2010 Viburnum Trend Water and Sediment Sampling
Hines Emerald Dragonfly Survey

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Natural Resource Damage Assessment and Restoration

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INTRODUCTION

The Viburnum Trend is an active lead (Pb) and zinc (Zn) mining district within the Southeast Missouri Lead Mining District (SEMOLMD), which is the largest producer of Pb in the nation. There are eight major tailings impoundments (tailings are mill waste produced by separating ore from host rock), ten mines, and a secondary Pb smelter in the Viburnum Trend within the Black River and Meramec River watersheds. Releases of heavy metals from the tailings impoundments, mines, and smelter have been documented into tributaries of these streams. The wetlands along the tributaries of the Black and Meramec River are habitat for the Hines Emerald Dragonfly (*Somatachlora hineana*), a federally-listed endangered species. These releases may have contaminated soil, sediment and water in the habitat of the Hines Emerald Dragonfly (HED). This Statement of Work will describe sampling activities designed to discern whether HED habitat has been contaminated by releases from mines, mills, or smelters within the Viburnum Trend.

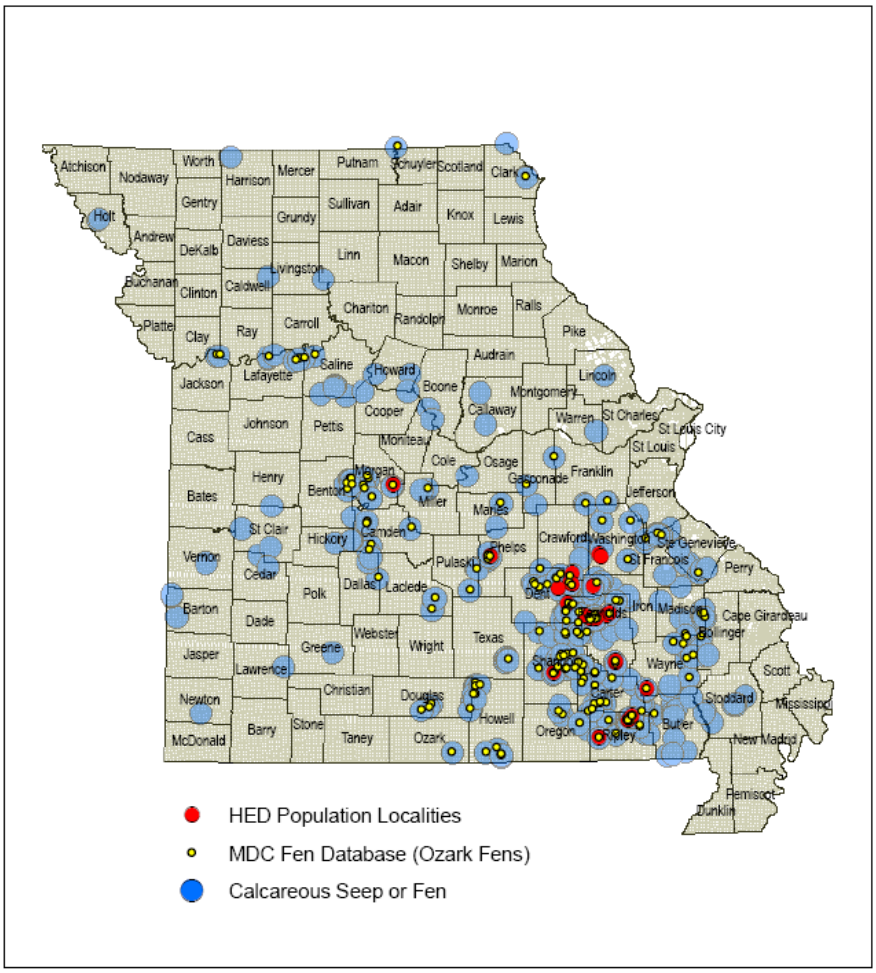
The HED inhabits spring-fed calcareous fens with dolomite rock. The HED is only found within dolomite fens in scattered locations in Missouri, Illinois, Wisconsin, Michigan and Ontario. The dragonfly spends the majority of its two to four year life in its larval stage as an aquatic nymph. The dragonfly nymph lives in the muddy sediment of the fen, and inhabits wet burrows of crayfish during dry periods. The dragonfly nymph is carnivorous, feeding mainly on other invertebrates living in the fen. Releases of hazardous substances from mining, milling, and/or smelting in the Viburnum Trend could potentially negatively affect HED as a result of contaminated sediment and water transported during high water events, or soil contaminated by aerial transport or fallout of smelter emissions and wind-blown tailings dust. Consequently, the USFWS proposes to examine water and sediment contamination in the known habitat of the HED to inform the continuing natural resource damage assessment of the Viburnum Trend.

