The distribution of heavy metals in known and potential Hine's emerald dragonfly (*Somatachlora hineana*) habitat near the Viburnum Trend mining district of southeast, Missouri, USA.

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ABSTRACT

The Viburnum Trend mining district in southeast Missouri, USA is one of the largest producers of lead in the world. Previous biological surveys in the district have found evidence demonstrating metal exposure of birds, insects, fish and crayfish. This study examined heavy metal concentrations in the sediment and water of freshwater wetlands known to be or potentially occupied by the federally endangered Hine's Emerald Dragonfly (*Somatachlora hineana*). Sediment samples were collected from thirteen sites to assess the potential exposure of the dragonfly to mining-derived metals. Water samples were also collected at the sampling sites when sufficient surface water was available for collection. Concentrations of metals (lead, zinc, cadmium, nickel, *et al.*) were analyzed in the surface water and sediment. Mean concentrations of lead in sediments were significantly greater ($P < 0.01$) at sites potentially impacted by mining compared to reference sites. Sediment concentrations of lead exceeded consensus-based threshold effects concentrations at eight of ten sites potentially impacted by mining. Concentrations of dissolved metals in surface water samples did not exceed Aquatic Life Criteria established by the State of Missouri. These findings suggest that metals associated with mining activities in the Viburnum Trend may have the potential to negatively impact Hine's Emerald Dragonfly populations in and around the district.

INTRODUCTION

The Viburnum Trend (VT) is an active lead (Pb) and zinc (Zn) mining district within the Southeast Missouri Lead Mining District, which is the largest producer of Pb in the United States. Extensive mining for Pb, Zn, and (to a lesser degree) other metals, in the VT began in the 1950s and continues presently (Seeger 2008). In the VT, the Black River and Meramec River watersheds house eight major tailings impoundments (produced by the separation of ore from host rock), ten mines, and a secondary Pb smelter (U.S. Fish and Wildlife Service and Missouri Department of Natural Resources 2009). Releases of heavy metals from the tailings impoundments, mines, and smelter have been documented in the soils, sediments and waters of these watersheds. Elevated concentrations of metals in the aquatic food chain, including fish, and benthic invertebrates represent a risk to wildlife. Deleterious effects on benthic invertebrate and fish communities have been documented by Schmitt et al. (2007a, 2007b). Previous studies (Allert et al. 2008a, 2008b; Besser et al. 2006, 2009; Brumbaugh et al. 2007; Schmitt et al. 2007b) have documented the release of metals from mining districts in Missouri that are linked to toxic effects on aquatic organisms; lower densities or absence of benthic macroinvertebrates including crayfish have been documented downstream of mining sites.

Hine's emerald dragonfly (*Somatochlora hineana*, or "HED" -- for the remainder of this report) is one of the most imperiled odonates in the United States (Cashatt and Vogt 2001). The HED currently exists in only a remnant of its historical area. It is presently extant in Illinois, Michigan, Missouri, and Wisconsin, but is presumed extirpated in Ohio, Indiana, and Alabama, where populations historically existed. (USFWS 2001). Based on the HED's limited distribution and specific habitat requirements, HED was listed as endangered under provisions of the Endangered Species Act of 1973 (US FWS 2001). It is afforded a global rank of G2G3, signifying that this species has a moderate to high risk of extinction due to a restricted range, few remaining populations, and recent, widespread or steep population declines (Trial and Belshe 2002). In Missouri, HED is given a numeric state rank of S1, meaning it is critically imperiled in the State or state endangered; this designation is typically afforded to species with five or fewer occurrences (or very few remaining individuals, i.e., less than 1,000 individuals) (Missouri Department of Conservation 2007). Figure 1 shows the location of known populations as of 2007.

Hine's emerald dragonfly belongs to the Corduliidae family, the emeralds and baskettails (Bridges 1994). This family contains 384 species, 39 of which are Somatochlorans; 26 occur in the United States (Bridges 1994). Six *Somatochlora* species have been documented in Missouri (Trial and Belshe 2002). Hine's emerald dragonfly has brilliant green eyes, a dark metallic green thorax, two distinct yellow lateral lines, and specialized terminal appendages or ovipositor (USFWS 2001). Adults of the species are approximately 60-65 mm in body length and have a wingspan between 90 and 95 mm (USFWS 2001).

