Work Plan to Assist the U.S. Fish and Wildlife Service in identification of the depth of mine tailings contamination of streambed sediments in the Viburnum Trend mining district of southeastern Missouri, USA.

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Southeast Missouri Lead Mining District Natural Resource Damage Assessment and Restoration

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Introduction

The Viburnum Trend (VT) in southeast Missouri, USA is mined for lead-zinc sulfides containing the major and minor metal constituents of Lead (Pb), Zinc (Zn), Nickel (Ni), Cobalt (Co), Cadmium (Cd), Arsenic (As) and Copper (Cu). The average depth to the ore is about 1,200 feet (ft) and the deposits average about 30 to 85 thick and 200 to 2,000 ft wide (Seeger, 2008). Background concentrations of ore-related metals are relatively small (Lee, 2008). The waste material produced from the mining is stored behind impoundments in headwater valleys area streams and thus maybe transported downstream into larger streams and rivers. Three recent sampling efforts by the U.S. Geological Survey indicate that that ore-related metals are significantly enriched in surficial streambed-sediments downstream from mine-waste impoundments (Brumbaugh et al., 2007; Femmer, 2008; Lee, 2008). The degree of this enrichment depends both on the metal considered and the distance downstream from mining activities. The studies reached similar conclusions using slightly different methods for collection and analysis of streambed sediment. Femmer (2008) and Lee (2008) reported metals concentrations in the less than 0.063 millimeter (mm) size-fraction of streambed sediments. Brumbaugh et al. (2007) reported metals concentrations in the fine fraction of sediment that was collected by pumping sediments from the streambed using a diaphragm pump with a suction hose covered with a 2 mm pore- size screen. The slurry pumped from the streambed was transferred to polyethylene tanks where the sediment was allowed to settle for 30 minutes before the overlying water was decanted using a drain valve. The Brumbaugh et al. method (2007) included sediments between 0.063 mm and 2 mm whereas Femmer (2008) and Lee (2008) did not. However, sediments analyzed by Brumbaugh et al. (2007) may have slightly smaller amounts of very fine sediments that would not have settled within the 30- minute period. To assess the toxicity of sediments to aquatic life, metals concentrations are typically compared to the Probable Effects Concentration or PEC (MacDonald et al, 2000). Metals concentrations typically increase with decreasing grain-size of the sediment. Depending on the metal contents in various size fractions of the sediment, comparing only data from the <0.063 mm size fraction to the PEC could result in misidentification of some sediment as contaminated above the PEC because the PEC is based on fine sediment, but not exclusive to sediments less than 0.063 mm.

Lee (2008) indicated that near-mining stream sites (within 7.5 miles of mining activity) are enriched significantly in Co, Pb, Ni, and Zn. Statistical analysis indicated the distribution of Ni and Zn in non-mining and distal-mining sites were similar, but these metals are significantly enriched in near-mining sites (Lee, 2008). This indicates concentrations of these metals in streambed sediment at sites within 7.5 miles of mining activity are elevated, but return to baseline-like conditions at distal-mining sites (distances of 7.5 miles or more downstream from mining activity). However, cobalt and lead concentrations did not decrease to the lower non-mining concentrations at the distal-mining sites, but remained slightly elevated. In the Lee (2008) and Femmer (2008) studies, metal concentrations in the <0.63 mm size-fraction were compared to the PEC and 11 of the more than 25 sites sampled had Pb concentrations exceeding the PEC (Lee, 2008).

While the general extent of mine contaminated surficial sediments in the Viburnum Trend is known, the depth of contamination and volume of contaminated sediments is not known. Evaluation of potential restoration options requires estimates of the depth that contamination might extend; identification stream features where fine contaminated sediments accumulate, and

the volume of contaminated sediments. In addition, there is some uncertainty about the comparability of metal concentrations in the <0.063 mm size-fraction reported in most previous studies to more recent data collected by the Missouri Department of Natural Resources that used the <2 mm and <0.250 mm size-fraction. The US Fish and Wildlife Service (USFWS) is beginning a study with Missouri State University (MSU) to estimate the amount of mining contaminated sediment on floodplains within the VT and estimate the volume of contaminated sediments within the stream channels. MSU investigators are adapt at geomorphic analysis and using X-ray fluorescence spectrometer (XRF) identify screen for metals in the <2 mm size-fraction. However, MSU has limited capability to evaluate the depth of contaminated sediments beneath the water table or determine metals contents in various size-fractions of sediments.