STUDY OBJECTIVES

This study will seek to:

1. Characterize heavy metal contamination of sediment, soil, and surface water of fens above and below mines, mills, and smelters in the Viburnum Trend;
2. Compare media concentrations to known toxicological benchmarks relevant to HED;
3. Compare media concentrations of known HED fens to sites without HED;
4. Survey sites for presence or absence of HED if sediment, soil, or surface water of fens exceed toxicological benchmarks relevant to HED.

Figure 1 Hine's Emerald Dragonfly (HED) in Missouri, 2007.



Source: Missouri Department of Conservation, 2007.

METHODS

1. Extent of Heavy Metal Contamination in Sediment and Soil

The U.S. Fish and Wildlife Service (Service) will use an X-ray Fluorescence (XRF) meter, combined with confirmatory laboratory analysis using Inductively Coupled Plasma or Atomic Absorption Spectroscopy, to characterize heavy metal contamination of soils and/or sediment within fens below mining and smelting sites. The XRF will be used as a field screening tool and as a final analytical instrument for soils and sediment. A separate analytical laboratory will be used to analyze 10% of the samples to confirm the accuracy of metals analysis of the XRF.

1.1 Screening level survey of metals with XRF

Field screening will be used to identify fens that are contaminated and areas of sediment/soil contamination within the fen. Approximately 16 fens identified (in Table 1) as existing or potential HED habitat within five miles of mining or smelting related discharges will be targeted for sampling. At least one fen above the influence of mining or smelting will also be sampled for reference comparison. If field screening indicates contamination is occurring less than or greater than five miles from the mine/mill/smelter site, the geographic scope of sampling will be expanded to additional fens further downstream, or contracted to focus on fens closer to the mine/mill site, in order to represent likely contaminated areas.

Samples for field screening will be collected of unsaturated wetland soil adjacent to potential HED nymph habitat. Composite soil samples will be collected less than 10 cm (4 inches) deep. Each sample will contain no less than five aliquots collected within approximately a one hundred square meter area. Soil subsamples will be collected using a Teflon or plastic scoop (or large spoon) and placed on a paper plate or other non-metallic vessel in the open air for short-term drying to approximately 20% moisture or less based on visual estimation. (Twenty percent moisture is approximately equivalent to a moist soil.)

Samples will be analyzed in the field by placing the sample in contact with the XRF analytical window for approximately one minute after air drying. Concentrations of Pb, Zn, cadmium (Cd), copper (Cu), and nickel (Ni) will be recorded in a logbook and stored in the meter using a discreet sample number. After analysis with the XRF, the sample will be placed in a plastic zip-lock bag and labeled with the discreet sample number previously recorded in the logbook. Samples will be placed on ice and transported back to Columbia, MO for additional analysis.

Sediment samples for XRF will be analyzed using a 2007 Thermo Niton Xl3t 600 XRF (Thermo Scientific, Billerica, MA). Samples analyzed by XRF will be allowed to air dry for at least 1 week in the laboratory until totally dry. Samples will be thoroughly mixed within the Ziploc® bag by shaking and/or by hand manipulation. Each sample will then be analyzed for 90 s by placing the sample bag directly against the XRF analytical aperture in Thermo Niton's "Portable Test Stand" (Thermo Scientific, Billerica, MA), a fully shielded device that allows for computer controlled hands-free operation of the meter. An arithmetic mean will be calculated from three separate readings for each sample, with the sample fully mixed and shaken between each reading and used as the best representation of the sample metals concentrations.

A suite of calibration verification check samples will be used to check the accuracy of the XRF and to assess the stability and consistency of the analysis for the analytes of interest. Thermo Niton XRFs are internally calibrated prior to each use employing Compton normalization. Check samples will be analyzed at the beginning of each working day, during active sample analyses, and at the end of each working day. For the calibration verification check to be acceptable, the measured value for each target analyte must be within ±10 percent (%D) of the true value. If a measured value falls outside this range, then the check sample will be reanalyzed (USEPA 1998). If the measured check value again falls outside of the acceptable range, then the

instrument will be internally calibrated again until the check sample falls within the acceptable error range.
The number of samples collected from each fen will vary with the size of the wetland. Personnel will collect one sample from fens of one acre in size or less; two to three samples from fens of one to five acres, three to five samples from fens over five acres. The exact number of samples collected within the prescribed range will be determined by the relative heterogeneity or homogeneity of hydraulic and soil conditions present at each site. Relatively homogeneous sites can be represented by fewer samples.

A GPS reading and one or more photographs will be taken at every sample location. The GPS reading will be recorded in the logbook.