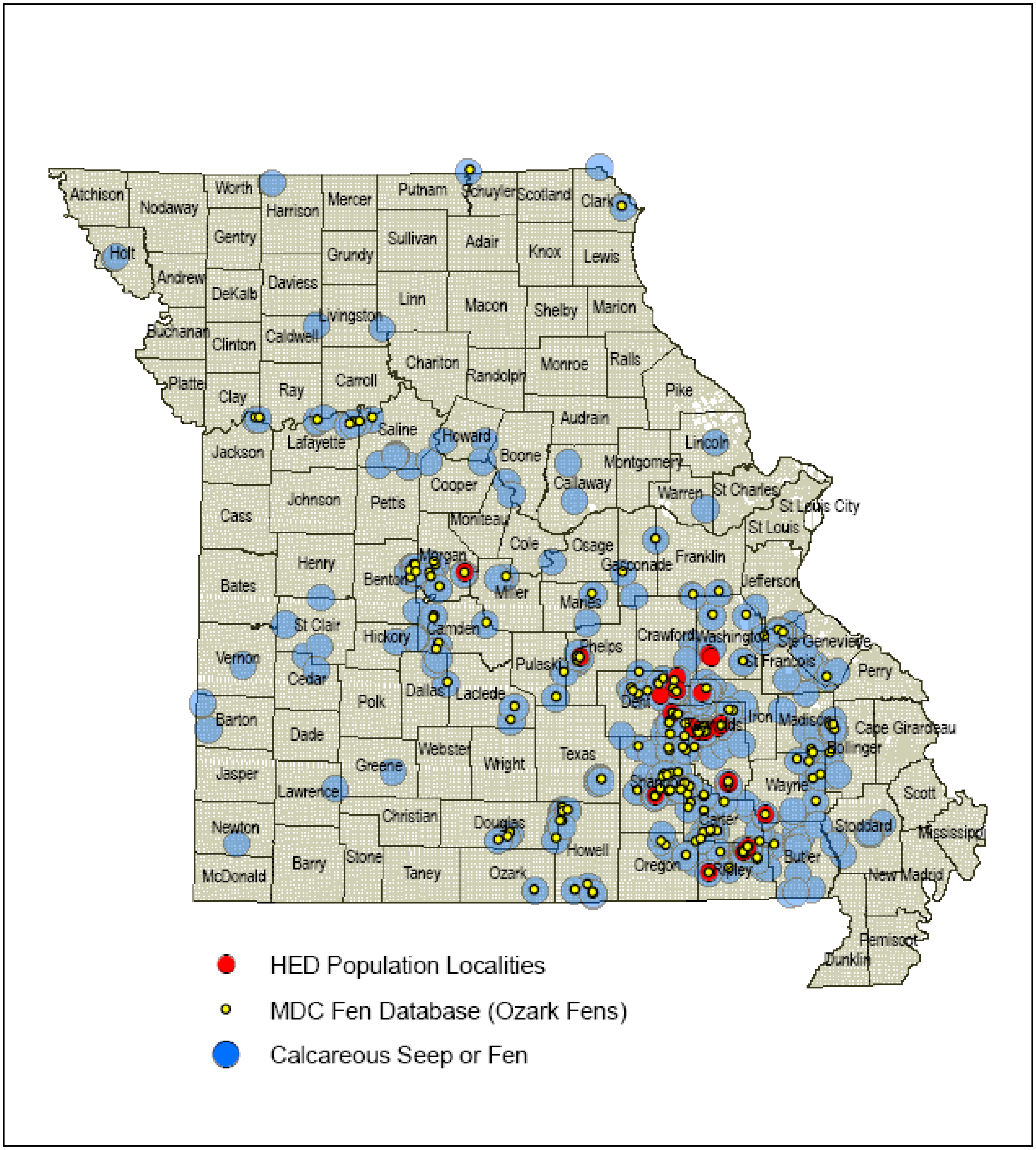
The life cycle of HED is comprised of the following stages: aquatic egg, aquatic larva, and a terrestrial/aerial adult (Corbet 1962). After an egg is hatched, the larvae may spend 2 to 4 years in small streamlets and wetlands, foraging and molting as they grow (Soluk et al. 1996, 1998). Upon completion of larval development, the larvae begin to emerge as adults as early as late May in Missouri and continue to emerge throughout the summer (Vogt and Cashatt 1994, Soluk et al. 1996, Mierzwa et al. 1997). Fully adult HED can live at least 14 days and may live 4 to 6 weeks (Mierzwa et al 1997). As with most dragonflies, adult HED feed, establish territories, mate, and oviposit (Corbet 1962). Most dragonfly adults are general predators throughout their life cycle, feeding primarily on insects they can capture while flying.

