Natural Resource Damages Sampling and Analysis Plan

Sediment and Surface Water Sampling of the Viburnum Trend Lead Mining Sites in Iron, Crawford, Washington, Reynolds, Shannon and Dent Counties, Missouri

Prepared For:
Missouri Department of Natural Resources
Division of Environmental Quality
Hazardous Waste Program

Prepared By:
Missouri Department of Natural Resources
Division of Environmental Quality
Environmental Services Program
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1.0 Introduction

Pursuant to the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Superfund Amendments and Reauthorization Act of 1986, the Missouri Department of Natural Resources (MDNR), Hazardous Waste Program (HWP), Natural Resource Damages (NRD) program is conducting an NRD site assessment on selected streams located in and around the Viburnum Trend Lead Mining Sites (VTLMS). The streams selected for this study are potentially impacted by hazardous substances releases from the VTLMS. Furthermore, limited or no sediment and surface water sampling data exist for these streams at the present time. This assessment does not seek to address all streams potentially impacted by the VTLMS; it intentionally excludes streams (as a matter of prioritization) that were previously sampled as part of other sampling events.

The NRD program requested that the MDNR, Environmental Services Program (ESP) prepare and implement a sampling plan for the selected VTLMS streams. The scope of the assessment includes collecting sediment and surface water samples at selected sites and analyzing them for a suite of mining-derived metals. This assessment is intended to provide stream-specific information about the presence and concentration of hazardous substances in the selected VTLMS streams.

2.0 Site Information

2.1 Description

The VTLMS are in six counties and comprise a mixture of properties owned by mining companies, the U.S. Forest Service (USFS) and private landowners. Approximately 45 miles of streams are included in this assessment and are typical of the stream types found in the area. They are primarily medium to fast running streams that vary greatly in volume depending upon the amount of rainfall occurring in the area. Sediment is primarily comprised of cobble, gravel, and sand with a small amount of fines (silt- and clay-sized particles) in slower depositional areas.

2.2 History

The VTLMS contain historic lead, zinc and barite mine locations listed in the Missouri Inventory of Mines, Occurrences and Prospects (IMOP) database. Both surface and underground mining occurred throughout the area historically within the State of Missouri. Mining is still occurring in the Viburnum Trend.

2.3 Contaminants of concern

The contaminants of concern that are associated with the mining activities at these sites are arsenic, copper, cadmium, lead, nickel and zinc.
3.0 Site Reconnaissance

Site reconnaissance was conducted by ESP and HWP personnel at some of the VTLMS. Personnel from the ESP and HWP arrived at the VTLMS on May 24, 2011 and met with personnel from The Doe Run Company. The DNR and Doe Run personnel traveled along the area roads and consulted maps to determine access points to each of the creeks selected for this assessment. Access points included areas where the creeks passed under bridges or where the creek was close enough to a road for sample equipment and personnel to be transported to the creek. A total of 36 access locations were found, with the breakdown per creek as follows: Bill’s Creek - 6, Sweetwater Creek - 3, Neal’s Creek -10, Left Fork Neal’s Creek - 3, Crooked Creek - 5, Mill Rock Creek - 1, and Indian Creek - 6. In addition to locating sampling access points, the team also collected sediment samples at five locations in order to help establish the sampling protocol and quality control measures.

4.0 Field Sampling

Non-random sampling will be conducted to determine whether hazardous substances releases have occurred, and the types and concentrations of hazardous substances present. This plan directs field personnel to collect sediment and surface water samples.

4.1 Sampling location

The VTLMS are located along several stretches of streams primarily in Iron County near the town of Viburnum. These streams include Neals Creek, Left Fork of Neals Creek, Crooked Creek (with a small portion located in Dent County), Indian Creek (with a small portion located in Washington County), Mill Rock Creek (primarily in Crawford County, with a small portion in Iron County), Bills Creek (primarily in Reynolds County, with a small portion in Iron County), and Sweetwater Creek (primarily in Reynolds County with a small portion in Shannon County). Refer to Appendix B (site map) for the locations of the streams that will be sampled (subject to change based on field conditions and observations).

