AN ASSESSMENT OF FRESHWATER MUSSEL (BIVALVIA: MARGARITIFERIDAE AND UNIONIDAE) POPULATIONS AND HEAVY METAL SEDIMENT CONTAMINATION IN THE BIG RIVER, MISSOURI.

Andrew D. Roberts[1], Dave Mosby[1], John Weber[1], John Besser[2], Josh Hundley[1], Steve McMurray[3], and Scott Faiman[3]

[1]U.S. Fish and Wildlife Service, Columbia Missouri Ecological Services
[2]U.S. Geological Survey, Columbia Environmental Research Center, Columbia Missouri
[3]Missouri Department of Conservation, Resource Science Center, Columbia Missouri

ABSTRACT

This assessment was conducted in the lead mining-impacted Big River basin of Missouri to: 1) determine the downstream extent of heavy metal contamination of sediment; 2) determine distribution, diversity, and abundance of freshwater mussel species; and 3) evaluate the relationship between heavy metal concentrations in sediment and the abundance and species diversity of unionid mussels. Sediment samples were collected at 39 locations in the Big River and its tributaries and analyzed for metal concentrations by x-ray fluorescence and inductively-coupled mass spectrometry. Fine sediments (particles <0.25 mm diameter) from the Big River exceeded 2000 ppm lead (Pb) in over 24 km (15 mi) of stream, 1000 ppm in over 96 km (60 mi) of stream; and exceeded the Probable Effects Concentration (PEC) for Pb (128 mg/kg) from the upstream extent of mining to the confluence with the Meramec River over 180 km (113 mi) downstream. Zinc (Zn) and cadmium (Cd) concentrations in sediments were greatest below the uppermost mining inputs and exceeded PECs for approximately 80 km (50 mi) downstream. Lead (Pb), Zn, and Cd occurred at higher concentrations in the finest (<63 µm diameter) grain size fraction at almost all locations.

Timed mussel surveys (average time per site = 3.2 hours) found a total of 2198 living specimens representing 33 unionid species at 19 study reaches in the Big River. Overall catch per unit effort (CPUE) was 36.6 living mussels per person-hour. Nine species of conservation concern were found in the Big River including 2 federally endangered species (*Lampsilis abrupta* and *Leptodea leptodon*) and 1 federal candidate (*Cumberlandia monodonta*). Sites in a reach extending 158.7 km (98.6 river miles) downstream from mining sites were determined to have impacted mussel communities, based on reduced species richness. Comparison with past mussel sampling indicated that mussel abundance has declined since 1979 at the sites furthest downstream, suggesting that sediments containing toxic metal concentrations continue to migrate downstream. A comparison of mussel species richness and CPUE with sediment toxicity among timed survey sites in the Big River showed a broad-based negative association with metals in sediments. Quantitative mussel sampling (quadrat counts) conducted at 6 sites downstream of mining areas and 2 reference sites yielded a total of 236 living mussels representing 24 species. Mean mussel densities (average densities ranged from 0-0.4 individuals/m^2) at all quantitative study sites downstream of mining areas were significantly lower ($p<0.0001$) than at either of the reference sites (average densities ranged from 1.9–9.1 individuals/m^2).

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INTRODUCTION

The rivers of the United States support the most diverse freshwater mussel fauna in the world, with 297 recognized species (Turgeon *et al*. 1998). However, the diversity and abundance of these animals have declined in many areas of the country. Over 70% of the mussel species in the United States are considered to be extinct, endangered, threatened, or of special concern (Williams *et al.* 1993). This decline has been attributed to several factors including the construction and operation of impoundments, sedimentation, channelization, dredging, water pollution, and invasive species (Williams *et al*. 1993, Neves *et al*. 1997, National Native Mussel Conservation Committee [NNMCC] 1998). In general, environmental contaminants are considered to be one of the main causes for this decline (Havlik and Marking 1987, Bogan 1993, Williams *et al.* 1993, NNMCC 1998), and thus, mussels recently have been the subject of increased scientific focus in the field of ecotoxicology.

The Big River in Missouri, which is the largest tributary of the Meramec River, drains the largest historic lead producing mining area in the United States (USGS 1998), and therefore, heavy metal contamination has long been suspected to be affecting freshwater mussel populations and other aquatic biota. Elevated levels of bioavailable heavy metals have been documented in the water and river sediments and have been documented within tissues of aquatic biota downstream of mining sites (Zachritz 1978, Gale and Wixson 1986, Gale *et al*. 1973, Schmitt and Finger 1982, Duchrow 1983, Czarnezki 1985, Niethammer *et al*. 1985, Czarnezki 1987, Schmitt *et al*. 1987, Meneau 1997, Gale *et al*. 2002, Department of Natural Resources [MDNR] 2003, Besser *et al*. 2007). During extensive mussel surveys of the Meramec and Big River basins in the late 1970's and early 1980's, Oesch (1995) and Buchanan (1979*b*) both noted a noticeable reduction in the diversity and abundance of mussels in the Big River and attributed this decline to the effects of lead mining. Roberts and Bruenderman (2000) surveyed some of the same locations as Buchanan (1979*b*) in the Big River and noted additional declines in mussel populations. Mosby *et al*. (2008) demonstrated that mussels are less abundant and less diverse in sampling locations below mining impacts where sediment concentrations exceeded the Probable Effects Concentration (PEC) for lead (Pb) and/or zinc (Zn) during a screening level survey in 2007 of mussel populations and sediment metal concentrations in the Big River. Lastly, recent mussel sampling indicated declines to mussel populations at locations further downstream of previous studies (Missouri Department of Conservation [MDC] Unpubl. Mussel Database 2008).

Freshwater mussels are considered good indicators of ecological integrity and toxicological stressors affecting the aquatic benthic community (Van Hassel and Farris 2007). They have been shown to be among the most sensitive to heavy metals (Havlik and Marking 1987, Keller and Zam 1991, Naimo 1995, Wang *et al*. 2007*a*, Wang *et al*. 2007*b*), and as benthic, filter-feeding animals, they are directly exposed to metals in contaminated sediments where they live and in the water column from which they obtain their food (Naimo *et al.* 1992). Mussels generally live in the same area for their entire adult life, and therefore, can indicate the condition of local environmental conditions by their presence. The shell material left behind by dead mussels can provide a record of past existence in the vicinity. Lastly, mussels are abundant in terms of biomass and are ecologically important, serving as structural and functional components of the benthos (Vaughn and Hakenkamp 2001, Vaughn *et al*. 2004). Recently, the diversity and abundance of mussels have been demonstrated to be negatively correlated with heavy metal contaminated sediment in the Tri-State Mining District of Missouri, Kansas, and Oklahoma and were found to be good indicators of these impacts (Angelo *et al*. 2007).

The objectives of this assessment (study) were to (1) provide a full characterization of the longitudinal downstream extent of heavy metal contamination of sediment; (2) to determine distribution, diversity, and abundance of freshwater mussel species in the Big River (including federally listed species); and (3) evaluate the relationship between heavy metal concentrations in sediment and mussel populations.

Study area

The Big River (Figure 1) is part of the Meramec River system, which consists of clear, gravel-bottomed streams of the Ozark region in east-central Missouri. The Big River originates in northern Iron County, Missouri and flows 225 km (140 mi) north to its confluence with the lower Meramec River in St. Louis County, Missouri. The Big River watershed drains approximately 1537 km^2 (955 mi^2) of the upper Mississippi River Basin in portions of 6 Missouri counties. The main tributaries of the Big River include Mineral Fork and Terre Bleue and Cedar creeks. The Big River drains the "Old Lead Belt", which is an historic mining subdistrict within the current Southeast Missouri Lead Mining District (district).

There is a long history of lead and zinc mining in the Big River watershed, beginning with the first French settlers. Historically, the district had the highest production of lead in the United States (U.S. Geological Survey 1998). While the mining has ceased in the Old Lead Belt portion of the district, the process accumulated approximately 227 million metric tons of fine-grained dolomitic tailings divided among 6 large piles adjacent to the Big River and its tributaries contaminating the surrounding land and water. Small dams were constructed to hold back the mining wastes, but most were improperly constructed or maintained. Among the 45 dams constructed by the U.S. Army Corps of Engineers, only 1 was considered safe from failure if flooding was to occur, and 27 received the lowest rating. The poor condition of the dams has led to large influxes of mine waste into the Big River from dam collapse (Meneau 1997). For example, in 1977, a mine tailings dam near Desloge ruptured and discharged 63,000 cubic meters (81,000 cubic yards) of mine tailings into the Big River, which covered 40 km (25 mi) of stream bottom and negatively impacted freshwater mussels and other aquatic organisms inhabiting the lower 129 km (80 mi) of the river (Buchanan 1980). These releases contaminated sediment in over 90 river mi (RM) of the Big River and its tributaries (MDNR 2007) with Pb and Zn in excess of PECs established by MacDonald *et al*. (2000).