Objective:

1- Determine if significant difference exist between mining-related metal concentrations in the <0.063 mm size fraction compared to the <0.250 mm and <2mm size-fraction at selected sites previously sampled by the US Geological Survey (USGS).

2- Assist the USFWS and MSU in evaluating the depth of mining-related metal contamination in larger gravel bar deposits downstream from mine waste impoundments in the VT by determining vertical profiles of metals and the fraction of fine-grain sediments (<2mm) within the specific gravel bars evaluated.

3- Provide analytical services as a quality assurance (QA) validation of the MSU study by analyzing duplicate field and laboratory samples collected and processed by MSU to independently determine grain-size and metals concentrations in various size fractions.

Approach:

The overall project will be to collect data that will complement the VT-wide geomorphic screening being conducted by the USFWS and MSU. Three tasks have been identified for the USGS part of the project and are described below.

<u>Task 1 - Characterization of near surface streambed material samples at selected existing UGSS sample sites</u>

Near surface (less than 5-inches) samples will be collected from a subset of sites previously sampled by the USGS (Lee, 2008; Femmer 2008). Samples will be target to depositional areas of finer-grained sediments (as was done in previous USGS studies). These near surface samples will be collected with a non-metallic or stainless steel hand sampler from 20 sub-sample sites at each location and composited into a single sample for sieving and analysis. The composite samples will be taken to the USGS Laboratory in Rolla, Missouri where they will be dried and processed for analysis. Processing will involve an initial sieving each sample through a 25.0 mm then a 2.0 mm sieve (Figure 2). The total weight of sample greater than 25 mm and greater than 2.0 mm will be measured in addition to the weight of material passing the 2.0 mm sieve. The <2mm fraction of the sample will be split into two subsamples (A and B) using a stainless steel sediment splitter (Gilson model SP-171X precision splitter). Subsample A will be weighed, homogenized and 2-3 g (grams) removed for chemical analysis of the < 2 mm size fraction. The remaining split A will be sieved through a 0.250 mm sieve and 2-3 g a passing the sieve collected for chemical

analysis of the <0.250 mm size fraction. The remaining material passing the 0.250 mm sieve will be retained for possible recombining with material from split B if insufficient mass of <0.063 mm material is available.

Split B will be weighed then split again into two splits--B1 and B2. Split B2 will be archived. Split B1 will be sieved through a stacked assembly of 0.0250 mm and 0.063 mm stainless steel sieves placed on a mechanical sieve shaker (Gilson model SS-30) and the weights in each fraction (>0.250 mm, 0.250 to 0.063 mm, and < 0.063 mm) recorded. Material passing the 0.063 mm sieve will be collected for chemical analyses.

The grain-size and chemical composition of each sample collected in task 1 will be reported as dry weight percent (grain-size) and chemical composition of the <2mm, <0.250 mm, and <0.063 mm size-fractions. In addition, the weight percent of material > 25 mm and > 2 mm also will be reported. XRF screening will be done using the USFWS Thermo Niton Scientific XL3T portable XRF unit (Billerica, MA) at the Rolla office or by transporting samples in sealed bags under custody seal to the USFWS office in Columbia, Mo.

Sampling, handling, sieving, weighing, etc. will be done according to standard USGS Missouri Water Science Center sediment laboratory procedures. Blank samples of clean silica sand and silica flour will be processed in an identical manner as streambed sediment samples. The silica sand-silica flour samples will be sieved through nylon sieves in nylon or non-metallic sieves or sized material purchased directly from a manufacturer. A subsample from each size fraction will be submitted for metals analysis, then the remaining silica material analyzed for metals in the <2mm, <0.250 mm, and <0.063 mm size fractions after passing through the splitter several times and at least three passes through the stainless steel sieves used for routine sample processing.

Subsamples collected for chemical analysis will first be scanned for metal contents by the USFWS using XRF. After XRF scanning, all samples will be submitted for total digestion and analyses of a suite of XX metal analysis by the USGS Geologic Division laboratory in Denver, Colorado. The sample digestion, analytical method, and list of elements and reporting limits are provided in attachment A1.

