Sampling and Analysis Plan for the 2009 Tri-State Transition Zone Assessment Study

Kansas, Missouri and Oklahoma

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A sampling and analysis plan (SAP) consists of three primary elements, including a quality assurance project plan (QAPP), a field sampling plan (FSP), and an associated health and safety plan (HSP). The QAPP describes the policy, organization, functional activities, quality assurance and quality control protocols necessary to achieve project data quality objectives (DQOs) dictated by the intended use of the data, while the FSP provides guidance for all fieldwork by defining in detail the sampling and data gathering methods to be used on the project. This document includes the essential elements of both an FSP and a QAPP. This document describes the sampling and analysis that will be conducted in November 2009 to assess quality conditions in the Transition Zones in Tri-State. More specifically, this document includes:

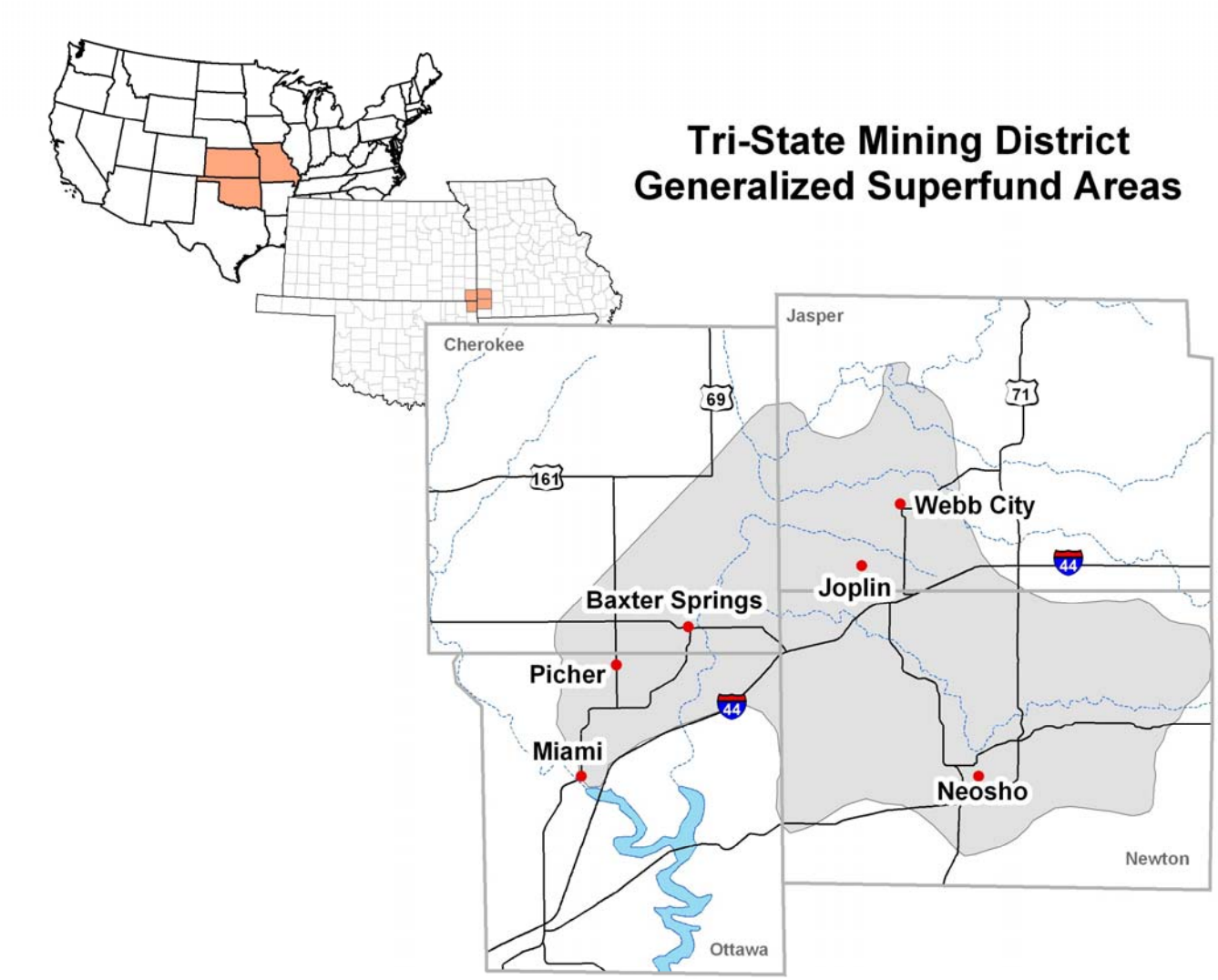
- Introduction (Section 1);
- Sampling objectives (Section 2);
- Sampling program design (Section 3);
- Sampling locations and frequency (Section 4);
- Sampling timing (Section 5);
- Sample designation (Section 6);
- Sampling equipment and procedures (Section 7);
- Sample handling and analysis (Section 8)
- Chemicals of potential concern (Section 9);
- Roles and responsibilities of the sampling team (Section 10);
- Quality assurance (Section 11);
- Examples of forms and instructions for filling out that paperwork (Section 12);
- References cited (Section 13).