Despite nation-wide declines of freshwater mussels, the Meramec River basin in Missouri remains a stronghold of mussel diversity and abundance, with 45 species known from the basin (Buchanan 1979*b*, Roberts and Bruenderman 2000). The Meramec Basin includes two major tributaries, the Bourbeuse and Big Rivers, which support a diversity and abundance of mussels. The Big River supports 36 of mussel species, including the federally endangered pink mucket (*Lampsilis abrupta*) and scaleshell (*Leptodea leptodon*) and two species that are currently candidates for federal listing (Table 1). The effects of Pb and barite ($BaSO_4$) mining have been hypothesized as the reason the Big River has a lower mussel species diversity and abundance throughout a significant portion of its length (Buchanan 1980).

MATERIALS AND METHODS

1. Sediment collection preparation and analysis (2008)

From July through October 2008, composite sediment samples were collected from 21 sites in the Big River, 2 sites in the Bourbeuse River, and 2 sites in the Meramec River above and below the confluence with the Big River (Figure 1, Table 2). In addition, 4 sediment samples were collected from 2 Big River tributaries; Mill Creek and Mineral Fork. At some sites, multiple sediment samples were collected to characterize changes affecting sedimentation within a reach of the river (i.e. above and below mill dams, low water crossings, or tributaries). Sediments were collected from relatively slow-moving water near physically adequate mussel habitat consisting of riffle/run complexes with relatively stable gravel sized particles. Each composite sample contained no less than 5 subsamples collected within an approximately 100 m^2 area, from water less than 15 cm (6 inches) 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 transfer to the laboratory for further analysis. Used HDPE vessels and collecting scoops were then placed in a storage bag for cleaning and nitric acid rinse for later reuse.

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/verification. One quality control (QC) sample was collected for every tenth sample, or one QC sample was collected by each team per day, whichever number was greater. For these samples approximately 1.5- 2.0 kg was required: 2 separate bags were prepared with alternating scoops of homogenized sediments placed in each bag. QC samples were collected for verification of both by X-ray fluorescence (XRF) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analytical results.

In addition to the QC samples identified in Table 2, 10 sediment collection sites on the Big River were identified for particle size fraction and ICP-MS analysis of metals content at each size fraction. At these sites, 18.9 L (5 gallons) of site water and 11.4 L (3 gallons) of homogenized sediments were collected in HDPE buckets with watertight lids. Buckets and lids were pre-cleaned with nitric acid and rinsed to remove any possible existing metal contamination. Sediment size fraction samples were stored in a walk-in refrigerator until analysis at the laboratory.

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

a. Meramec River

Field screening of sediments was used to identify the portion of the Meramec River that represents the leading edge of sediment contamination originating from the Big River. The leading edge of contamination was defined as sediment concentrations above the Threshold

Effects Concentrations (TEC), according to MacDonald *et al*. (2000), but below the PEC. Samples were collected downstream from the confluence with the Big River at approximately 3.2 km (2 mi) intervals or at suitable mussel habitat. When concentrations of any of the metals of concern were detected above their respective TEC, a downstream sample location was selected and the procedure was repeated. Downstream sampling was discontinued when sediment concentrations of all of the metals of concern were below their respective TEC. Approximately 45 km (28 mi) of the Meramec River downstream from the confluence with the Big River were sampled in this manner.

Field screening samples were collected with the same methodology discussed above, homogenized, and placed in a HDPE vessel in the open air for short-term drying to approximately 20% moisture or less based on visual estimation, which is approximately equivalent to a moist soil (Rawls, *et al.,* 1982). The samples were analyzed *in situ* by placing the sample in contact with the XRF analytical aperture for 90 s after air drying. Concentrations of Pb, Zn, Cd, and Ba were recorded. After analysis with the XRF, the sample was placed in a labeled plastic Ziploc® bag.

c. Big River

Sediment samples were analyzed by XRF meter and QC samples were analyzed by both XRF and by ICP-MS in a 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 totally 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 a 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, with the sample fully mixed and shaken between each reading and used as the best representative 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 was to 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).

Additionally, a portion of each bulk sediment samples was sieved to <0.25 mm particle size fraction using a USA Standard Sieve Series (Number 60), ASTM E11 sieve. The fine samples were placed in Thermo Niton Series 1500 Top Loading XRF Sample Cups (Thermo Scientific, Billerica, MA) and analyzed in triplicate in the same manner as the bulk samples.

d. Quality control samples

Bulk sediment QC samples were analyzed by XRF as described above. In addition, bulk QC samples were submitted to the United States Geological Survey's Columbia Environmental Research Center (USGS-CERC) for ICP-MS analysis of total Pb, Zn, Cd, Ba, and Nickel (Ni) following the methods outlined in Brumbaugh *et al.* (2007). Samples of several particle-size fractions were obtained by wet–sieving using site water to determine the percentage of sediments (and associated metals concentrations) in the following fractions: <62 µm, 62-250 µm, 250 µm-2mm, and >2 mm (Table 3).

2. *Mussel survey methods*

a. *Timed searches*

Timed searches were used to evaluate species richness and distribution of freshwater mussels in 19 stream reaches in the Big River (Table 2). Timed searches are used to produce a more complete list of species at a given location, including the detection of rare species (Strayer *et al.* 1997, Vaughn *et al.* 1997, Obermeyer 1998, Strayer and Smith 2003). In addition to species richness, a measure of mussel abundance can be expressed as CPUE (Catch Per Unit Effort, expressed as number of mussels per person hour) and the relative abundance of each species can be expressed as a percentage of the total catch.

Timed searches involved visual searching and tactile searches for live mussels while snorkeling, or wading if water was too shallow to snorkel. Visual searches also included disturbing and fanning gravel substrates by hand and moving cobble and large flat rocks. These techniques were necessary to increase collections of juveniles, smaller species, and individuals that were buried in the substrate. Mussels were identified and recorded as they were found. On-shore searches of dead shell material were also conducted on gravel bars and in raccoon/muskrat middens. All dead shells on the stream bottom that were not represented by living species were collected during timed searches for voucher purposes. All habitats were searched at each site until at least 1.5 person-hours of search time failed to increase the number of mussel species present. However, sampling times always at least matched or exceeded past sampling times for a given site to allow some comparisons to past data (Buchanan 1979*b*, Roberts and Bruenderman 2000. All sites were surveyed by at least 2 biologists experienced with mussel sampling and familiar with the regional fauna. Searches were conducted during periods of low flow when aquatic habitats were accessible for visual searches.

Dead specimens of mussel species not represented by live individuals were classified as either fresh dead, dead, or subfossil. Fresh dead shells represent individuals in which the soft anatomy has not fully decomposed, and indicate the individual has recently perished. Dead shells have some luster to the nacre (innermost layer of the shell) and have a relatively intact periostracum (outermost layer of the shell). Subfossil shells have a chalky and lusterless nacre and the periostracum has peeled off considerably (Buchanan 1979*b* and 1980). The rate at which shell material decomposes following the death of a mussel depends on a variety of factors, including whether the shell was above or below the substrate, whether the shell was in the water or immersed, species, and shell thickness. In general, dead shells represent mussels that have been dead for less than a year and subfossil shells represent mussels that have been dead for more than a year.

At each survey reach the sampling method(s), total sampling effort, the number of living specimens of each species found, and species represented by shell material only. Subjective descriptions were also made of the habitat in which each mussel species was found and of the surrounding stream habitat conditions. If a distinct concentration of mussels ("bed") was found, the approximate dimensions, location, and general water depth of the concentration was described.

Sampling reaches for timed searches were selected for assessment based on the presence of suitable mussel habitat and previous reports of mussel abundance (Buchanan 1979*b*, Roberts and Bruenderman 2000, MDC Unpubl. Mussel Database). New reaches were surveyed as deemed necessary to gain a better understanding of present conditions. Three reference sites were chosen to determine an aquatic baseline from current conditions. These included the upper Big, lower Bourbeuse, and middle Meramec rivers. The upper Big River site was located upstream from all mining operations. While the mussel community at this site can be compared to sites in the upper stream reaches, it is not representative of sites in the middle and lower Big River because mussel diversity and abundance naturally increases in a downstream direction (Watters 1992). Therefore, the Bourbeuse and Meramec rivers were also chosen as reference streams to provide a more accurate baseline conditions for lower Big River stream reaches. These sites were selected based on similar characteristics of geography and biology to the Big River, except for mining impacts. Geographic factors that are important in selecting a reference stream include similar land-use patterns, basin size, topography, and gradient. The important biologic factors considered for these reference streams were mainly similarities in faunal assemblages, or species composition, fish host assemblages, and physical mussel habitat.

b. Quantitative mussel sampling

Quantitative mussel sampling was conducted at 8 of the 2008 timed survey sites to provide estimates of mussel densities (individuals/m^2). These sites included 6 sites in the Big River located downstream from mining operations and at 2 reference sites (upper Big River and lower Bourbeuse River). Each site was delineated such that only the portion of the channel with suitable, occupied mussel habitat was sampled. First, the length and width of the sampling area was measured and plotted. Then, a tape measure was anchored parallel with the stream channel at the upper and lower ends of the sampling reach. Quadrat coordinates were determined successively from a list of random numbers and located in the stream by using a second tape measure and a large T-square to measure 90 degrees off the anchored tape. A 0.25 m^2 quadrat, which was the most efficient size quadrat (Strayer and Smith 2003), was positioned on the stream bottom and all visible mussels were collected. Following this initial search, cobble and flat rocks were removed by hand and gravel substrates were searched by mixing and fanning by hand until no mussels remained. Mussels were identified, enumerated, and replaced into the substrate within the quadrat location. The lengths of mussels from every other quadrat were also measured.