<u>Potential stream sites to be sampled in task 1 (site designations from Lee, 2008):</u>

A1 – Middle Fork Black River at Redmondville	B1 – Courtois Creek near Courtois
B2 – Strother Creek near Goodland	B3 – Neals Creek near Goodland
B4 – Strother Creek near Redmondville	B5 – Bills Creek near Redmondville
B6 – West Fork Black River at West Fork	C3 – Middle Fork Black River at Black B8
B8– Logan Creek near Corridon	C4 – Middle Fork Black River near Black
C6 – West Fork Black River near Centerville	C7 – West Fork Black River at Centerville

Task 2 - Stream bar characterization

Vertical profiles of metal and grain size in selected gravel bars. Up to six gravel bars will be evaluated. Bars will be selected in conjunction with USFWS staff after initial reconnaissance of the VT streams by MSU. One or more bars in Strother Creek and the West Fork of the Black River downstream from the Buick and West Fork Mines will be included. Bars in Bee Fork will not be included. The surface area of each bar will be estimated from aerial photographs and by sub-meter global positioning system GPS. The overall volume of the bar will be estimated using a hand level to estimate average height. A level survey may be needed for bars with complex topography. The overall grain-size nature of the bar will be evaluated using the Wolman pebble count method (Bunte and Abt, 2001; Daniels and McCusker, 2010; Kondolf et al., 2003). Depending on the size of the bar, pebble counts will be done along one or two longitudinal sections, and at least three cross sections of the bar with a target goal of 300 to 400 counts per bar.

Vertical profiles of each bar will utilize variety of methods triaged as discussed in the QAPP prepared for assessment of stream sediments in the Tri-State District (Slifer et al. 2010). The depth of the bars will be estimated at six to 15 locations using a tile probe or solid probe to refusal. Subsurface characterization of grain-size and metal contents of each bar will be done by collection of core samples from 3 locations (upstream end of the bar, middle section, and downstream end of the bar). Core samples will be collected such that samples for grain-size and metals can be collected representing the composition for each 1-ft of depth. For larger bars such as exist along the West Fork of the Black River, additional cores may be done to provide additional representativeness of the bar deposit. Samples from the bars will be processed in a similar manner as task 1, expect that metal contents will be determined only in the <2mm fraction and split B will be used entirely for grain-size analyses and archiving after recombining the sieve splits.

Task 3 – Quality assurance of selected MSU samples

The USGS will provide quality assurance (QA) checks of selected MSU samples. Two types of samples are anticipated: field duplicate samples, and laboratory duplicate samples. MSU will collected duplicate samples from 5-10 field sites and provide USGS the raw, unprocessed sample as it were to be received at the MSU laboratory. USGS will process these samples in an identical manner as task 1 samples with grain-sizing, XRF screening of the <2mm, <0.25 mm, and <0.063mm fractions. Inductively coupled plasma – mass spectrometry (ICP-MS) will be run on either the <2mm or <0.25 mm fraction of each of the submitted QA samples.

In addition to submittal of field duplicate samples, MSU will submit 10 laboratory duplicate samples that MSU has processed and sized (either <2mm or <0.25mm fraction). USGS will submit these laboratory duplicate samples for ICP-MS analysis as a QA check on MSU analytical data.

General project QA

Duplicate samples - Complete recollection of samples will be done at three task 1 sites and processed and analyzed as described in task 1. The duplicate samples will provide an estimate of the variability in collecting multiple samples from the same location.

Equipment blanks – Before processing samples, an equipment blank consisting of a mixture of clean silica sand and silica flour will be analyzed for metals before and after passing at least twice through the Rolla laboratory sample splitters and sieves.

Method blank – To verify proper decontamination between sediment samples, three blank samples of silica sand/flour mixture will be processed after every 20 to 25 environmental samples.

Laboratory duplicates- Duplicate samples will be submitted for ICP analysis at a rate of 1 duplicate per 20 samples.

Summary of Sample Analyses:

Near-surface composite samples from the 12 sites will be analyzed for the following:

- Grain size (>25mm, >2,mm, 0.25-2mm, 0.063-0.25 mm, <0.063mm fraction)
- XRF (USFWS) screening of all samples (<2mm, <0.25 mm, <0.063 mm fraction)
- ICP-MS metals (<63um fraction, <250 um fraction, < 2mm fraction; 36 total samples)

Sediment Core samples

- Composite samples over each 1-ft depth increment (3-6 cores per bar, est. max 6 ft deep)
- Grain Size ((>25mm, >2,mm, 0.25-2mm, 0.063-0.25 mm, <0.063mm fraction) XRF (USFWS) screening of all samples (<2 mm fraction)
- ICP-MS metals in < 2 mm fraction (1-2 samples per borehole, est. 36 total samples)

MSU split samples

Field split (5-10 samples)

- Grain-size size (>25mm, >2,mm, 0.25-2mm, 0.063-0.25 mm, <0.063mm fraction)
- ICP-MS (<2mm fraction)

Laboratory split (10-12 total samples)

- ICP-MS (<2mm fraction or <0.250 fraction)

Deliverable:

Data will be summarized and interpreted in an Administrative Letter Report to the USFWS by May, 2013. Subsequent USGS publication with additional FY2013-14 funds to cover publication costs.