Appropriate reference samples will be collected from locations determined to be unaffected by any previous site activities of the media collected. Reference sample locations will be collected from three streams; Bee Fork (above Fletcher Mine) in Reynolds County, Tom’s Creek (a tributary to West Fork Creek) in Reynolds County and Middle Fork of the Black River (above Strother Creek) in Iron County.

All sampling locations will be recorded on a site map; the corresponding global positioning system (GPS) coordinates will be recorded.

4.2 Record of sampling

Field personnel shall note all observations, sample locations, descriptions, and methods in a bound field logbook.
4.3 Sampling methods

All aspects of sampling shall be performed using standard operating procedures (SOPs) established within the ESP, Environmental Emergency Response/Field Services Section (EER/FSS) for the collection, preservation, and transport of various media sampled. Modifications to the following sampling methods may be made in the field based upon conditions encountered. Any modifications to the methods will be noted in the field logbook and the final sampling report submitted to the NRD program.

4.4 Sampling order

Wherever sediment and surface water samples are collected, personnel will collect surface water grabs prior to the corresponding sediment grabs to minimize sediment disturbance.

4.5 Surface water sampling

Field instruments to be used during water sample collection, including pH, specific conductivity, Oxidation-Reduction Potential (ORP), and temperature meters, will be calibrated daily on-site per manufacturers’ specifications.

Surface water grab samples (500 ml) will be collected by immersing the sample containers into the stream water. The sample containers will be rinsed with a small volume of site (stream) water before collection of the grab sample. When entering the stream, personnel will approach the water sampling location from downstream so as not to increase turbidity in the water sample during collection. A portion of the collected sample (about 250 ml) will be reserved for analyses of total metals. The remainder of the sample (about 250 ml) will be filtered back at the sampling vehicle and preserved for dissolved metal analysis. This portion of the sample (about 250 ml) will be passed through a 0.45 micron filter via the use of a peristaltic pump to remove additional suspended particulates from the sample. All pump tubing and filter devices will be dedicated, single-use equipment to eliminate cross-contamination.

Nitric acid will be used in the field to chemically preserve the water samples collected for both total and dissolved metals. The container for total metals will be acidified immediately upon collection, while the container for dissolved metals will be acidified after filtration. Water samples will also be preserved in the field by putting the containers in a cooler on ice after collection.

4.6 Sediment sampling

Sediment samples will be collected at the same general locations as surface waters. All sampling locations will be assessed prior to stream entry to determine if sufficient sediment sample can be safely collected. Sediment composite samples will be collected at locations of apparent sediment deposition in pools and backwater areas along the stream within a 100 m² area, centered generally around the point where the surface water sample was collected. Sediment will be
collected from within the 100 m² area using a 3-inch diameter by 24-inch length polyvinyl chloride (PVC) scoop sampler constructed by USGS staff (see Appendix A). Three to five scoops will be collected of the shallow stream sediment to a depth of 8 cm with an attempt to minimize the loss of finer-grained particles. The scoops of sediment will be poured into a sieve bucket equipped with a US #10 (2 mm) stainless steel screen at the bottom, with the finer-grained sediment captured in a clean five-gallon bucket placed directly below the sieve bucket. The sediment in the five-gallon bucket will be homogenized with a large Teflon spoon. Because each sediment sample will be split between MDNR personnel and mining company representatives (i.e. replicate split samples), the sieved sediment in the five-gallon bucket will then be poured into two pans joined side-by-side, making an effort to equally divide both the water and the sediment between the two pans. Each pan of sediment and water will then be placed in another clean bucket and covered with a secure lid. One bucket containing a replicate split will remain in the possession of MDNR personnel, while another bucket containing the other replicate split will be given to the mining company representatives. The MDNR sample bucket of collected sediment will be labeled with a unique sample number and returned to the ESP laboratory for further post processing.