3. Habitat evaluation

Physical habitat was evaluated at each mussel survey site using the habitat assessment protocol described by Barbour *et al.* (1999). From this method a numerical score is generated representing habitat quality by rating the various stream parameters on a scale of 0 to 20 with the habitat quality increasing with number. The following stream habitat parameters were evaluated: Epifaunal substrate/cover, embeddedness, velocity/depth regime, sediment deposition, channel flow status, channel alteration, frequency of riffles, bank stability, bank vegetation, and riparian zone (see Appendix A for definitions of habitat parameters). Ratings for each parameter were determined by averaging the values independently assigned by three surveyors familiar with the regional stream conditions following visual inspection of the targeted stream reach. The final physical habitat score is the sum of the averaged ratings for each of the habitat parameters (theoretical maximum = 200). Together with reach-specific environmental chemistry data from sediment samples, these scores provide a general basis for distinguishing between contaminant-limited and physical habitat-limited mussel populations.

4. Sediment chemistry data analysis

a. XRF Sediment Chemistry Quality Assurance/Quality Control

All calibration verification check samples used to check the accuracy of the XRF instrument were within the target accuracy and precision (±20 percent of the true value [%D]). This indicated that the XRF was acceptably accurate, stable and consistent for the analysis of the metals of interest (USEPA 1998). See Table 13 of Appendix B for XRF calibration data.

b. Bulk sediment XRF: ICP-MS laboratory comparison

Three laboratory replicate XRF readings of metal concentrations were combined into a mean metal concentration for each sample location. XRF analyses were then compared to ICP-MS laboratory analysis as a quality assurance measure. See Tables 1-12 of Appendix B for ICP-MS data and QA/QC evaluation.

The data quality objective for the XRF metals analysis for a bulk whole sediment sample is +/– 30% of the laboratory value. If the analysis met these criteria, the XRF sample was considered valid and the XRF sample was used for further data evaluation. If the XRF sample for the bulk sediment sample was not within 30% of the bulk laboratory value, the laboratory sample was to be substituted for the XRF value and used for further data analysis.

The comparison of XRF versus ICP-MS metals was focused on Pb and Zn. Cadmium method detection limits are too high for the XRF to make comparisons relevant (Thermo Scientific, 2008), and Ba and Cu are not toxicologically important to the Big River aquatic ecosystem. Lead was greater than 30% different from the ICP-MS analysis for 7 out of 11 samples. Zinc was greater than 30% different from the ICP-MS analysis for 5 out of 11 samples.

The prescribed QA measures also allowed for a statistical trend analysis comparing laboratory ICP-MS and XRF data. A regression analysis showed very good correlation between XRF and ICP-MS ($R^2 = 0.94$ for Pb and 0.99 for Zn), but with XRF results averaging slightly lower than results obtained by ICP-MS. For the paired XRF and ICP samples, XRF Pb was 17% lower than ICP-MS on average and XRF Zn was 11% lower on average. Therefore, instead of adjusting individual data points, regression lines were used to adjust the entire XRF data set for

Pb and Zn. For results below the XRF detection limit, the regression equation transformation would result in a negative number. In those cases, either an ICP-MS value was used, if available, or the number was adjusted by the mean percent difference of the 2 data sets. The laboratory ICP-MS analysis for total Ba showed poor recovery of the spikes. Therefore, the XRF Ba data were not transformed.

c. <0.25 mm XRF: ICP-MS laboratory comparison

The XRF metal concentrations in the <0.25 mm sediment samples had much poorer correlation with their paired samples analyzed by ICP-MS than did the bulk sediments ($R^2 = 0.3929$ and $R^2 = 0.9873$, respectively). A subset of these samples were re-analyzed using XRF and were not significantly different from the earlier result.

The poorer correlation is contrary to what was expected since sieved samples normally have less variability than bulk sediments (Horowitz and Elrick, 1988). It is suspected that the reasons for the lower correlations are due to differences in sieving methods. Samples analyzed by XRF were dry-sieved, whereas the ICP-MS samples were wet-sieved using site water. Wet sieving is suspected to be a superior method since the drying process employed in the XRF analyses may cause finer metallic particles to differentially aggregate into coarser particles or otherwise adhere to coarser particles (Horowitz and Elrick, 1988). Further the XRF fine fraction concentrations were inconsistent in their distribution compared to the bulk, with no discernable trend. In contrast the ICP-MS concentration distribution was consistently lower in the finer fraction than in the bulk. Therefore the relationship established by a regression analysis between bulk and <0.25 mm samples as analyzed by ICP-MS was used to estimate the <0.25 mm XRF results for Pb and Zn based on the bulk XRF results. The <0.25 mm XRF results were converted to Probable Effects Quotients (PEQ) by dividing the concentration of a given metal result by its respective PEC.

d. Cd estimated concentrations from Cd:Zn ratio correlation

XRF meters typically have high detection limits for Cd relative to eco-toxicologically relevant concentrations (Thermo Scientific, 2008). The Niton Xl3t 600 used for this assessment had a detection limit of 10 ppm, which is amongst the lowest achievable with an XRF, but still above the PEC for Cd of 4.98 mg/kg (Thermo Scientific, 2008). It was necessary to estimate a Cd concentration to facilitate the evaluation of injury and ecological risk in areas of the Big River where ICP-MS sediment samples were not collected. Cadmium and Zn concentrations in mining sites are frequently well correlated (Dames & Moore 1995), since Cd usually co-occurs as an impurity within Zn minerals. Twenty-eight samples were analyzed for Cd and Zn (and other metals) by ICP-MS. There was significant correlation between Cd and Zn ($R^2 = 0.98$) for the <0.25 mm sediment. Therefore, the regression equation was used to estimate Cd concentrations based on XRF Zn results.

5. Mussel survey data analysis

a. Reference envelope analysis for mussel species richness:

Impacts on mussel species richness in the Big River were determined by comparing the number of live mussel species collected during timed sampling in 2008 to the total number of mussel species documented (live or dead) from 50 sites in the Big River, based on all available data (samples collected between 1979 and 2008; Buchanan 1979*b*, Roberts and Bruenderman 2000, MDC Unpubl. Mussel Database). This determination was complicated by two factors: (1) the natural increase in mussel species expected to occur in streams with distance downstream from the headwaters (Watters 1992) and (2) the absence of mussel survey data prior to the disturbance in the watershed due to mining. The first factor was addressed by performing a regression of all past species-richness data versus river mile, which approximates the natural decrease in species with increasing river mile (i.e., with distance upstream). A plot of all species richness data for the Big River, arranged in downstream-upstream order shows both an overall trend of greater mussel species richness at downstream sites and the very low species richness in the reach downstream of mining, compared to both downstream and upstream reaches (Figure 2a). To estimate the natural decrease of mussel species richness in the Big River with distance from the confluence with the Meramec River, sites with less than 5 documented mussel species (presumed to represent either anthropogenic impacts or unsuitable headwater habitat) were excluded and the remaining species richness data were plotted versus river mile, with the X-axis log transformed to produce a linear relationship (Figure 2b). This regression was assumed to be a conservative estimate of the natural reference condition for mussel species richness in the Big River, and sites from the 2008 timed sampling that fell below the 95% confidence interval (the "reference envelope") for the regression were considered to be "impacted".

b. *Quantitative mussel survey data*

Mean mussel densities from quantitative mussel survey data were compared among study sites by conducting a one-way ANOVA with rank-transformed data and Tukey's test for pair-wise comparisons of the means (Conover and Iman 1981).

c. *Mussel community associations with sediment metals and habitat quality*

Statistical approaches used to evaluate associations of timed mussel survey data (taxa richness and CPUE) with sediment metal concentrations and habitat scores included: (a) rank correlation analysis; (b) principal component analysis of the correlation matrix; and (3) multiple regression analysis. These analyses were conducted using SAS/STAT (version 9.2) (SAS; Cary, North Carolina) with statistical significance based on a type I error rate of less than 5% ($p \leq 0.05$). Rank correlation analyses (PROC CORR) examined relationships of taxa richness and CPUE with Pb, Zn, and Cd concentrations in both bulk and fine sediments and with habitat variables, including the total habitat scores and individual scores for the 13 individual habitat metrics. Principal components analysis (PROC PRINCOMP) was conducted on the matrix of correlations among taxa richness, CPUE, and 6 sediment variables that had significant rank correlations (Pb, Zn, and Cd concentrations in fine sediments (<0.25 mm); embeddedness; sediment deposition; and channel status). Multiple regression analysis (PROC REG) was used to generate predictive models for the dependent variables, taxa richness and CPUE, based on explanatory variables (sediment metal concentrations and habitat indices) that had significant rank correlations. Sediment metal concentrations were log-transformed before the regression analysis. Variables were added to the models by forward selection, starting with the strongest single explanatory variable and continuing to add variables (with a minimum significance value of p=0.05) as long as they significantly improve the fit.