2.0 Sampling Objectives

The 2009 Tri-State Transition Zone Study is intended to provide the information needed to determine the extent of soil degradation from historic mining operations in the Tri-State Mining District (see figure 1). More specifically, the objectives of the sampling program are to:

> 1) Obtain real-time data on the concentrations of target metals in 250 soil samples collected from Cherokee, KS; Jasper/Newton, MO and Ottawa, OK counties in areas of potential deposition of heavy metal from historic mining operations (i.e., analysis of dried samples using a portable X-ray fluorescence (XRF) for metals as described in EPA Method 6200.)

Figure 1 – Tri-State Mining District



2) Confirm the results of XRF-based metal analyses of samples through analysis of a sub-set of the collected samples for target metals. Samples will be sieved to <250 microns, digested following EPA Method 3052, and analyzed by Inductively Coupled Plasma/Atomic Emission Spectrometry (ICP-AES, EPA Method 6010B).

3.0 Sampling Program Design

Soil sampling will take place in November and December 2009 over the course of two to three weeks. Three sampling teams of two to three people will collect approximately 250 samples. Each sample will be analyzed using XRF technology, as indicated in Section 7.0. A subset of samples will be corroborated through laboratory analysis. In situ field screening will also be performed by XRF in order to determine when background concentrations are achieved in the field and to provide real time data.

4.0 Sampling Locations and Frequency

The sampling locations for the 2009 Tri-State Transition Zone Study will be selected based on the following parameters:

- Surrounding land use (i.e. agriculture, prairie, wooded, roads etc)
- Height of chat pile (i.e. chat base vs. standing chat)
- Remediation status of the chat pile
- Proximity of other chat piles/bases
- Previously sampled chat piles for comparison
- Chat pile ownership

Landowners will be contacted for permission to sample on sites that best meet the above parameters. When potential sites are identified land owners will be contacted to obtain permission to access their property. Once access is granted the samples will be collected at each of the sampling sites unless it is not possible to access the site due to unsafe conditions.

If it is not possible to sample a site, then the samples may be collected at an alternate site (alternate sites will be located prior to sampling). The coordinates of the alternate sampling station should be recorded once an acceptable sample has been collected. If an acceptable sample cannot be collected at the adjusted sampling location, the station should be abandoned and no sample will be collected at the station.

5.0 Sampling Timing

The soil sampling to support the 2009 Tri-State Transition Zone Study will be conducted in late November to early December 2009. Approximately 250 Transition Zone soil samples will be collected. Soil metal concentrations from historic mining are stable relative to time frames measured in months. Time considerations at this scale should not have a significant affect on results. One exception could be in the case of anthropogenic land disturbance, which is taken into account as described in section 4.0 above.