4.7 Sample quantity
A total of 36 access locations were identified during the May 24, 2011 reconnaissance event. At a minimum, samples will be collected at the access points (immediately upstream of any stream modifications, e.g., bridge or road crossing); at a location a half mile upstream from the access location; and a half mile downstream from the access location, for a total of 108 samples. Additional access locations may be added to the sampling, once property access has been provided by property owners.

4.8 Decontamination
Clean or field decontaminated equipment will be utilized for each separate sample collected to minimize the possibility of cross-contamination. Clean disposable nitrile gloves will be worn by sampling personnel for each sample collected. All reusable sampling equipment (e.g., sieve buckets, scoops) will be thoroughly rinsed with stream water at the sampling location. Decontaminated equipment will be allowed to air dry until used again.
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4.9 Sample container and preservation requirements
Refer to the following tables for container and preservation requirements on all samples.

### Water Samples

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Container(s)/Volume</th>
<th>Preservative(s)</th>
<th>Holding Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Metals</td>
<td>1 / 250-ml nalgene bottle</td>
<td>HNO₃ to pH&lt;2, Cool</td>
<td>6 months</td>
</tr>
<tr>
<td>Hardness (Ca and Mg)</td>
<td>1 / 250-ml nalgene bottle</td>
<td>HNO₃ to pH&lt;2, Cool</td>
<td>6 months</td>
</tr>
<tr>
<td>Dissolved Metals</td>
<td>1 / 250-ml nalgene bottle</td>
<td>Filter (0.45 µm), HNO₃ to pH&lt;2, Cool</td>
<td>6 months</td>
</tr>
</tbody>
</table>

Note: total metals and hardness will be combined into one sample container

### Sediment Samples

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Container(s)/Volume</th>
<th>Preservative(s)</th>
<th>Holding Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Metals</td>
<td>1 / 8-oz glass jar</td>
<td>None</td>
<td>6 months</td>
</tr>
</tbody>
</table>

* Sediment samples will initially be collected in five-gallon buckets with lids and returned to the ESP laboratory for drying, sieving and XRF analysis. Any samples turned in to the laboratory for lab analysis of metals will be transferred to 8 ounce glass jars.

4.10 Chain-of-custody
All submitted samples will receive a numbered label and the corresponding number entered onto a chain-of-custody form indicating the description, location, date and time of collection, and analytes requested. Water samples will be stored and transported on ice in coolers. Sediment samples will remain in 5-gallon buckets until post processing. The ESP field personnel will maintain custody of the samples until relinquishing them to a sample custodian at the State’s environmental laboratory within the Environmental Services Program in Jefferson City for the analyses.

5.0 Laboratory Sampling
After sample preparation, sediment samples will be screened with an X-ray Fluorescence (XRF) analyzer, with a portion later submitted to the ESP laboratory for confirmatory analyses.

5.1 Screening sediment metals by XRF
Sediment samples will be returned to the ESP laboratory and prepped for XRF screening. Excess water will be pumped off the sample via the use of a peristaltic pump and tubing. Water will be pumped off of the sample in a manner that will minimize the removal of fine-grained
particulates. Samples will be spread out in aluminum foil pans and allowed to dry until the sample contains less than twenty percent of the moisture. The percent moisture will be assumed to be less than 20% when all moist areas contained in an individual sample appear dried. Once the samples have dried they will be placed in a plastic bag and analyzed for metal concentrations using an XRF analyzer. Samples will next be sieved using a standard #60 soil sieve (250 μm openings). Sieved sediment will then be placed in a plastic bag and analyzed for metal concentrations using an XRF analyzer.

5.2 Confirmatory analyses
After samples have been sieved and dried (as previously described), 20% of the samples that were analyzed by XRF, will be submitted to the laboratory for confirmatory analysis. Based on the history of the VTLMS, all submitted samples will be analyzed for total metals (arsenic, copper, cadmium, lead, nickel and zinc). Water samples will also be further analyzed for dissolved metals and hardness (calcium and magnesium).