RESULTS AND DISCUSSION

1. Longitudinal sediment distribution in the Big and Meramec Rivers

In general XRF results showed highly elevated concentrations of Pb and Zn (10 times greater than PECs) in the reach extending 16 to 32 km (10 to 20 mi) downstream from St. Francois County tailings disposal sites (Figure 3) (Table 1 of Appendix C). The most pronounced peak for Pb and especially Zn and Cd was immediately below Eaton Branch, which drains the Leadwood Tailings pile. Zn and Cd concentrations declined more rapidly than Pb, which remained extremely high and showed a second peak at Hwy K below the confluence with Flat River Creek. Bulk XRF Pb remained above the PEC until above Morse Mill dam (116 ppm at RM 30.7), although lab adjusted bulk Pb (159 ppm) was just above the PEC. Big River sediment concentrations continued to fluctuate above and below the PEC in the lab adjusted bulk fraction all the way to 0.40 km (0.25 mi) above the confluence with the Meramec River. Bulk XRF Pb declined to 120 ppm below the Byrnes Mill dam at RM 8.3, and remained below the PEC for the remaining downstream reach of the Big River. Figure 4 shows the PEQ by river mile for Pb, Zn, and Cd in the <0.25 mm fraction compared to their respective PECs (Figures 1 and 2 of Appendix C).

Estimated mean sediment concentrations in the <0.25 mm fraction were calculated from multiple samples collected at the Leadwood site at 2680 ppm, 9781 ppm and 170 ppm, with PEQ values of 20.9, 21.3 and 34.2, for Pb, Zn, and Cd, respectively. Maximum Pb, Zn, and Cd PEQ values at Leadwood were 30.9, 47.7, and 77.0, respectively (Table 4). Caution should be used in evaluating the upper limits of the < 0.25 mm fraction results, since they are transformed from correlations between ICP-MS and XRF analyses, and bulk and <0.25 mm metals results. Samples collected at RM 113.3 and 113.2 were located just below the confluence of Eaton Branch, which drains the Leadwood Tailings Pile. This tributary heavily influences metal concentrations at these locations (Figure 5).

Concentrations of Pb, Zn, and Cd decline rapidly below the confluence of Eaton Branch, but are still highly elevated (PEQ of 22.0, 3.7, and 6.4, for Pb, Zn, and Cd, respectively) (Table 4) over 25 km (16 mi) below Leadwood at Hwy K. Lead concentrations in the <0.25 mm fraction decline gradually with distance downstream, but remain above the PEC to the confluence with the Meramec River. Zn and Cd concentrations show a more rapid decline with distance downstream, but remain above their respective PECs until the Brown's Ford site, over 96 km (60 RM) below Leadwood.

Bulk XRF Ba averaged between 150 to 300 ppm, with the exception of two distinct peaks (601 ppm Ba at RM 50.9 and 1533 at RM 75.5) below the confluence of Mill Creek and Mineral Fork tributaries, respectively (Figure 6). These tributaries drain $BaSO_4$ mining areas from the Washington County Lead Mining District. The most upstream Ba peak was at Hwy CC at Blackwell, which is just over .80 km (0.5 mi) below the confluence with Mill Creek. The downstream peak occurred at Brown's Ford, which lies approximately 15 mi downstream from

Mineral Fork. Several other tributaries draining Washington and Jefferson County $BaSO_4$ and Pb mining sites enter the Big River in this approximately 24 km (15 mi) reach without an associated Ba or Pb peak. There are less pronounced peaks in Pb concentrations co-located with these Ba peaks. However, Pb concentrations within the $BaSO_4$ influenced tributaries themselves are not elevated in Pb. Accordingly, Mill Creek and Mineral Fork were determined to be major loading sources of Ba to the Big River, but not Pb (Figure 3).

Meramec River sediments collected in 2008 did not exceed the PECs at any sampling point. Sediments collected at the Jedburg high water island site (Meramec River Mile 29.50) approached but did not exceed the PEC for Pb (Pb =122 ppm, Zn = 71 ppm). Results from the Meramec River field screening can be found in Table 2 of Appendix C.

2. Sediments collected above and below mill dams

Sediment sampling conducted in 2007 identified mill dams located in the lower Big River in Jefferson County as potentially important fine sediment traps (Table 3 of Appendix C). Trapping efficiency was expected to be reflected in metal concentrations in samples collected above and below mill dams. Samples collected above the Byrnesville and House Springs mill dams (101 ppm and 379 ppm bulk laboratory adjusted Pb, respectively) were higher than the paired samples collected below the dams (89 ppm and 76 ppm bulk lab adjusted Pb, respectively). Samples collected below the Morse Mill dam (377 ppm laboratory adjusted Pb) and the Byrnes Mill dam (212 ppm Pb in the eddy pool and 163 ppm Pb, 45.7 km [50 yards] below dam) were higher than the respective samples collected above the mill dam. The mill dams at Byrnesville and House Springs are more intact and presumably better sediment traps than the Morse Mill and Byrnes Mill dams. The Morse Mill dam appeared physically degraded since sampling in 2007 and this was reflected in 2007 results discussed below.

3. Comparison of Big River sediment metals in 2007 vs. 2008.

There is good general agreement between the longitudinal distribution of metals in the Big River in the 2007 (Mosby *et al.* 2008; Table 4 of Appendix C) and 2008 sample results. Sediment data collected in 2007 indicated bulk Pb concentrations above the PEC from the Desloge tailings impoundment to the Byrne's Mill Dam site, a length of more than 120 km (75 river mi). Bulk sediment data from 2008 indicated exceedances of the PEC for Pb from the Leadwood tailings impoundment to the Klondike Road site below Morse Mill, a length of approximately 136 km (85 river mi).

At the Morse Mill Dam site in Jefferson County, 2007 sediment samples indicated roughly similar concentrations of Pb in bulk sediments above the mill dam (199 ppm) and below (224 ppm). Conversely, 2008 sediment samples revealed a large difference in bulk Pb concentrations above (145 ppm) and below (330 ppm) the mill dam. Significant flooding during the spring months of 2008 may have contributed to the degradation of the Morse Mill dam and potentially the downstream migration of contaminated sediments in the Big River.

4. Sediment particle size distribution

Table 5 of Appendix C contains the size fraction distribution by weight percent as gravel (>2mm), medium to coarse sand (2mm-0.25 mm), fine sand (250-63 micron), and silt to clay (<63 micron). Gravel and/or coarse sand dominated the sediment collected at all sites except above the House Springs mill dam (Rockford Beach). Silt made up a very small percentage of the sediment fraction, except below Morse Mill (6.85%) and especially above House Springs mill dam (25.4%). Notably the silt content in samples collected at highly contaminated sites at Leadwood (0.54%), Hwy K (0.65%), and Hwy E (1.37%) was similar to the reference site above Irondale (0.58%) and the low-level contaminated site 0.25 mi above the confluence with the Meramec (1.36%).

5. *ICP metals distribution by size fraction*

Metals were analyzed in the >2mm, 2mm-0.25 mm, 250-63 micron, and <63 micron size fractions Figures 7-10). In general, the metals concentrations in the finest fraction (<63 µm) were the highest concentration at all sites. Lead concentrations in the <63 micron fraction exceeded the PEC by 7 fold (907 mg/kg) all the way to the confluence with the Meramec River. The finest fraction was the highest in concentration for all metals of interest at all locations with the exception of Ba at Hwy CC and in the Mineral Fork, and Cd at Leadwood. These locations are close to mining sources of metals, so the higher concentrations in coarser fractions are not unexpected. The Leadwood sample was collected just below the confluence of Eaton Branch. The Hwy CC and Mineral Fork samples were collected either just below or within tributaries affected by $BaSo_4$ mining.