Figure 1. Estimated Costs (do not include indirect charges):

Items	Task 1	Task 2	Task 3	Admin	Totals
Salaries	$8,700	$14,300		$13,700	$36,700
Travel/vehicles	$1,500	$3,500		0	$5,000
Supplies/equipment/shipping	$4,600	$1,500	$500	0	$6,600
Lab/analytical support	$8,325	$12,570	$4,200	0	$25,095
Total Net Cost	$23,125	$31,870	$4,700	$13,700	$73,395
Allowable Indirect (7 %)					$5,138
Total Cost					$78,533

Timeline:

Samples will be collected within 6 months of an approved agreement. Lab analyses and administrative letter will be completed within 13 months of the signed agreement.

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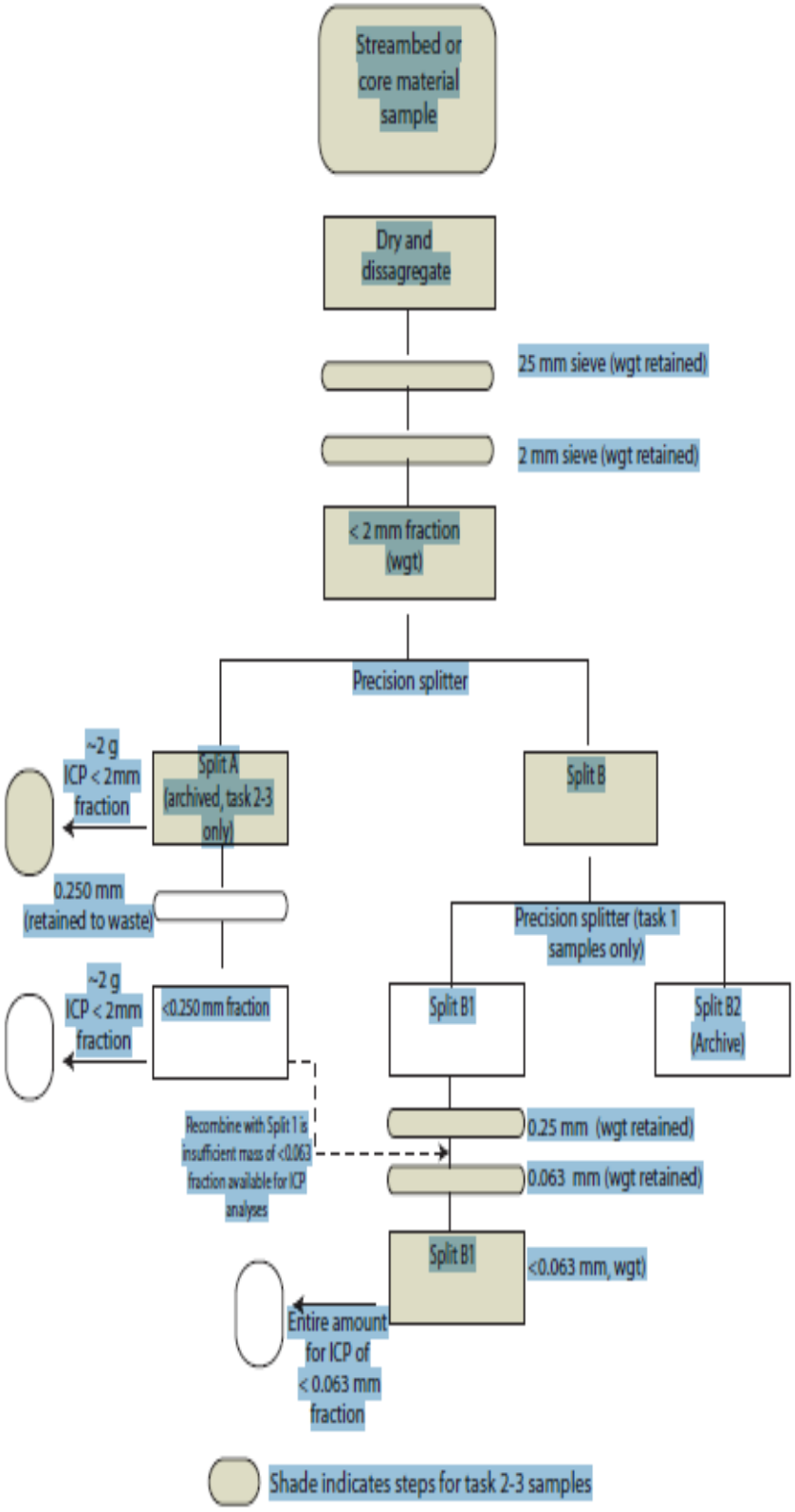