1.2 Sediment and soil sample collection

A minimum of seven fens will be selected for further study based on screening level XRF results. A minimum of ten soil/and or sediment samples will be collected in plastic bags for further XRF and laboratory analysis. Sample collection techniques will be the same as described in 1.1 above, with one exception: Either soil and/or sediment samples will be collected, depending on wetland water levels and the conditions that best represent the media where HED nymphs are living. Approximately 0.5 kilograms of soil and/or sediment will be collected at each location. Samples will be given a unique label on the bag and recorded in a logbook or field datasheet, and chain-of-custody sheet. GPS readings and photographs will be taken and recorded as described above.

Additional sediment/soil material will be collected at sampling locations for the purpose of quality control/verification. One quality control (QC) sample will be collected for every ten samples, or one QC sample will be collected by each team per day, whichever number is greater. An additional sample volume of approximately 1.5- 2.0 kilograms will be required. Two separate bags will be collected with alternating spoonfuls of sample placed in each bag. Duplicate samples for XRF analysis will be collected at a rate of ten percent, or at least one per team per field sampling day. An additional ten percent of total samples will be collected for confirmatory analysis using Inductively Coupled Plasma Mass Spectrometry or Atomic Adsorption using EPA method 3050b, “Acid Digestion of Sediments, Sludges, and Soils”.

1.4 Surface water sampling and analysis

One water sample will be collected from each wetland. Samples will be collected by filling a one-liter plastic container (after rinsing with site water) at the deepest point of standing water at each fen. Samples will be given a unique label and recorded in a logbook and chain-of-custody as mentioned above. Samples will be preserved with nitric acid (HNO_3) and stored on ice until analyzed at a laboratory.

Surface water quality analyses (i.e., temperature, pH, conductivity, dissolved oxygen) will be measured in situ at each fen within a site with a multi-parameter water quality instrument (e.g., YSI 556).

Water samples will be analyzed in the laboratory for total and dissolved Pb, Zn, Cd, Cu, and Ni, and total hardness. Samples analyzed for dissolved metals will be field filtered using a 0.45 micron filter prior to preserving with HNO_3.

2. Hines Emerald Dragonfly Survey

All sites will be evaluated for the presence of HED during sampling by visual surveys or sampling of crayfish burrows. If sampling occurs during the time of year when adults are present (June through July), visual surveys of flying insects will be conducted. If sampling occurs during other times of the year, surveys for the nymphs will be conducted following methodology first used in Missouri by Landwer and Vogt (2002). Personnel will survey for dragonfly nymph by pumping water and detritus out of crayfish burrows and identify extracted larvae to species. Both adult and larval dragonfly surveys will be conducted by a biologist experienced with identification of larvae in the genus *Somatochlora*.

Photographs will be collected of all observed HED. Notes on the presence or absence of HED will be recorded in a logbook.

Table 1: Hines Emerald Dragonfly Soil/Sediment Sampling Location

Stream Name	**No. or Name of Fen(s)**	**Site Identifiers**	**Known HED Site**	**Sampling Rationale/Location**
Neals Creek	Barton Fen	BF	Yes	1 mile below Magmont Tailings
Neals Creek	5 fens	NC-1 through NC-5	No	2 ½-5 miles below Magmont Tailings
Strother Creek	1 fen	SC	No	1 mile below Buick Mine/Mill Tailings
Bills Branch	3 fens	BB-1 through BB-3	No	¼-2 ½ miles below Brushy Creek Mine/Mill Tailings
West Fork of the Black River	1 fen	WF	No	4 miles below West Fork Mine/Mill Tailings
Bee Fork	3 fens	BF-1 through BF-3	No	½-4 miles below Fletcher Mine/Mill Tailings
Adair Creek	1 fen	AC	No	½ mile below Sweetwater Mine/Mill Tailings
Bee Fork	1 fen	BFR	Yes	Reference site 1 mile above Fletcher Mine/Mill Tailings

3. DATA ANALYSIS

1. *Sediment Chemistry*

The three laboratory replicate XRF readings of metal concentrations will be combined into a mean metal concentration for each sample location.

Laboratory XRF analysis will be compared to ICP-MS laboratory analysis. If the XRF metals analysis for a bulk whole sediment sample is ±30% of the laboratory value, the XRF sample will be considered valid and the XRF sample will be used for further data evaluation. If the XRF sample for the bulk sediment sample is not within 30% of the bulk laboratory value, the laboratory sample will be substituted for the XRF value and used for further data analysis. If greater than 20% of the comparative laboratory analyses are outside of the data quality precision range, an additional 10 % of the samples will be submitted for laboratory analysis. Samples rejected on the basis of QA review will be flagged and noted in data reports. A statistical trend analysis will be performed comparing laboratory and XRF data. If there appears to be a biased trend in the correlation between the XRF and laboratory analysis, the XRF values may be adjusted to account for the bias.