Bulk sample metal results were consistently lower than any given size fraction that contains the highest concentration of metals. This indicates that using only bulk sample results to evaluate metals distribution or potential biological effects significantly underestimates contamination and its potential biological availability in the Big River.

6. *Overall Diversity and abundance of mussels in the Big River and reference locations*

Timed mussel surveys were conducted at 19 survey reaches in the Big River and 2 reference locations outside of the Big River (Meramec and Bourbeuse rivers) between August and October 2008 (Table 2). A total of 2198 living specimens were found representing 33 unionid species in the Big River (Table 5). The most abundant unionid species found in the Big River (percentage of total live catch) were: *Actinonaias ligamentina* (mucket) (43.4%), *Elliptio dilatata* (spike) (14.6%), *Lampsilis cardium* (pocketbook) (7.5%), *Amblema plicata* (three ridge) (6.9%), and *Cumberlandia monodonta* (spectaclecase) (5.2%). With the exception of *L. cardium*, the majority of individuals of these species were found at the lower 3 Big River sites (Table 1 of Appendix D). Nine species of conservation concern were found in the Big River including 2 federally endangered species (*Lampsilis abrupta* [pink mucket] and *Leptodea leptodon* [scaleshell]) and 1 federal candidate (*C. monodonta*). Of the 33 species found, 27 were represented by living individuals and 6 species were only represented by dead shells (*Alasmidonta viridus* [slippershell], *Elliptio crassidens* [elephantear], *L. abrupta*, *L. leptodon*, *Pyganodon grandis* [giant floater], and *Toxolasma parvus* [lilliput]). Timed survey results for survey reaches in the Meramec and Bourbeuse rivers are summarized in Table 2 of Appendix D.

7. Distribution and abundance of federally listed mussel species

One objective of this assessment was to determine the current status and distribution of federally listed mussel species known to occur in the Big River. The habitat and distribution of these species are discussed below followed by the timed survey results of the current study.

Lampsilis abrupta: The federally endangered pink mucket inhabits medium to large rivers, but is most associated with larger rivers. It has been reported in habitats ranging from silt to boulders, rubble, gravel, and sand substrates in moderate to fast-flowing water at depths ranging from 0.5 to 8.0 meters (U.S. Fish and Wildlife Service [USFWS 1985]). It historically occurred in the Tennessee, Ohio, and Cumberland River basins with occasional records from the Mississippi River drainage. While the species was widespread, it never was known to occur in large numbers from any one location, and, therefore, it has usually been considered rare (USFWS 1985). In Missouri, it has been reported from the lower reaches of the Osage, Gasconade, Meramec, and Big rivers (Buchanan 1979*b*, Grace and Buchanan 1981, Roberts and Bruenderman 2000), and from the St. Francis, Sac, Black, and Little Black rivers (Buchanan 1979*a*, MDC Unpubl. Mussel Database). The Meramec and Osage rivers in Missouri, along with the Tennessee and Cumberland rivers in Tennessee, are believed to support the largest remaining populations of the species (USFWS 1985).

In the Meramec River basin, living pink mucket was originally known only from the lower 88 km (55 mi) of the Meramec River. The pink mucket is rare in the Big River and, at present, appears to be restricted to the lower 8 km (5 river mi). The first report of the species in the Big River was a subfossil specimen at RM 4.8 (Buchanan 1979*b*). In 1997, a living specimen was collected at RM 1.3 (Roberts and Bruenderman 2000). Subsequently, 8 living specimens were collected at RM 1.3 during 6 visits to the site between 2001 and 2002 (MDC Unpubl. Mussel Database). In the present assessment, no living individuals were found in the Big River, but a weathered dead shell was collected at RM 1.3. One living and one subfossil specimen were collected in the Meramec and Bourbeuse river sites respectively.

Leptodea leptodon: The federally endangered scaleshell occurs in medium to large rivers and is primarily found in stable riffles and runs with slow to moderate current velocity (USFWS 2004). It is considered a typical riffle species, occurring only in clear, unpolluted streams with stable substrate (Oesch 1995, USFWS 2004). The species was historically wide-ranging within the Mississippi River drainage and occurred in 56 rivers in 13 states (USFWS 2004). Currently, the only streams where the species can be found with any consistency, although still rare, are in three Missouri streams: the lower Meramec, Bourbeuse, and Gasconade rivers.

In the Meramec River basin, the scaleshell is known from the lower 180 km (112 mi) of the Meramec River and lower 124 km (77 mi) of the Bourbeuse River (Buchanan 1979*b*, Roberts and Bruenderman 2000). In the Big River, the species has a more restricted distribution to the lower reach of the river, where it has only been documented from the lower 16 km (10 mi). It has been collected at RM 0.4 and 10.3 in 1978 and 1980 respectively (Buchanan 1979*b* and MDC Unpubl. Mussel Database). More recently, the scaleshell has been collected alive in 1997 from the Big River at RM 1.3 (Roberts and Bruenderman 2000) and in 2002, a dead specimen was also collected from the same site (MDC database). In the present study, only a single fresh-dead shell was found in the Big River at RM 10.3; no other evidence of the species was found in the Big River. Six and 4 living specimens were found in the Meramec and Bourbeuse river sites respectively.

Plethobasus cyphyus: The sheepnose is currently a candidate species proposed for federal listing. It occurs in medium to large rivers in gravel or in mixtures of sand and gravel (Cummings and Mayer 1992). Its distribution includes the Ohio, Cumberland, and Tennessee River systems and the Mississippi River drainage west to Iowa and north to Minnesota (Burch 1973). Its current distribution in Missouri includes the Whitewater, Gasconade, Meramec, and Bourbeuse rivers (Buchanan 1979*b*, Buchanan 1994, MDC Unpubl. Mussel Database).

In the Meramec River basin, it occurs throughout the lower 241 km (150 mi) of the Meramec and lower 144 km (90 mi) of the Bourbeuse Rivers. In the Big River, this species is restricted to the lower reach; a living specimen was found in 1978 at RM 4.8 and subfossils shells were collected at 0.4 and 14.4 (MDC Unpubl. Mussel Database). No evidence of the sheepnose mussel was found in the Big River during the present study. However, it was found at both sites surveyed in the Meramec and Bourbeuse rivers where 20 and 2 living specimens were found respectively.

Cumberlandia monodonta: The spectaclecase is a candidate proposed for federal listing. The spectaclecase has been collected from a variety of habitats in medium to large rivers (Parmalee 1967, Stansbery 1973). In the Meramec River basin, it has been found in rubble and boulder, or boulder substrate in shallow (less than 1 meter in depth) or deeper water (up to 4 m). In the Meramec River, the species can be found in large numbers based on specimens that were observed crowded into a small space between or under rocks (Buchanan 1979*b*, Roberts and Bruenderman 2000). The spectaclecase is generally distributed in the Cumberland and Tennessee River systems and the Mississippi River drainages from Minnesota and western Pennsylvania south to the Gulf of Mexico (Burch 1973, Parmalee and Bogan 1998). Possibly the largest population in North America exists in Missouri in the Meramec and Gasconade rivers (Buchanan 1979*b*). It also occurs, although not abundant, in the Bourbeuse, Big, Osage, and Salt rivers and in Joachim Creek (Utterback 1917, Buchanan 1980). Utterback (1917) reported it from the Mississippi River, northwest Missouri lakes, and in the Osage and Platte River basins.

In the Meramec River basin, the spectaclecase is most common in the Meramec River where it is found throughout the stream, and has only been collected from 1 site in the Bourbeuse River (Buchanan 1979*b*, Roberts and Bruenderman 2000). In the Big River, it has been collected live from RM 1.3 (Roberts and Bruenderman 2000) and a subfossil shell has been reported from RM 0.4 (Buchanan 1979*b*). In the present survey, the spectaclecase was observed at RM 1.3 where 115 living specimens were found. It was not found living at the Meramec or Bourbeuse river survey sites, but a subfossil specimen was collected at the Meramec River site.

8. Mussel community comparisons of reference sites vs. sites downstream of mining areas

Both timed and quantitative mussel survey data show that mussel populations are suppressed below mining areas in the Big River. Results of timed surveys at sites in the Big River showed reductions in mussel species richness and CPUE that correspond to elevated sediment Pb concentrations in much of the Big River downstream of mining areas (Figures 11 and 12). Based on the regression of mussel species richness vs. river mile for the Big River, 15 of 18 sites located downstream the mining areas fell below the reference envelope (lower 95% confidence interval) and can be considered impacted relative to the historic reference condition (Figure 13). These sites occur in a reach that extends from Leadwood (RM 113) downstream to Byrnesville (RM 14.4). In contrast, mussel species richness at the upstream reference site (Irondale) and the three sites furthest downstream from mining areas fell within the reference envelope.