6.0 Data Quality

To help ensure precise, accurate, representative, complete, and comparable data are achieved, all field work and analyses will be conducted in accordance with the Quality Assurance Project Plan (QAPP) for Natural Resources Damages, Revision 3, April 13, 2011. Unless otherwise noted in this sampling plan, ESP field personnel will utilize SOPs established within the ESP for all samples collected.

6.1 Quality Assurance/Quality Control (QA/QC) samples
The ESP has established the following definitions for QA/QC samples routinely included/collected during sampling events.

6.2 Duplicate (co-located) water samples
Duplicate water samples are used primarily to assess the precision associated with sampling methodology and, to a lesser extent, sample heterogeneity and analytical procedures.

ESP personnel routinely collect duplicate water samples at a rate of 10% of the total number of water samples collected or at least one for each day of sampling. Each duplicate sample will be collected at the same location and time as its true sample, using similar equipment and technique. Each duplicate sample will receive a numbered label, be entered onto the chain-of-custody form, and submitted for the same analyses as its companion sample.

6.3 Replicate/Duplicate sediment samples
Replicate (split) samples are used primarily to check instrument precision and accuracy of a laboratory analysis and, to a lesser extent, sample handling procedures. Replicate samples
(sediment) are collected by dividing or splitting one sample that has been mixed or homogenized into two samples for separate analyses. It is anticipated that ESP and mining company representatives will be splitting each stream sediment sample.

ESP personnel routinely collect replicate and duplicate samples at a rate of 10% of the total number of samples collected. For this project, ESP will collect duplicate samples at a rate of 10%. Duplicate sediment samples will be collected in the following manner. The first sample (or true sample) will be collected and split as previously described in Section 4.6. Then a second sample will be collected from the same 100 m² area as the first sample, following the same procedures as described in Section 4.6. In addition to assessing sample homogeneity, precision and accuracy, duplicate samples help assess the representativeness of the sample collection procedures.

A post processed replicate sample will also be collected for those samples sent to the ESP laboratory for confirmatory analysis. This replicate sample will be collected after samples have been dried, sieved, and screened using XRF analysis. From the samples selected for confirmatory analysis 10% will be selected for post processed replication. The selected sample will be split into two separate samples and submitted for laboratory analysis. Each post processed replicate sample shall receive a numbered label, be entered onto the chain-of-custody form, and submitted for the same analyses as its true sample.

7.0 Investigation Derived Wastes (IDW) Plan

Efforts will be made to minimize IDW generation. The IDW may include sediment, aqueous liquids (surface water), decontamination fluids, disposable sampling equipment, and disposable personal protective equipment (PPE).

Field personnel will attempt to return unused sediments to their source immediately after generation or, if warranted, containerize and return to the ESP laboratory for proper disposal. Disposable PPE and disposable sampling equipment will generally be handled as solid waste, containerized, and properly disposed. Wash and rinse waters generated during equipment decontamination will generally be discharged to the ground on-site or, if warranted, containerized and returned to the ESP laboratory for proper disposal.

8.0 Site Safety

A safety briefing will be held on-site prior to initiating field activities and field personnel will be required to read and sign the site-specific health and safety plan. The site safety plan is attached as Appendix C.

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The analytical results of samples collected will be presented, along with methods of collection and observations, in a formal report submitted to the HWP.
Submitted by:  

Kenneth Hannon  
Environmental Specialist  
Field Services Unit  
Environmental Services Program

Date:  

7/20/11

Approved by:  

Frances Klahr  
NRD Coordinator  
Hazardous Waste Program

DH:kh.

c: Frances Klahr, NRD Coordinator, HWP
APPENDIX A
Photographs
Sediment and Surface Water Sampling of the Viburnum Trend Lead Mining Sites in Iron, Crawford, Washington, Reynolds, Shannon and Dent Counties, Missouri
Figure 1- Sample scoop and sieve bucket

Figure 2- Close up of sample scoop
APPENDIX B
Site Map
Sediment and Surface Water Sampling of the Viburnum Trend Lead Mining Sites in Iron, Crawford, Washington, Reynolds, Shannon and Dent Counties, Missouri
APPENDIX C
Health & Safety Plan
Sediment and Surface Water Sampling of the Viburnum Trend Lead Mining Sites in Iron, Crawford, Washington, Reynolds, Shannon and Dent Counties, Missouri
SITE HEALTH AND SAFETY PLAN

1.0 INTRODUCTION
This plan has been prepared for implementation by DNR employees, using operating procedures for which they are specifically trained. Any use of the plan by other agencies, organizations, or private individuals is at their own risk.