6.0 Sample Designation and Procedures

6.1 Sample Collection Procedures

The sample locations (i.e. chat piles/bases) will be identified prior to sampling using the parameters in Section 4. At each sample location the sampling will occur in transects away from the chat pile/base. An attempt will be made to sample in four opposing directions (i.e. north, south, east, west, or northeast, southwest, northwest, southeast). If it not possible to sample in all four directions a minimum of sampling in two directions is acceptable A map of current and historic chat piles/base will be used to indicate where to begin each transect.

Samples will be taken at 50 foot intervals away from the chat pile/base until two consecutive samples are at or below background concentrations (Tidball 1984, Dames & Moore, 1995). A portable XRF unit will be used during sampling to determine when background concentrations have been reached unless samplers encounter a stream, chat pile or other barrier that would preclude sampling. In situ XRF meter analyses will be conducted just below the vegetated zone and/or duff layer.

At each sampling location all plant material and organic detritus will be removed from the surface, the sampler (e.g. sharp shooter, shovel, and trowel) will be used to gather the sample from a depth of 1-6 inches. A description of whether the soil is native or vegetated chat or tailings will be made in the log book.

The material will be placed into a 1 liter zip lock bag and labeled appropriately. A split sample will be collected at a subset of samples for quality assurance and confirmatory laboratory analysis, requiring two bags. One sub-sample will be transported to an off-site location where it will be homogenized, dried to consistent moisture content as determined by weight taken before and after drying, and analyzed with the XRF to determine metal concentrations. The other sub-sample will be sent to a qualified lab for analysis by EPA Method 3052 to confirm the results of the field chemistry results.

At each sampling station along a transect, the sampler will be cleaned by removing any excess soil, then it will be inserted into the soil near the sample location. Between each transect, the sampler will be rinsed with deionized water, then with Alconox, and finally with deionized water then placed in a stainless steel tray for transport between transects.. Alternatively, a pre-cleaned dedicated sampling spoon or scoop will be used at each sampling location.

Table 1 lists the equipment that will be used to collect samples for the 2009 Transition Zone sampling program (see Appendix A). The following information should be recorded following retrieval of the sample:

- Unusual events that occurred during sampling ;
- Sample depth;
- Description of sample (i.e. sandy, clay etc);
- Description of sample color (i.e., black, brown, etc.);
- Sample processing procedure used (i.e., total volume collected, type of containers used).

6.2 Precautions to Avoid Exposure to Contaminated soil

It is anticipated that contaminated soil will be routinely encountered during sampling throughout much of the study area. As such, the sampling crew should take precautions to minimize exposure to potentially toxic substances. At a minimum, steps that should be taken include:

- Handling sampling equipment and samples carefully;
- Avoiding direct dermal contact with samples; and,
- Wearing protective equipment, such as gloves, safety glasses, long-sleeved shirts, long pants, rubber boots, and/or rain gear.

More detailed guidance on avoiding hazards during sampling and minimizing the potential for personal injury is provided in the project Health and Safety Plan.

6.3 Other Precautions to Avoid Sample Contamination

Generation of reliable data soil quality conditions is a primary objective of the sampling program. As such, all reasonable efforts should be made to minimize the potential for sample contamination during the sample collection, handling, and processing process. At a minimum, steps that should be taken to avoid sample contamination include:

- Ensuring that samples do not come in contact with any item that has not undergone the approved decontamination process;
- Ensuring that any utensils that are used in the sampling process do not come in contact with any item that has not undergone the approved decontamination process;
- Fully decontaminating all sampling equipment after sampling has been completed; and,
- Prohibiting any activity that could result in sample contamination (e.g., smoking, consumption of food or drinks during the sampling process; Note: there will be a cooler for food and drinks that are to be consumed at appropriate times).