Freshwater mussel densities estimated by quantitative sampling also showed pronounced differences between sites below mining areas and reference sites. A total of 236 living mussels representing 24 species were found while excavating 538 0.25 m^2 quadrats at 8 sites. These sites include 6 sites downstream from mining in the Big River, 1 reference site in the Big River upstream of mining areas, and 1 reference site in the Bourbeuse River (Table 2). Maximum recorded densities at both reference sites (44 and 12 mussels per m^2 at the Bourbeuse River and Big River reference sites respectively) is contrasted with maximum densities at sites below mining areas of 4 mussels per m^2. Mean mussel densities at all quantitative study sites downstream of mining areas were significantly lower than at reference sites (One way ANOVA with rank-transformed data [$p<0.0001$] and Tukey's test for pair-wise comparisons of the means) (Table 6). These differences are pronounced as the mean mussel densities at the downstream-most sites (RM 30.5 and 20.2) are much lower than the upper reference site (RM 129). Given the natural increasing trend in mussel abundance with distance downstream, mussel density would be expected to be much lower at the reference site compared to the downstream impacted most sites.

9. Mussel community comparisons of past and present mussel data

In 1979 an extensive mussel survey was conducted on the Big River (Buchanan 1979*b*). The availability of this survey data allows general comparisons of mussel species richness and CPUE between the past and present sampling results to be made. However, only gross differences in CPUE between the surveys are noted because of possible differences in sampling efficiency (i.e., Buchanan [1979*b*] often employed water scopes, which are less efficient than the snorkeling used in the present study).

The marked decline of mussels downstream of mining areas observed in the present study is consistent with past mussel survey results. Buchanan (1979*b*) also showed a clear decline in species richness and CPUE of mussels beginning at sites directly downstream of mining areas (Figure 14). The present study and Buchanan (1979*b*) show a similar species richness at each site throughout the river (Figure 15). However, species richness at the lowest site (RM 10.3) was considerably higher in the present study. This could be an indication that sampling was more efficient in the present study because mussels were found to be much less abundant at this site. The similar overall species richness among sites between the surveys is expected because the mussel fauna was already impacted at the time of Buchanan (1979*b*), which was conducted after a major dam collapse released large amounts of lead tailings into the Big River. The two surveys also had similar CPUE among sites throughout most of the river, with the exception of RM 28.3, 10.3, and 14.4) (Figure 15). The sites at RM 10.3 and 14.4 had a CPUE of 70 and 24, respectively, in 1979, and 36.4 and 3.1 mussels per person-hour, respectively. This difference in CPUE could be an indication that contamination has recently increased at these sites due to downstream migration of lead tailings, and is currently impacting mussel populations there. The reach at RM 28.3 appears to have been a strong-hold for mussels in 1979, but live mussels were not found at that site in 2008 and only shell material remained.

Discerning any trends in the presence of individual species and metal contamination among sites is difficult because species richness naturally increases from upstream to downstream. Some species have broad distributions longitudinally, while others are naturally restricted to upper or lower stream reaches. Species that are present at reference sites above mining impacts are a mixture of broadly distributed and headwater species. The absence of both these species groups is evident at sites close to mining areas during both present and Buchanan's study (Buchanan 1979b) (Figure 16 and 17). The downstream distribution of these species ends abruptly at the point of mining impacts. The distribution of the broadly distributed species then recovers at some distance downstream. This trend can be easily seen in *Alasmidonta marginata* (elktoe), *E. dilata*, *L. cardium*, *Lasmigona costata* (flutedshell), *Strophitus undulatus* (creeper), and *Venustachoncha ellipsiformis* (ellipse) (Figure 16 and 17). The gap in distribution is larger in some species than others suggesting that species differ in their sensitivity to heavy metals. For example, *S. undulatus* was not found upstream from RM 66.3, but was common at the sites upstream of mining areas in both studies. In contrast, the distribution of *L. cardium* recovers within a shorter distance and appears to be one of the most tolerant species to metals in the Big River. This species has also been suspected to be the most metal-tolerant species in other similar studies (Angelo 2007).

10. Habitat evaluation

Physical habitat scores varied among the mussel survey sites in the Big River, ranging from 165.7 (82.9% of the theoretical maximum score) at RM 129 to 103.7 (51.9% of the theoretical maximum) at RM 75.5 (Table 7, Figure 18). Physical habitat scores at 2 sites in the Meramec and Bourbeuse rivers were 158.3 (79.2% of theoretical maximum) and 137.7 (68.9% of theoretical maximum) respectively (Table 8). The average score among all sites, including reference sites was 138.1 (69.0% of the theoretical maximum).

11. Mussel community associations with sediment metals and habitat quality

a. Rank correlation analysis

Characteristics of mussel communities in the Big River and reference sites were significantly correlated with metal concentrations in sediments ($p = 0.05$). Rank correlation coefficients for both species richness and CPUE of live mussels collected during timed searches indicated significant negative associations with Pb, Zn, and Cd in both bulk sediments (<2 mm fraction) ($p = 0.05$) and fine sediments (<0.25 mm) ($p = 0.05$) (Table 9). These correlations indicated significant trends for lower species richness and lower CPUE at sites with greater sediment metal concentrations.

Associations of mussel community variables with habitat parameters were less consistent. Neither species richness nor CPUE were significantly correlated (p = 0.05) with the total habitat score determined from multiple habitat parameters, as described by USEPA (Barbour *et al*. 1999) (Table 9). However, scores for 3 of the 13 individual habitat metrics (embeddedness, sediment deposition, and channel flow status) had significant, positive correlations with both mussel species richness and CPUE (p = 0.05, p = 0.05). These associations (of the habitat *scores*) indicated that mussel species richness and CPUE were greater at sites with lesser deposition of fine sediments, lesser embeddedness of coarse substrates and lesser degree to which the channel is aggraded with sediment.

The observed association between mussels and sediment deposition, embeddedness, and channel flow status is likely a reflection of large amounts of fine mine tailings present within survey reaches. These 3 habitat parameters were related to the presence of fine sediments within each survey reach. In the present study, the fine sediment observed was in the form of Pb contaminated tailings. While fine sediment can have negative physical effects to mussel habitat (i.e. can physically smother mussels), it was largely observed in pools and depositional areas within the survey reaches. Significant deposition of tailings was not often seen in suitable mussel habitat where most mussel species occur (well established riffles and runs). However, sand particles intermixed with gravel was usually a significant component of substrates throughout the other habitats of the survey reaches (Table 5 of Appendix C). While fine silt (< 63μm) could adversely affect substrate for mussels, sand particles mixed with gravel (and not burying gravel) are the typical substrate supporting diverse mussel beds in the Meramec River and are thought of as a favorable substrate for mussels, unless contaminated (Buchanan 1979*b*, Roberts and Bruenderman 2001). Silt was a minor constituent (ranging from 0.58 to 3.10%) of the substrate of the mussel habitat sampled, and the only areas of elevated silt fraction were associated with mill dams (Table 5 of Appendix C).

The correlation analysis does not provide complete information on the relative importance of metal contamination and habitat parameters in determining mussel community status. The strength of significant positive correlations of mussel variables with habitat variables (r-values from 0.467 to 0.830) was similar to correlations of mussel variables with sediment metals (r-values from -0.526 to -0.824). These similar associations are not surprising, because scores for the habitat variables mentioned above had significant negative correlations with all metal variables tested (r-values from -0.479 to -0.645; data not shown).

b. Principal components analysis

In an attempt to better understand interactions among mussel community impacts, metal contamination, and habitat parameters, we conducted principal components analysis on the correlations among the 2 mussel variables, 3 significant habitat variables, and metal concentrations in the fine sediment fraction. This analysis allowed us to express 83% of the total variation in the dataset in terms of 2 new variables, or principal components (PC1 and PC2), each of which represented the influence of multiple variables (Figure 19). The mussel sampling sites fell along a gradient along PC1 (the X-axis), which explains 67% of the total variation in the data. Sites with negative values for PC1 had impacted mussel communities and high sediment metal concentrations, whereas sites with positive values on PC1 axis had relatively unimpacted mussel communities, low metal concentrations, and high values for the habitat indices. Sites with the most negative values for PC1 were Big River sites immediately downstream of the Desloge-Flat River mining area, whereas sites with the most positive values were reference sites farther downstream on the Big River. PC1 did not provide information about the relative contribution of metals and habitat, because these two groups' variables fell into tight groups on opposing ends of the axis. PC2 (Y axis, Figure 19), explained a much smaller proportion of the total variation (16%). Dispersal of sites along this axis suggested a small interaction of metals and habitat influences, with embeddedness falling on the opposite (negative) end of the axis from both high metal concentrations and high values for mussel community variables. One interpretation of this contrast is that mussel communities at sites with negative values on PC2 (e.g. sites B2, B10, and B13-B16) may be influenced by a combination of moderately high metal contamination and low embeddedness.