Somatochlora hineana is a species restricted to calcareous areas where limestone or dolomite bedrock lies close to the surface. The species occupies wetland habitat types characterized by sandy or marly saturated soils that are extremely hydric; wetlands typically associated with the HED are sustained by free-flowing limestone/dolomite spring natural communities (Nelson 2005, Moorehead 2000). Ozark fens, prairie fens, forested fens, seeps, marshes, and sedge meadows are natural communities that support populations of HED. *Fens*, strictly defined, are "a minerotrophic, enriched peatland with organic soils >15 inches deep; more generally in Missouri applied to similar wetlands lacking, or with only superficial, organic soils." (Nelson 2005). In Missouri a fen could be commonly defined as "any wetland that is perennially (or nearly perennially) saturated by groundwater discharge" (Nelson 2005). Figure 1 shows the location of fens and calcareous seeps in Missouri.

Certain fens along the tributaries of the Black and Meramec Rivers are known habitat for the HED. Releases of hazardous substances from mining, milling, and/or smelting in the Viburnum Trend could potentially negatively affect adult and larval 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. Another potential exposure route for HED, particularly HED larvae is consumption of smaller aquatic macroinvertebrates which may carry a body burden of mining related contaminants. Consequently, the U.S. Fish and Wildlife Service (Service) designed a screening level study to examine water and sediment contamination in the known and potential habitat of the HED to inform the continuing natural resource damage assessment of the Viburnum Trend. The objectives of the study were:

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. Sediment Sampling

From September 2010 through April 2011, composite sediment samples were collected from ten sites in the VT (Figure 2, Table 1). At some sites, multiple sediment samples were collected to characterize a larger fen. Each composite sample contained no less than 5 subsamples collected within an approximately 100 m^2 area, from water less than 15 cm deep. Collected subsamples were deposited into a high density polyethylene (HDPE) mixing vessel using a plastic scoop, homogenized, and then spooned into a Ziploc® brand 1-gallon size freezer bag. Samples were labeled and placed on ice for temporary storage until transferred to the laboratory for further analysis.

Approximately 0.5-1.0 kg of sediment was collected at each location. Additional sediment material was collected at certain sampling locations for the purpose of quality control/quality assurance. One quality control (QC) sample was collected for every ten samples, or one QC sample was collected by each team per day, whichever number was greater. Approximately 1.5-2.0 kg of sediment was required for sample analysis: two separate bags were prepared with alternating scoops of homogenized sediments placed in each bag. QC samples were collected for verification of X-ray fluorescence (XRF) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analytical results.

The investigators completed a qualitative description of each site including the current weather, stream conditions, site location, number and identification of samples collected, and collaborators on site. A global positioning system (GPS) reading and one or more photographs were taken at every sample location. The GPS reading was stored internally on a Garmin GPSMap device and recorded in a log book.