Figure 2. Generalized process for handling streambed and core material samples

ATTACHMENT A1

Method 22 - 55 Element ICP-AES-MS sodium peroxide sinter

Summary:

Fifty-five major (except Si and Na), rare earth and trace elements are determined in geological materials by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). The sample is decomposed using a sodium peroxide sinter at 450oC. The resultant cake is leached with water and acidified with nitric acid. After an addition of tartaric acid, aliquots of the digested sample is aspirated into the ICP-AES and the ICP-MS. The concentrations of the optimal elements from the ICPAES and ICPMS are determined. Calibration on the ICPAES is performed by standardizing with digested rock reference materials and a series of multi-element solution standards. The ICPMS is calibrated with aqueous standards, and internal standards are used to compensate for matrix affects and internal drifts.

Sample weight: 0.10 g

Reporting limits for 55 elements by ICP-AES-MS:

Element	Concentration Range	
Aluminum, Al	0.01%	25%
Antimony, Sb	0.1 ppm	500 ppm
Arsenic, As	30 ppm	10%
Barium, Ba	0.5 ppm	1%
Beryllium, Be	5 ppm	0.25%
Bismuth, Bi	0.1 ppm	0.1%
Cadmium, Cd	0.2 ppm	1%
Calcium, Ca	0.01%	40%
Cerium, Ce	0.1 ppm	1%
Cesium, Cs	0.1 ppm	1%
Chromium, Cr	10 ppm	10%
Cobalt, Co	0.5 ppm	1%
Copper, Cu	5 ppm	5%
Dysprosium, Dy	0.05 ppm	0.1%
Erbium, Er	0.05 ppm	0.1%
Europium, Eu	0.05 ppm	0.1%
Gadolinium, Gd	0.05 ppm	0.1%
Gallium, Ga	1 ppm	0.1%
Germanium, Ge	1 ppm	0.1%
Hafnium, Hf	1 ppm	1%

Holium, Ho	0.05 ppm	0.1 %
Indium, In	0.2 ppm	0.1%
Iron, Fe	0.01%	50%
Lanthanum, La	0.1 ppm	1%
Lead, Pb	5 ppm	5%
Lithium, Li	10 ppm	5%
Lutetium, Lu	0.05 ppm	0.1%
Magnesium, Mg	0.01%	30%
Manganese, Mn	10 ppm	10%
Molybdenum, Mo	2 ppm	1%
Neodymium, Nd	0.1 ppm	1 %
Nickel, Ni	5 ppm	1%
Niobium, Nb	1 ppm	1%
Phosphorous, P	0.01%	1%
Potassium, K	0.01%	25%
Praesodynium, Pr	0.05 ppm	0.1 %
Rubidium, Rb	0.2 ppm	1%
Samarium, Sm	0.1 ppm	0.1%
Scandium, Sc	5 ppm	5%
Silver, Ag	1 ppm	1%
Strontium, Sr	0.1 ppm	1%
Tantalum, Ta	0.5 ppm	1 %
Thallium, Tl	0.5 ppm	0.1%
Thorium, Th	0.1 ppm	0.1%
Thulium, Tm	0.05 ppm	0.1%
Tin, Sn	1 ppm	1%
Titanium, Ti	0.01%	25%
Tungsten, W	1 ppm	1%
Terbium, Tb	0.05 ppm	0.1 %
Uranium, U	0.05 ppm	0.1%
Vanadium, V	5 ppm	1%
Ytterbium, Yb	0.1 ppm	0.1 %
Yttrium, Y	0.5 ppm	1%

Zinc, Zn	5 ppm	5%
Zirconium. Zr	0.5 ppm	1%

Analytical Performance

Data is deemed acceptable if recovery for all 55 elements is ±15% at five times the Lower Limit of Determination (LOD) and the calculated Relative Standard Deviation (RSD) of duplicate samples is no greater than 15%.