6.4 Information to be collected at Sampling Stations

The following basic information will be collected and recorded at each sampling station:

- Sample station name and number;
- Sampling date and time;
- Latitude and longitude coordinates in WGS84 datum using decimal degrees
- Weather conditions, including precipitation, temperature etc.;
- Type of sampler used;
- Names of sampling personnel
- Soil type/ soil genesis (i.e. native soil or formed over mine waste)
- In-situ XRF results for Pb, Zn, and Cd.

7.0 Sample Handling and Preparation

Procedures for handling and preparing samples for metal analysis should follow the procedures described in ASTM (2004; also Appendix A -Tablele 2). Samples should be carefully packed and transferred to the appropriate laboratory for storage along with the appropriate chain of custody forms. If samples are shipped, an inventory must be maintained of all samples that are shipped each day to facilitate confirmation of receipt the following business day.

8.0 Chemicals of Potential Concern

Previous studies in the TSMD have identified cadmium, lead,, and zinc as the primary constituents that are elevated due to mining activity (Dames & Moore, 1995). The adverse biological effects of these metals are well documented (Eisler 2004). In order to identify potential injury from mining activity, samples will be analyzed for these target metals. The list of priority analytes and associated data quality objectives for the chemical analyses are presented in Appendix A - Table 3.

9.0 Roles and Responsibilities of Sampling Team

Samples to support the Transition Zone Study will be systematically collected within the sampling area. The sampling teams will each include two to three who will be responsible for collecting and preparing samples, conducting on-site analyses of samples, and preparing and shipping samples for lab analysis. Quality assurance and control (QA/QC) for the field portion of this investigation will be directed by Suzanne Dudding, John Miesner and Dave Mosby of the U.S. Fish and Wildlife Service.

The sample collection crew will be responsible for ensuring that all necessary sampling equipment and associated supplies are loaded onto the sampling vehicle(s) each day, verifying the locations of the stations that are sampled (using handheld GPS), collecting sufficient volumes of sample to support analyses of soil chemistry, preparing and labeling samples, decontaminating the samplers between sites, and following the completion of sampling activities at each station. It is anticipated that one person will run the XRF unit, a second person will collect the sample and decontaminate the sampler and the third person will take GPS readings and collect field notes.

Samples should be transported in a secure manner to avoid damage to the sample. Any sub-samples that are lost or damaged during transport must be identified by sampling station and recorded. If a commercial shipping service is used, sub-samples may be shipped on Monday, Tuesday, Wednesday, Thursday, and Sunday only (to avoid weekend delivery to laboratories). Any sub-samples that are not shipped on the date of collection must be held and shipped on the next appropriate shipping day. Unused portions of samples should be disposed of at the station that the samples were collected.

Sample collection and disposition will be clearly documented. At each sampling station, the data collection form will be filled out (see example in Addendum 1A). Samples will then be stored in appropriate containers. Samples transported to a laboratory will be packaged with a chain of custody (COC) manifest will be prepared (see example in Addendum 2B). A copy of the COC will be maintained with the sample records, and the initial disposition will be noted on the data

collection form. The laboratory will also return a copy of the updated COC to the sender upon receipt and acceptance.

10.0 Quality Assurance

Generation of good quality chemistry data is essential for supporting the 2009 Tri-State Transition Zone Study. To avoid problems associated with data reliability, it is necessary to implement adequate quality assurance measures in the sampling program, during data collection and analysis. In this study, the quality of data analyzed by portable XRF will be evaluated by conducting laboratory analysis of a sub-set of the field-collected samples. Samples for XRF analysis will be dried to a constant weight at the FWS field office in Tulsa, OK. The samples will be sieved to <250 microns and analyzed at the FWS field office in Columbia, Missouri. XRF analysis of all samples will be performed using EPA Method 6200 by FWS personnel, after completion of the field collection. FWS personnel in the Missouri office will direct quality assurance and control during XRF analysis.

Split samples, discussed in section 6.1 above, will be collected by placing alternating spoonfuls of soil into different bags, or placing half of each scoop into each bag. Split samples will be collected at a frequency of 10% of all samples. And a minimum of one split sample will be collected per day of sampling.

