined to allow the selenium results to be reported on a dry weight basis. Percent moisture is determined as the percent ratio of wet to dry weight for the entire sample. Dry weights will be determined by placing the wet sample in a pre-tared, pre-cleaned sample container, lyophilizing (freeze drying) the entire sample, and then recording the change in weights.

B. Low-Level Trace Metals Analysis

The required analytical method for analyzing selenium in the macroinvertebrate samples is EPA Method 270.3, gaseous hydride atomic absorption.

Sample preparation must include:

- lyophilizing the samples and then homogenizing them using a ball-mill prior to digestion
- digesting an aliquot of approximately 0.5 g of each dried, homogeneous sample by combining with nitric and hydrochloric acids (aqua regia) in a Teflon vessel and heating in an oven at 130°C ($\pm 10^\circ\text{C}$) for a minimum of eight hours
- diluting with deionized water to achieve analysis volume, then submittal of analysis.

The digested samples must be analyzed for selenium using hydride generation flow injection atomic absorption spectroscopy (HGAA-FIAS).

- All results will be determined and reported in units of mg/kg on a dry-weight basis.
- The detection limit for selenium in the macroinvertebrate samples will be based on a methods detection limit (MDL) and reporting limit (RL) study performed by the

laboratory. MDLs for trace metals are determined in accordance with 40 CFR Part 136 Appendix B.

- The RL is calculated by multiplying the target analyte MDL by 3.18. The value 3.18 is based on the Student's-t value for 7 to 10 replicates, the number of replicates usually analyzed to generate the MDL.
- The MDL for tissues must be less than 0.02 mg/kg dry weight with an RL less than 0.07 mg/kg dry weight.

C. Laboratory Quality Control

Internal quality control (QC) is an important part of the measurement system to ensure that analytical results are reliable and that data integrity is maintained. Laboratory performance will be evaluated through analysis of laboratory quality control samples (in conjunction with field quality control samples, as appropriate).

The analytical performance of the laboratory will be validated by reviewing the results from analysis of the blank, matrix spike, duplicate, and quality control check samples. The following describes the batch preparative quality control samples that are required by the analytical method.

- **Method Blank (MB):** A Method Blank consists of Type II ASTM water that is subjected to the sample preparation or extraction procedures and analyzed as a sample. It serves to measure contamination associated with preparation and analysis. One MB is required for the 20 or fewer samples. If the analyte of interest is above the RL, corrective action must be taken.
- **Matrix Spike (MS):** A Matrix Spike is an aliquot of sample to which a known amount of analyte has been added. It is subjected to the sample preparation or extraction procedures and analyzed as a sample. The stock solutions used for spiking are purchased or prepared independently of calibration standards. One MS is required for every 20 or fewer samples analyzed. The spike recovery measures the effects of interferences in the sample matrix and reflects the accuracy of the determination.
- **Matrix Spike Duplicate (MSD):** A Matrix Spike Duplicate is an additional aliquot of sample to which known amounts of analyte have been added and subjected to the same preparation and analytical scheme as the original sample. The Relative Percent Difference (RPD) between MS and MSD measures the precision of a given analysis. One MSD will be required for every 20 or fewer samples analyzed.
- **Laboratory Control Sample (LCS):** Laboratory Control Sample is created from a standard reference material which is a material similar in nature to the sample being processed [traceable to the National Institute of Standards and Technology (NIST) or other agencies, to the extent possible]. A known amount of analyte is added to an aliquot of Type II ASTM water. The LCS is subjected to the sample preparation or extraction

procedure and analyzed as a sample. One LCS will be required every 20 or fewer samples analyzed.

- **Laboratory Replicate Sample (LRS):** Laboratory Replicate Samples are used to assess the homogenization techniques. Samples are homogenized, and then divided into two equal parts for analysis. Care is taken to make both samples representative of materials present, including heterogeneities. If possible, at least one sample will be prepared and analyzed as a LRS.

Laboratory results will be available approximately 45 days after the samples have been received. The laboratory will provide the results to Stoller in electronic form.

V. Laboratory Test Analyses – Surface Water

Surface water samples will be submitted to a contracted analytical laboratory for analysis of selenium by ICP-MS (inductively coupled plasma-mass spectrometry, EPA SW-846 6020). The laboratory reporting limit (0.1 µg/L) will be consistent with previous and current monitoring for selenium in OUIII water samples.

Laboratory data reporting will conform to the applicable requirements and formats described in the LM Sampling Plan.

VI. Data Report

A summary report will be prepared by S.M. Stoller and submitted to DOE by September 30, 2010. The report will include the following information.

- A summary of the dates, times and locations of the field sampling activities
- A summary of the field activities performed, including locations of sampling points
- A summary of the laboratory test analyses including results, methods, detection limits, and laboratory qualifiers
- Comparison of results from macroinvertebrate samples to benchmark values, previous data, and known background values
- Recommendation for follow-on activities
- References

The summary will be reviewed by DOE, EPA and UDEQ and included in the 2010 Annual Groundwater Report.