c. Multiple regression analysis

Multiple regression analysis quantifies the contributions of multiple explanatory variables (such as metal concentrations and habitat variables) to values of variables of interest (such as mussel species richness and CPUE). Multiple regression analysis with forward selection starts with the strongest single explanatory variable and continues to add additional variables as long as they significantly improve the model. Results of multiple linear regression analyses produced similar models for predicting species richness and CPUE. In both cases, the forward-selection process produced two-parameter models that included 1 metal variable and 1 habitat variable. These models explained 67% of the variation in species richness and 68% of the variation in CPUE. For species richness, the explanatory variables were Zn in fine sediments and channel flow status. For CPUE, the explanatory variables were Cd in fine sediments and channel flow status. Although the strongest explanatory variables were different for the two-variable models (Zn for species richness, channel flow status for CPUE), single-variable models with either the metal variable or the habitat variable had similar explanatory power (range: 47% to 58%).

d. Integrated discussion of statistical analyses

All three statistical analyses discussed above (rank correlation, principal components, and multiple regression) indicated that indicators of mussel community status (species richness and abundance) had significant ($p = 0.05$) negative relationships with metal concentrations in sediments. Mussel community status was not significantly associated with overall habitat scores, but both species richness and CPUE had significant positive associations with scores of habitat variables including sediment deposition, coarse substrate embeddedness, and channel flow status.

Available statistical methods cannot determine the relative contribution of metal contamination and habitat quality to the overall status of mussel communities in the study area. This is due to the strong inter-correlation of mussel community variables, habitat variables, and sediment metal concentrations. To a large extent, sites with the most degraded mussel communities had highest concentrations of Zn, Cd, and Pb in sediments. These sites also possessed higher levels of embeddedness, sediment deposition, and channel flow status. However, as previously stated above, sand-sized particles (typical of St. Francois County mine tailings) that contributed to these habitat parameters, did not pose a physical habitat problem in suitable mussel habitat within survey reaches. This suggests that habitat parameters were not the primary constraint on mussel species richness and CPUE. Further, the pronounced increase in both mussel species richness and CPUE in the lower reaches of the Big River coincided with a sharp decline in Pb and Zn concentrations in bulk sediments (Figure 11 and 12). In contrast, habitat scores in this stream reach remained within the range observed at upstream locations and did not differ greatly across the study sites (range of scores: 10.7 to 17.7 out of possible 20) (Figure 18). This strongly suggests that metal toxicity is a predominate factor in limiting mussel species richness and CPUE in the areas within the 20 sites sampled.

The results of this assessment are consistent with other studies. Angelo *et al.* (2007) also documented the reduction or elimination of mussel communities in streams with metal-contaminated sediments in the Spring River basin in Kansas and Missouri. The toxicity of high sediment metal concentrations to juvenile freshwater mussels has been well documented in laboratory studies (Keller and Zam 1991, Naimo *et al.* 1992, Naimo 1995, Wang *et al*. 2007*a*, Wang *et al*. 2007*b*, Besser *et al*. 2009, Wang *et al*. In Prep.). Specifically, Besser *et al*. (2009) found that mussel toxicity in the laboratory was strongly associated with metal concentrations (Zn, Cd, and Pb) in Big River sediments. These results corresponded closely to the reduced mussel taxa richness in field surveys in this assessment. Laboratory results by Besser *et al.* (2009) agreed with mussel field survey results for 80% of sites that are common to both studies (Figure 1).

CONCLUSIONS

Big River sediment is extensively contaminated with toxic metals from historic Pb mining operations in terms of both magnitude of concentration and downstream extent. Specifically:

- Maximum Pb concentrations in the <0.25 mm fraction exceeded 4000 ppm sediment <0.25 mm exceeded 2000 ppm Pb in over 24 km (15 mi) of stream; exceeded 1000 ppm in over 96 km (60 mi) of stream; and exceeded the PEC for Pb (128 mg/kg) all the way from the upstream extent of mining in St. Francois County to the confluence with the Meramec over 180 km (113 mi) downstream.
- Zn and Cd contamination is severe just below the uppermost St. Francois County mining inputs from the Leadwood site. Estimated mean maximum sediment concentrations in the <0.25 mm fraction were 9781 ppm and 170 ppm, with a PEQ of 21.3 and 34.2, for Zn and Cd, respectively. Although Zn and Cd concentrations decline dramatically downstream from Leadwood, they still exceeded PECs for approximately 80 km (50 river mi).
- Pb, Zn, and Cd are concentrated in the <63 µm grain size fraction at all locations, with the exception of Cd at Leadwood, which was highest between the 0.25 mm and 2 mm size fraction.
- Washington County tributaries contained elevated Ba concentrations, but not elevated Pb concentrations, and do not appear to contribute significantly to the Pb, Zn, or Cd concentrations in sediment in the Big River.

Mussel communities are significantly degraded due to releases of heavy metals to sediment in the Big River. Specifically:

- Both mussel species richness and abundance had significant negative correlations with heavy metal contamination in sediment.
- Both mussel species richness and CPUE had significant positive correlations with habitat scores determined from estimates of channel flow status, coarse substrate embeddedness, and degree of sedimentation in riffles.
- Primary components analysis and regression analysis indicated that Zn and Cd concentrations were highly predictive of low mussel species richness and abundance.
- Mussel densities at all quantitative study sites downstream of mining areas were significantly lower than at reference sites
- Sites with impacted mussel communities (reduced species richness and abundance) occur in a reach that extends 158.7 km (98.6 stream mi) downstream from mining areas (river mile 113 to 14.4).
- It appears that mussel abundance has declined at two sites in the lower river (RM 10.3 and 14.4) based on CPUE of the present survey compared to past survey data suggesting that metal contamination continues to migrate downstream.

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TABLES AND FIGURES

Table 1. Freshwater mussel species found in the Big River in past and current studies (Utterback 1917, Buchanan 1979b, Roberts and Bruenderman 2000, Missouri Department of Conservation unpubl. Data).

Status: CC = Species of Conservation Concern; FC = Federal Candidate; FE = Federally Endangered

Shell condition: L = Live animal;WD = weathered shell; FD = fresh-dead shell; SF = subfossil shell

Scientific name	Common Name	State Status[2]	Federal status[2]	Previous Serverys[3]	Present Study
Actinonaias ligamentina	mucket			L	L
Alasmidonta marginata	elktoe	CC		L	L
Amblema plicata	threeridge			L	L
Cumberlandia monodonta	spectaclecase	CC	FC	WD	L
Cyclonaias tuberculata	purple wartyback			L	L
Ellipsaria lineolata	butterfly			L	L
Elliptio crassidens	elephantear	CC		-	SF
Elliptio dilatata	spike			L	L
Fusconaia ebena	ebonyshell			-	L
Fusconaia flava	pigtoe			L	L
Lampsilis abrupta	pink mucket	CC	FE	L	WD
Lampsilis cardium	pocketbook			L	L
Lampsilis reeviana brittsi	broken ray	CC		L	L
Lampsilis siliquoidea	fat mucket			L	-
Lampsilis teres	yellow sandshell			L	L
Lasmigona complinata	white heelsplitter			L	L
Lasmigona costata	fluted shell			L	L
Leptodea fragilis	fragile papershell			L	L
Leptodea leptodon	scaleshell	CC	FE	D	FD
Ligumia recta	black sandshell	CC		L	L
Megalonaias nervosa	washboard			L	L
Obliquaria reflexa	three-horn wartyback			L	L
Plethobasus cyphyus	sheepnose	CC	FC	L	-
Pleurobema sintoxia	round pigtoe			L	L
Potamilus alatus	pink heelsplitter			L	L
Potamilus ohiensis	pink papershell			L	-
Pyganodon. grandis	giant floater			L	SF
Quadrula metanevra	monkeyface			L	L
Quadrula pustulosa	pimpleback			L	L
Strophitus u. undulates	creeper			L	L
Toxolasma parvus	lilliput			L	SF
Tritogonia verrucosa	pistolgrip			L	L
Truncilla donaciformis	fawnsfoot			WD	L
Truncilla truncate	deertoe			L	L
Utterbackia imbecillis	paper pondshell			L	-
Venustaconcha ellipsiformis	ellipse			L	L

Table 2. Sediment and mussel survey sites in the Big, Bourbeuse, and Meramec rivers that were sampled in 2008.