2. Surface Water Sampling

In addition to the sediment collection, surface water was sampled in seven of the ten fens where surface water was present at the time of collection. One water sample was collected from each wetland where water was available. Samples were collected by filling a 500-ml polyethylene Nalgene container (after rinsing with site water) at the deepest point of standing water at each fen. Filtered water samples for dissolved metals were collected using a GeoTech DisposaFilter, 0.45 µm high capacity capsule filter. Metal samples were preserved to a pH <2 using ultrapure nitric acid prior to delivery to the analytical facility. Field parameters were collected prior to laboratory samples and recorded in the field log and chain of custody. Water quality parameters, including dissolved oxygen, pH, conductivity, and temperature, were collected at each site using a YSI 556 Multiparameter Water Quality Instrument (YSI Incorporated, Yellow Springs, Ohio) that was calibrated at each collection site.

Figure 2. HED Sampling Locations in 2010 and 2011.

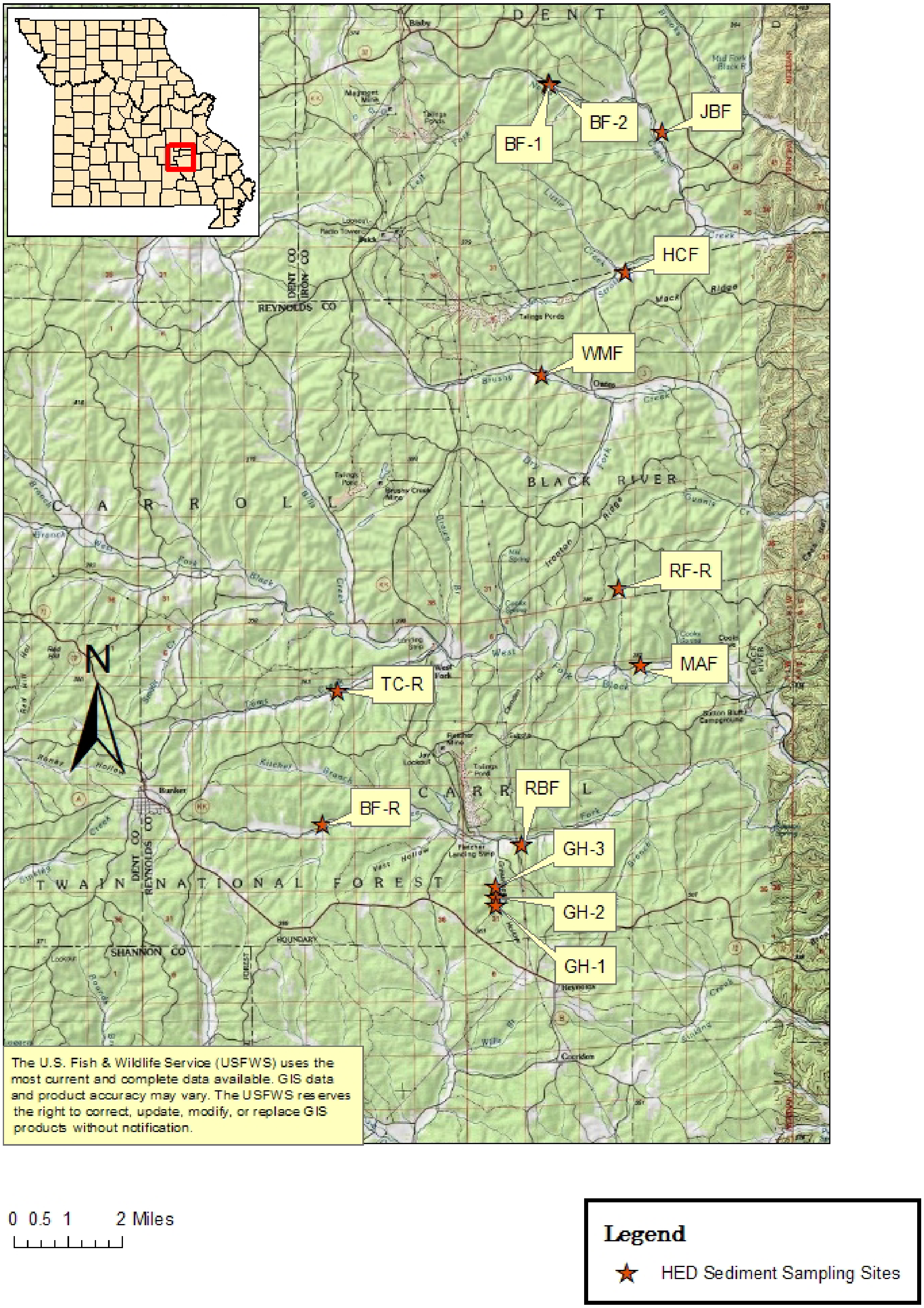


Table 1: Hines Emerald Dragonfly Sampling Location

Stream Name	Name of Fen	Site Identifiers	Known HED Site	Water Sample Collected	Sampling Rationale/Location
Potentially Impacted Sites					
Neals Creek	Barton Fen	BF-1, BF-2	Yes	Yes	1 mile below Magmont Tailings
Neals Creek	J. Barton Fen	JBF	No	Yes	2 ½ miles below Magmont Tailings
Strother Creek	H. Crocker Fen	HCF	No	No	2 miles below Buick Mine/Mill Tailings
Brushy Creek	W. Mason Fen	WMF	No	Yes	5 miles from Buick Smelter
West Fork of the Black River	McAdams Fen	MAF	No	No	5 miles below West Fork Mine/Mill Tailings
Bee Fork	R.Bryant Fen	RBF	No	No	½ miles below Fletcher Mine/Mill Tailings
Bee Fork	Grasshopper Hollow	GH-1, GH-2, GH-3	Yes	Yes	½ mile below Sweetwater Mine/Mill Tailings
Reference Sites					
Bee Fork	Bee Fork Reference	BFR	No	Yes	Reference site 1 mile above Fletcher Mine/Mill Tailings
Tom's Creek	Tom's Creek Reference	TCR	No	Yes	Reference site 1 ½ miles above West Fork Mine/Mill Tailings
Unnamed tributary to the West Fork of the Black River	Radford Fen Reference	RFR	Yes	Yes	Reference site not hydrologically connected to mine impacted stream

3. Hines Emerald Dragonfly Survey