The samples that are selected for confirmatory chemical analysis will be sent to the laboratory for confirmatory and sieved to <250 microns. Analysis of metal content will be performed on the finer, sieved samples. Sieved samples will then be digested using EPA Method 3052 (Microwave assisted acid digestion of siliceous and organically based matrices) and analyzed by ICP-AES using EPA Method 6010B. Standard methods for XRF and laboratory analysis are appended to this document.

11.0 Examples of Forms for Sampling Program

Examples of forms that will be used in the sample program are presented as addenda, including the data collection form (Addendum 1A) and chain of custody form (Addendum 1B).

12.0 References

ASTM (American Society for Testing and Materials). 2004. Standard guide for collection, storage, characterization, and manipulation of s for toxicological testing and for selection of samplers used to collect benthic invertebrates. E1391-03. ASTM 2004 Annual Book of Standards Volume 11.05. West Conshohocken, Pennsylvania.

Dames & Moore, 1995, Final Remedial Investigation: Neck/Alba, Snap, Oronogo/Duenweg, Joplin, Thoms, Carl Junction, and Waco Designated Areas, Jasper County Site, Jasper County, Missouri.

Eisler, R. 2000. Handbook of chemical risk assessment Health hazards to humans, plants, and animals. Volume 1.

EPA. 1996 Standard Method 3052: Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices.

EPA. 1996 Standard Method 6010B: Inductively Coupled Plasma-Atomic Emissions Spectrometry

EPA. 1998 Standard Method 6200: Field Portable X-Ray Fluorescence Spectrometry for the Determination of the Elemental Concentrations in soil and Sediment. 31pp

Tidball, R.R., 1984. Geochemical Survey of Missouri, U.S. Geol. Survey Professional Paper - .- 954-8.1.

Appendix A -Tables

Table 1. Sampling equipment required to support the Tri-State Study	
Cleaning supplies	
• Alconox solution • Deionized/reverse osmosis water	• Polyethylene squeeze bottles or spray bottles • Long bristle scrub brush
Sampling supplies	
• Maps of the study area • Zip Lock bags - Liter • Sharp shooter • Stainless steel trowel • Sample collection forms	• Latex gloves - non-powdered • Stainless steel spoons • Stainless steel homogenization buckets - 2 x 1 L; 2 x 5 L • Sharpie pens
Measurement supplies	
• GPS (handheld)	
Shipping and storage supplies	
• 48-L plastic coolers • FedEx labels for shipments - as needed • Paper towels	• Shipping manifests - as needed • Electrical tape
Personal supplies	
• Gloves • Rubber boots • Cooler for onsite food and beverage consumption • Tick spray and poison ivy lotion	• Long pants • Rain/ foul-weather gear
Miscellaneous supplies	
• Forms for data collection on samples • Sample book (write in rain)	• Digital camera with accessories (spare batteries; extra memory chips)

Table 2. Volume, container material, preservation specifications, and holding times for samples collected for Tri-State study.

Parameter Analyzed	Laboratory[1]	Approximate Volume	Container Material	Preservation Method	Holding Time
Metals (by XRF)	FWS facility	125 mL	Zip Lock bag	room temp	28-d
Metals (by EPA Method 6010B)	TBD	125 mL	Zip Lock bag	room temp	28-d

d = day; XRF = X-Ray fluorescence;

Table 3. Chemicals of potential concern and associated data quality objectives for the Tri-State Study (applies to confirmatory chemistry by Method 6010B only.)

Chemical of Potential Concern	Target Detection Limit (as µ/L in disgestate)	Target Mean Accuracy (Average % Recovery)	Target Precision (Relative Standard Deviation %)	Target Completeness
Metals (mg/kg)				
Cadmium	2.3	75-125	20	100%
Lead	28	75-125	20	100%
Zinc	1.2	75-125	20	100%