2.0 KEY PERSONNEL
MDNR OSC: Kenneth Hannon SAFETY OFFICER: Kenneth Hannon

OTHER MDNR PERSONNEL/TITLE:
Frances Klahr, Natural Resource Damages Coordinator
Amy Wright, Natural Resource Damages Analyst
Meagan Prestegard, Environmental Engineer
Sean Counihan, Environmental Specialist
Ben Frissel, Environmental Specialist

3.0 SITE INFORMATION
Site name Viburnum Trend Lead Mining Sites (VTLMS) County/City: Iron, Crawford, Washington, Reynolds, Dent, Shannon
Sampling date: 8/29/11 Through 9/2/11
Site Description: Historical and current mining activities impacting streams

3.1 Overall Incident Risk/Hazard Analysis
Chemical: Serious Moderate XX Low Unknown
Physical: Serious Moderate XX Low Unknown

3.2 Contaminant(s) of Concern: Lead (Pb), Cadmium (Cd), Copper (Cu), Nickel (Ni), Zinc (Zn), and Arsenic (As).

3.2.1 Physical State: XX Liquid XX Solid Sludge Gas/Vapor
Chemical Characteristics: (check all that apply)
a. _____ carcinogen b. biological c. corrosive d. combustible
e. _____ explosive f. flammable g. volatile XX h. poison
i. _____ radioactive j. reactive k. other:
3.2.2 Physical Hazards: (check all that apply)

a. overhead
b. below grade
c. confined space

* The need for confined space entry by ESP personnel shall be evaluated on a site-by-site basis. A confined space entry permit must be signed by the appropriate Unit or Section Chief prior to ESP employees entering a confined space (29 CFR 1910.146). Confined space entry shall be screened in at least Level B prior to downgrade. **Adequate resources must be available and specific planning and tasks determined before confined space entry is initiated.**

d. noise

e. splash
f. fire/burn
g. puncture

h. heat stress

i. cut

j. slip/trip/fall

k. cold stress

l. electrical

m. mechanical/heavy equipment

n. other: animals, insects, plants.

3.3 Task-Specific Risk Analysis (attach additional sheets as necessary)

<table>
<thead>
<tr>
<th>Task Description</th>
<th>Chemical Hazards</th>
<th>Physical Hazards</th>
<th>Level of Protection</th>
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</thead>
<tbody>
<tr>
<td>Sample Collection</td>
<td>h</td>
<td>e, h, j, n</td>
<td>D</td>
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</tbody>
</table>

4.0 MEDICAL SURVEILLANCE AND PERSONNEL TRAINING REQUIREMENTS

All ESP field personnel participate in a medical monitoring program and are trained at least to the level of "Hazardous Substance Emergency Response-Technician" as required and specified in the department's written health and safety program located in Section 2 of the MDNR-Hazardous Substances Emergency Response Plan (HSERP). The written policy satisfies requirements set out in 29 CFR 1910.120. MDNR ESP's respiratory protection program meets the requirements of 29 CFR 1910.134.

ESP personnel will ascertain as much information as possible regarding health and safety issues associated with the site prior to initial entry. Information shall include chemical and physical hazards as listed above, types and amounts of materials involved, and citizens/areas threatened by the incident.
5.0 PERSONAL PROTECTIVE EQUIPMENT

ESP shall utilize the Protection Level categories defined in 29 CFR 1910.120, Appendix B, and known as Levels A, B, C, and D. Refer to Section 2 of the MDNR-HSERP for definitions of Protection Levels. ESP personnel shall inspect APRs and self contained breathing apparatuses (SCBAs) at least monthly and maintain a record of such to ensure equipment is functional.