As none of the HED survey sites were found to have sediment concentrations of any of the metals of concern (Cobalt, Nickel, Copper, Cadmium, Pb, and Zn [Co, Ni, Cu, Cd, respectively]) exceeding the Probable Effects Concentration (PEC) established by McDonald *et al.* (2000), the Service opted to not conduct the HED Survey portion of the study, as consistent with the Study Objectives and protocol discussed in the introduction and the Sampling Analysis Plan.

4. Sample Analysis

A. Sediment analysis by XRF

Sediment samples were analyzed by XRF and QC samples were analyzed by both XRF and by inductively-coupled plasma-mass spectrometry (ICP-MS) in an EPA certified laboratory. Sediment samples for XRF were analyzed using a 2007 Thermo Niton Xl3t 600 XRF (Thermo Scientific, Billerica, MA). Samples analyzed by XRF were allowed to air dry for at least 1 week in the laboratory until dry. Samples were thoroughly mixed within the Ziploc® bag by shaking and/or hand manipulation. Each sample was then 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 was calculated from three separate readings for each sample; each sample was mixed between each reading and used as the best representation of the sample metals concentrations.

A suite of calibration verification check samples was 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 were 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 ±20 percent (%D) of the true value. If a measured value fell outside this range, then the check sample was reanalyzed (USEPA 1998). Sediment sample results for Pb were categorized into reference and potentially impacted sites, as shown in Table 1.

B. Quality control and surface water sample analysis by ICP-MS

QC and surface water samples were analyzed for Co, Ni, Cu, Zn, Cd, and Pb by ICP-MS (Brumbaugh et al., 2007). Method detection limits (MDLs) were: Co 0.009 μg/L, Ni 0.160 μg/L, Cu 0.064 μg/L, Zn 0.910 μg/L, Cd 0.012 μg/L and Pb 0.021 μg/L. Percent recovery of calibration verification standards ranged from 95% to 99%. Percent recovery of reference solutions used as laboratory control samples ranged from 94% to 100%. Percent recovery of analytical spikes ranged from 91% to 98%. Overall, quality assurance results indicated that the methods used provided acceptable accuracy and precision; thus, none of the sample results were corrected.