2. *Dragonfly/Sediment-Soil-Water Quality Correlation*

Ultimately the sediment and the HED data will be analyzed together to determine whether there are correlations between HED presence or absence and metals concentration.

3. *Experimental Design or Methodological Approach:*

Sampling sites will be selected based on National Wetland Inventory maps that identified dolomite fens in the region and proximity to mining/milling/smelting sites.

Study plan for HED was written with the assistance of an endangered species biologist. Study methods pose no threat of adverse effect to the HED.

4. *Listing of Critical Data:*

Collection location (including latitude and longitude determined by GPS); date; time; physical variables (i.e., depth, substrate particle size); water quality; sediment metals concentrations.

5. *Acceptance or Rejection Criteria for Results:*

Each endpoint will have its own quality assurance program that includes standards, reference materials, and blanks. Data outside the range of acceptable criteria will be clearly noted and discussed.

6. *Special Safety Requirements:*

Department of Interior (DOI) Regulations state that all personnel should wear flotation devices when near water. A first aid kit should also be present in all field vehicles.

7. *Quality Assurance Requirements:*

To the extent practicable, all analyses will comply with Good Laboratory Practices (GLPs). This includes descriptions of maintenance, inspections of instruments, and acceptance testing of instruments, equipment, and their components, as well as the calibration of such equipment and the maintenance of all records relating to these exercises. Documentation to be included with the final report(s) from each study will include field logs for the collection or generation of the samples, chain of custody records, and other QA/QC documentation as applicable.

8. *Endpoint of Study:*

The study will conclude when all chemical, biological, and statistical analyses; and project completion reports are finalized.

9. *Schedule of Study and Expected Outputs:*

Field collections will be conducted between September and October of 2010. Laboratory analyses will be completed by March 2010 with a draft report in review by May 2010.

10. *Place where Data will be Stored and Archived:*

U.S. Fish and Wildlife Service's Columbia, Missouri Field Office, 101 Park DeVille, Suite A, Columbia, MO 65203.

Table 2: Requirements for accuracy, precision and detection limits.

Parameter	**Estimated Accuracy for each matrix**	**Estimated Precision for each matrix**	**Precision Protocol for each matrix**	**Estimated Detection Limit**
Chemical	Measure Values within 95% of CI or 10% of Mean	Replicate Values within ± 25%	Analyze duplicate at least once per run	Temperature (0.3°C)
				pH (0.1 unit)
				Conductivity (100 μmhos/cm)
				Dissolved oxygen (0.1 mg/L)
				Metals (varies)
				GPS (10 m)

Procedures for calculating QC statistics are as follows:

Percent Relative Standard Deviation (%RSD) = SD/Mean x 100
Relative Percent Difference or RPD = (D1-D2)/Mean x 100
% Spike Recovery = (Total Measured – Background)/Spike Amount x 100
Method Limit of Detection = $3 \times (SD_b^2 + SD_s^2)^{1/2}$ where

SD_b = standard deviation of a blank or low level standard and
Sd_s = standard deviation of a low level sample.

Table 3: Proposed quality assurance samples for various matrices.

Type	**Matrix**	**Frequency**	**Analysis**	**Rationale**
Field Duplicates	Water	1 per run	YSI or Hydrolab®, water quality	Measures precision of sample collection and degree of environmental variability
Blanks	Sediment	1 per field samples	Metals	Monitors procedural contamination
Analytical duplicate	Sediment	1 per 20 analyses	Metals	Monitors instrumental precision
Analytical Spike	Sediment	1 per analytical run per matrix	Metals	Monitors instrumental accuracy
Laboratory Control Sample	Sediment	2 per analytical run	Metals	Monitors instrumental accuracy
Calibration Standard	Water, Sediment	1 per analytical run	Metals, YSI or Hydrolab® water quality	Monitors accuracy

Table 4: Proposed water quality, sediment, and biotic variables to be measured.

Matrix	Variable	No. Reps / Site	Where measured	Total Samples
Dragonflies	Presence/Absence	1.5 hrs survey	In situ	7-16
Soil	Screening Pb, Zn, Cd, Cu, Ni above PEC?	3-5	In situ	25-80
Sediment/Soil	Pb, Zn, Cd, Cu, Ni	1-3	Lab XRF	7-24
Sediment/Soil	Confirmatory Pb, Zn, Cd, Cu, Ni	1	Analytical Lab	1-3
Water	Total and dissolved Pb, Zn, Cd, Cu, Ni, and hardness	1	Analytical Lab	7-16
Site	GPS	1	In situ	7-16
Surface Water	Temperature	1	In situ	7-16
Surface Water	pH	1	In situ	7-16
Surface Water	Conductivity	1	In situ	7-16
Surface Water	Dissolved Oxygen	1	In situ	7-16

Literature Cited:

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