Levels of protection shall be reassessed and upgraded as conditions change and information is updated to comply with worker safety while performing site activities.

Action Levels for evacuation of work zone pending reassessment of conditions:
Level D: O₂ < 19.5% or > 25%; explosive atmosphere > 10% LEL; organic vapors > background levels; other________.
Level C: O₂ < 19.5% or > 25%; explosive atmosphere > 20% LEL; organic vapors (in breathing zone) > 5 m.u.; other______.
Level B: O₂ Explosive atmosphere > 20% LEL; unknown organic vapors (in breathing zone) > 500 m.u.; other______.
Level A: ESP personnel shall evaluate the need for entry on a site-specific basis and may utilize its emergency response contractor for Level A situations which may arise.

6.0 FREQUENCY AND TYPE OF AIR MONITORING/SAMPLING

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Contaminant of Concern</th>
<th>Sample Location (Area/Source)</th>
<th>Frequency</th>
<th>Odor Threshold/Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA</td>
<td></td>
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</table>
7.0 SITE CONTROL MEASURES

7.1 The "Buddy-System": ESP personnel performing any work activities within the exclusion zone shall employ the "buddy-system" at all times, as required and defined in Section 2 of the MDNR-HSERP. The "buddy-system" may not be required while an ESP staff member is observing or providing oversight of cleanup activities performed by a contractor or responsible party.

7.2 Safe work Practices: Refer to Section 2 of the MDNR-HSERP for written safety practices to be followed at all times by ESP personnel while on-site at an incident.

7.3 Site Communications: The use of two-way radios or establishment of hand signals for communications shall be determined prior to entering the work zone and followed by ESP personnel.

7.4 Radiation Safety: Due to the possibility of an unknown radiation hazard being present on a site, ESP personnel shall be required to wear radiation indicator badges (TLD badges) while on-site.

7.5 Work Zones: ESP personnel shall ensure work zones are established and be aware of their locations.

8.0 DECONTAMINATION PROCEDURE/SOLUTIONS:

Personnel: Gloves and clothing will be placed in a garbage bag and returned to Jefferson City for proper disposal.

Equipment: Returned to Jefferson City for proper decontamination.

Instruments: Returned to Jefferson City for proper decontamination or disposal.

Decontamination fluids/materials may be containerized for proper disposal.

9.0 EMERGENCY INFORMATION:

In the event of an emergency, notify the MDNR Environmental Emergency Response Office at 573/634-2436. The Duty Officer will make the appropriate notifications.
10.0 ADDITIONAL EMERGENCY INFORMATION/NUMBERS:

Hospital:  Salem Memorial Hospital, 35629 Highway 72, Salem, MO  (573) 729-6626  
Location/Specific directions from Site:  See Map directions.

<table>
<thead>
<tr>
<th>Name/Location</th>
<th>Telephone Number</th>
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<tr>
<td>Ambulance: Iron County Ambulance</td>
<td>(573) 244-5966</td>
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<tr>
<td>Police/Sheriff: Viburnum Police Department</td>
<td>(573) 244-5220</td>
</tr>
<tr>
<td>Fire: Quad County Fire Department</td>
<td>(573) 244-5440</td>
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Poision Control:  
Cellular Telephones/Other:  

1) Central Accident Reporting Office- WORK RELATED INJURY - 1-800-624-2354  
This number is to be called in the event of a NON LIFE THREATENING injury PROIR to seeking medical care.

11.0 SIGNATURES  
ESP personnel shall certify they have read the plan and addressed any questions regarding worker health and safety by signing and dating below followed by printing their name and title.

<table>
<thead>
<tr>
<th>Signature</th>
<th>Printed Name/Title</th>
<th>Date</th>
<th>TLD Badge</th>
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