RESULTS

1. XRF Sediment Analytical Results

The results of XRF analysis of sediments at potentially affected and reference sites are displayed in Table 2. Cadmium, Co, and Ni in sediments were not found above limits of detection for the XRF meter and are not reported. Concentrations of Pb in sediments, as determined by XRF, did not exceed the McDonald et al. (2000) Probable Effects Concentrations (PEC) at any of the sites; the PEC represents the concentration above which adverse effects are expected to occur more often than not (PEC Pb =128 mg/Kg) Eight of ten potentially mine impacted sites did exceed the McDonald et al. (2000) Threshold Effects Concentration (TEC) for Pb (TEC Pb= 35.8 mg/Kg), or the concentration below which adverse effects are not expected to occur.

A single-tailed Student's t-test of the XRF sediment results demonstrates a significant difference ($p<0.01$) between the mean Pb concentration at the reference sites (mean=23.7 mg/Kg Pb) (BF-R, TC-R, and RF-R) and the potentially mining impacted sites (mean=46.1 mg/Kg Pb).

2. Sediment ICP-MS Analytical Results

Concentrations of Pb in sediments, as determined by ICP-MS, did not exceed the McDonald et al. (2000) PEC at any of the sites. All three of the potentially mine impacted site sediments analyzed with ICP-MS exceeded the TEC for Pb (TEC Pb= 35.8 mg/Kg). Zinc TECs and PECs in sediments analyzed by ICP-MS were not exceeded at any sites. The MAF sample location had sediment concentrations of Cd that exceeded the TEC for Cd (TEC, Cd = 0.99 mg/Kg). The results of ICP-MS analysis of sediments at potentially mine impacted and reference sites are displayed in Table 3.

Table 2. XRF Analytical Results for Sediments

SAMPLE LOCATION	Pb (mg/Kg)	Zn (mg/Kg)
BF-R	14	58
RF-R	31	47
TC-R	26	36
GH-1	28	32
GH-2	23	27
GH-3	46*	92
BF-1	42*	41
BF-2	46*	38
JBF	43*	60
HCF	84*	61
WMF	37*	78
MAF	60*	97
RBF	52*	81

* Values exceed their respective Threshold Effects Concentration (TEC) as reported in MacDonald *et al.* (2000).

Figure 3. Exceedance of the Pb Threshold Effects Concentration at HED survey sites.

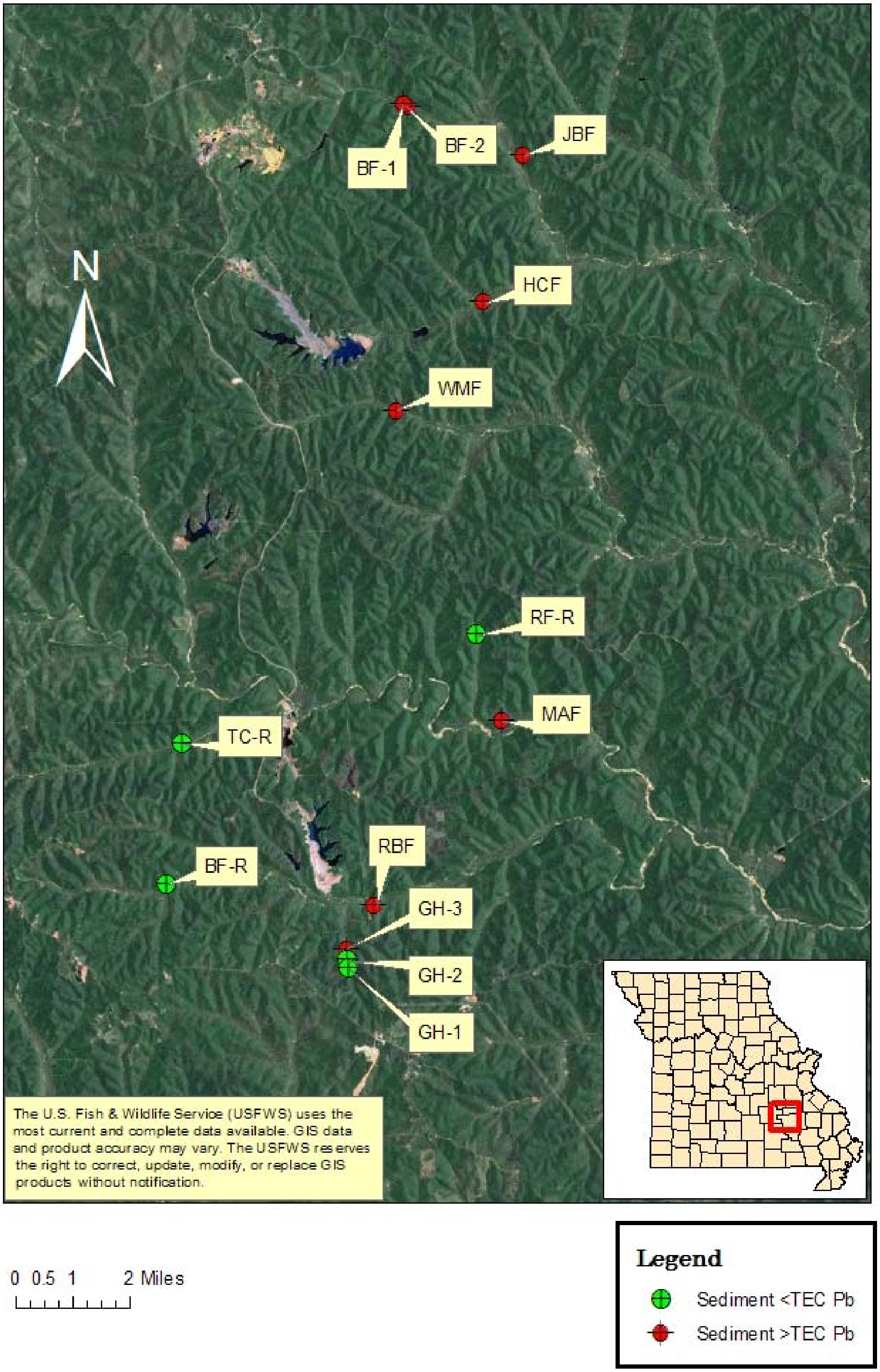


Table 3. ICP-MS Analytical Results for Sediments

Sample	Element	Result (mg/Kg)
BF-R	Chromium, Total	2.65
BF-R	Cadmium, Total	< 0.486
BF-R	Copper	5.68
BF-R	Lead, Total	5.85
BF-R	Nickel, Total	3.2
BF-R	Zinc, Total	6.95
TC-R	Chromium, Total	3.8
TC-R	Cadmium, Total	< 0.59
TC-R	Copper	11.72
TC-R	Lead, Total	18.40
TC-R	Nickel, Total	2.6
TC-R	Zinc, Total	7.32
BF-1	Chromium, Total	3.63
BF-1	Cadmium, Total	< 0.48
BF-1	Copper, Total	7.73
BF-1	Lead, Total	37.70*
BF-1	Nickel, Total	3.55
BF-1	Zinc, Total	18.80
GH-3	Chromium, Total	4.4
GH-3	Cadmium, Total	< 0.744
GH-3	Copper	7.63
GH-3	Lead, Total	38.00*
GH-3	Nickel, Total	5.30
GH-3	Zinc, Total	20.20
MAF	Chromium, Total	8.78
MAF	Cadmium, Total	4.45*
MAF	Copper, Total	16.23
MAF	Lead, Total	56.10*
MAF	Nickel, Total	3.94
MAF	Zinc, Total	49.70

* Values exceed their respective Threshold Effects Concentration (TEC) as reported in MacDonald *et al.* (2000).

3. Surface Water ICP-MS Analytical Results

Surface water samples were collected from the following fens: GH-2, BF-1, RF-R, JBF, WMF, BF-R, and TC-R. Concentrations of all total metals analyzed (unfiltered) in surface water at TC-R, BF-R, GH-2, and BF-1 did not exceed the MDL (15 µg/kg) for ICP-MS. Concentrations of total metals RF-R, JBF, and WMF are reported below in Table 4. Concentrations of all dissolved (filtered) metals analyzed in surface water did not exceed the MDL (15 µg/kg) for ICP-MS at any of the surface water sampling sites and are consequently not reported here.

Table 4. ICP-MS Analytical Results for Total Metals in Surface Water

Sample	Analyte	Result	Units	Reporting Limit	Analytical Method
RF-R	Hardness	286	mg eq CaCO3/L	9.92	SM 2340 B
RF-R	Cobalt, Total	88	µg/L	15	EPA 200.8
RF-R	Nickel, Total	21	µg/L	15	EPA 200.8
RF-R	Copper, Total	< 15	µg/L	15	EPA 200.8
RF-R	Zinc, Total	91	µg/L	15	EPA 200.8
RF-R	Cadmium, Total	< 15	µg/L	15	EPA 200.8
RF-R	Lead, Total	20	µg/L	15	EPA 200.8
JBF	Hardness	506	mg eq CaCO3/L	9.92	SM 2340 B
JBF	Cobalt, Total	342	µg/L	15	EPA 200.8
JBF	Nickel, Total	78	µg/L	15	EPA 200.8
JBF	Copper, Total	62	µg/L	15	EPA 200.8
JBF	Zinc, Total	125	µg/L	15	EPA 200.8
JBF	Cadmium, Total	< 15	µg/L	15	EPA 200.8
JBF	Lead, Total	61	µg/L	15	EPA 200.8
WMF	Hardness	211	mg eq CaCO3/L	9.92	SM 2340 B
WMF	Cobalt, Total	42	µg/L	15	EPA 200.8
WMF	Nickel, Total	< 15	µg/L	15	EPA 200.8
WMF	Copper, Total	< 15	µg/L	15	EPA 200.8
WMF	Zinc, Total	< 15	µg/L	15	EPA 200.8
WMF	Cadmium, Total	< 15	µg/L	15	EPA 200.8
WMF	Lead, Total	31	µg/L	15	EPA 200.8

DISCUSSION

The Black River System has been continuously exposed to mining-derived metals, including Pb, Zn, and Cd, for over 40 years (Gale *et al.* 1976; Allert *et al.* 2008a and 2008b). The results of this study, consisting of analysis of metals contamination in the sediment and water of known and potential HED habitat provides evidence that metals exposure in the Black River System may have the ability to impact HED populations in the future.

Concentrations of metals in sediments were consistently higher at sites identified *a priori* as potentially impacted by mining than at reference locations. Mean Pb concentration of potentially impacted sites was shown to be significantly greater ($P<0.01$) than mean sediment concentrations of Pb at reference sites. Additionally, eight of ten potentially impacted sites were found to have Pb concentrations which exceeded the TEC, though not the PEC. Exceedances of the TEC for Pb suggest there is a potential for HED to be exposed to metals as a result of the sediment pathway. A single exceedance of the TEC for Cd (TEC Cd=0.99 mg/Kg) was found at the MAF site. The Cd exceedance (4.45 mg/Kg) represents a potential threat to HED; however, the MAF site is not a known HED site. Further characterization of the site may be warranted if future funding exists for additional inquiries regarding the HED.

Concentrations of total and dissolved metals in surface water were generally below the MDL. Consequently, surface water is not suspected to be a pathway of concern for the HED at the sites sampled in this study.

As noted above, because of a dearth of exceedances of the PEC for contaminants of concern, the larval and adult dragonfly survey portion identified in the Sampling and Analysis Plan for this study was not conducted. Consequently, the full scope of habitat use by the HED in the VT remains unknown. Future research in this direction could repeat sampling and analysis of known HED habitat to insure that concentrations of heavy metals in sediments and surface water are not exceeding known toxicological thresholds for freshwater macroinvertebrates into the future.

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