					Sample collections			Mussel Surveys	
Site Name	River Mile	River Name	County	Site Description	Sediment	QC Sample	Sieved Sample	Timed	Quantitative
CON	0.3	Big	Jefferson	1/4 mi above confluence w/Meramec (CERC #18)	X	X	X		
HW	1.3	Big	Jefferson	Hwy W (CERC #17)	X			X	
BMB2	8.2	Big	Jefferson	400 yards below Byrne's Mill Dam	X			X	
BMA	8.5	Big	Jefferson	Above Byrne's Mill Dam	X				
RBB	10.3	Big	Jefferson	Below House Spring's Rockford beach (CERC #14)	X			X	
RBA	10.7	Big	Jefferson	Above House Spring's Mill Dam/Rockford Beach (CERC #13)	X		X		
BVB	14.4	Big	Jefferson	Below Byrnesville Mill Dam	X			X	
BVA	14.7	Big	Jefferson	Byrnesville Above Mill Dam	X				
CHB	20.2	Big	Jefferson	Below Cedar Hill Mill Dam (CERC #12)	X			X	X
BC	20.8	Big	Jefferson	Below Belew Creek	X			X	
KR	28.3	Big	Jefferson	Klondike Road	X			X	
MMB	30.5	Big	Jefferson	Below Morse Mill	X	X	X	X	X
MMA	30.7	Big	Jefferson	Above Morse Mill	X	X	X		
BF	50.9	Big	Jefferson	Brown's Ford (CERC #10)	X			X	
MA	62.7	Big	Jefferson	Mammoth Access (CERC #9)	X			X	
WSP	65.7	Big	Jefferson/ Washington	Washington State Park (above Mineral Fork)	X			X	
MC	NA	Mill	St. Francis	Mill Creek near confluence	X				
CC	75.5	Big	Jefferson/ St. Francois	Big River Hwy CC (Below Mill Creek) (CERC #7)	X			X	
CL	79.6	Big	Jefferson/ St. Francois	Cole's Landing	X			X	
HE	87.7	Big	St. Francois	Hwy E Below St. Francois State Park (CERC #6)	X	X	X	X	
67C	90.1	Big	St. Francis	Hwy 67 North of Bonne Terre (CERC #5)	X			X	
HK	96.7	Big	St. Francois	Below Flat River at Hwy K (CERC #4)	X	X	X	X	X
67D	102.7	Big	St. Francois	Above Flat River at Hwy 67 (CERC #3)	X			X	
LW	113	Big	St. Francois	Below Leadwood (CERC #2)	X	X	X	X	X
ID	129	Big	Washington	Above Irondale-Below Cedar Creek (Reference) (CERC #1)	X	X	X	X	X
MPP	51	Meramec	St. Louis	Meramec at Pacific Palisades (CERC #19)	X			X	
MTB	33.5	Meramec	St. Louis	Times Beach (CERC #20)	X				
BTB	32.3	Meramec	St. Louis	Meramec Below Times Beach (leading edge)	X				
Bref	0.4	Bourbeuse	Franklin	Bourbeuse reference site (CERC #21)	X	X		X	X

Table 3. Sediment Analytical Parameters for lead, zinc, cadmium, barium, and nickel for 2008 Big River sediment samples.

Sample Type	Stream	Analytical Method	Operator	Analytes	Fraction analyzed
Leading Edge Definition	Meramec River	Field XRF	USFWS	Pb, Zn, Cd, Ni, Ba	Bulk
Extent of contamination characterization	Big River	Laboratory XRF	USFWS	Pb, Zn, Cd, Ni, Ba	Bulk and <0.25 mm
QC samples	Big River	Laboratory XRF	USFWS	Pb, Zn, Cd, Ni, Ba	Bulk and <0.25 mm
QC samples	Big River	Laboratory ICP-MS	USGS-CERC	Pb, Zn, Cd, Ni, Ba	<62 µm, 62-250 µm, 250 µm-2mm, >2 mm, and Bulk fractions

Table 4. Probable effects quotients (PEQs) determined from concentrations of metals in Big River sediments sampled in 2008. Concentrations used for PEQ calculation were from analysis of the <0.25 mm particle size fraction. Site identifiers are defined in Table 1.

Site Name	River Mile	Pb PEQ	Zn PEQ	Cd PEQ
ID	129.0	0.6	0.1	0.1
LG	117.8	0.6	0.2	0.0
LWR	113.4	1.0	0.3	0.1
LWE	113.3	27.1	47.7	77.0
LWE2	113.2	30.9	36.9	59.5
LW	113.0	21.9	3.2	6.3
LWI	113.0	20.9	21.3	34.2
67D	102.7	19.1	4.2	6.4
HK	96.7	22.0	3.7	6.4
67C	90.1	10.6	1.7	2.8
HE	87.7	13.7	2.3	3.5
CL	79.6	11.3	2.0	2.9
SB	NA	3.6	3.4	5.1
MC	NA	3.0	2.9	4.3
CC	75.5	17.5	1.6	1.9
WSP	65.7	11.4	1.1	1.4
MFK	NA	2.0	0.8	0.2
MFC	NA	3.1	0.7	0.3
MA	62.7	10.6	1.1	1.3
BF	50.9	12.9	1.0	0.6
MMA	30.7	6.5	0.8	0.9
MMB	30.5	7.3	0.4	0.3
KR	28.3	3.7	0.5	0.4
BC	20.8	1.0	0.1	0.0
CHB	20.2	3.1	0.4	0.4
BVA	14.7	2.6	0.4	0.2
BVB	14.4	2.0	0.2	0.0
RBA	10.7	5.3	0.7	0.5
RBB	10.3	1.4	0.2	0.1
BMA	8.5	3.1	0.3	0.2
BME	8.4	5.5	0.5	0.4
BMB	8.3	3.4	0.4	0.2
BMB2	8.2	2.9	0.3	0.1
HW	1.3	2.7	0.3	0.2
CON	0.3	2.8	0.3	0.3
Bref	N/A	0.2	0.1	0.1
BU	N/A	0.4	0.3	0.2
MPP	N/A	0.3	0.1	0.0
MTB	N/A	0.5	0.1	0.0

Table 5. Relative abundance and number of sites at which each mussel species was found living during timed sampling in the Big River.

s = species represented by shell material only
* = less than 0.1

Species	Total No.	% of Total	No. Sites	% sites
Actinonaias ligamentina	953	43.4	6	31.6
Elliptio dilatata	321	14.6	6	31.6
Lampsilis cardium	165	7.5	14	73.7
Amblema plicata	151	6.9	4	21.1
Cumberlandia monodonta	115	5.2	1	5.3
Lampsilis reeviana brittsi	92	4.2	6	31.6
Venustachoncha ellipsiformis	66	3.0	4	21.1
Pleurobema sintoxia	64	2.9	3	15.8
Ligumia recta	44	2.0	4	21.1
Quadrula pustulosa	38	1.7	6	31.6
Potamilus alatus	27	1.2	8	42.1
Obliquaria reflexa	24	1.1	4	21.1
Fusconaia flava	23	1.0	5	26.3
Alasmidonta marginata	21	1.0	4	21.1
Ellipsaria lineolata	17	0.8	3	15.8
Lasmigona costata	15	0.7	3	15.8
Megalonaias nervosa	14	0.6	3	15.8
Cyclonaias tuberculata	10	0.5	1	5.3
Strophitus undulatus	10	0.5	4	21.1
Truncilla truncata	10	0.5	2	10.5
Leptodea fragilis	4	0.2	3	15.8
Tritogonia verrucosa	4	0.2	1	5.3
Quadrula metanevra	3	0.1	1	5.3
Truncilla donaciformis	3	0.1	1	5.3
Fusconaia ebena	2	0.1	1	5.3
Lampsilis teres	1	*	1	5.3
Lasmigona complinata	1	*	1	5.3
Elliptio crassidens	s	-	0	-
Lampsilis abrupta	s	-	0	-
Leptodea leptodon	s	-	0	-
Pyganodon grandis	s	-	0	-
Toxolasma parvus	s	-	0	-

Table 6. Statistical results for mean mussel density for quantitative survey sites in the Big River.
*Means with same letter are not significantly different (One way ANOVA with rank-transformed data [p<0.0001] and mean comparisons with Tukey's test).
**Due to the extended length and available suitable habitat, two different quantitative sample reaches were chosen to sample in this site.

				Mussels in quadrat counts				
Site Name	Stream	River Mile	Mean mussel density (mussels per square meter)	n	Standard error	Minimum	Maximum	Tukey's test*
ID	Big	129	1.9	58	0.36	0	12	b
LW	Big	113	0.1	60	0.07	0	4	c
HK	Big	96.7	0.0	79	0.00	0	0	c
HK**	Big	96.7	0.0	60	0.00	0	0	c
MA	Big	62.7	0.0	41	0.00	0	0	c
MMB	Big	30.5	0.4	80	0.14	0	4	c
CHB	Big	20.2	0.2	77	0.09	0	4	c
Bref	Bourbeuse	0.4	9.1	83	1.21	0	44	a

Table 7. Physical habitat scores for 19 mussel survey sites evaluated in the Big River in 2008. Habitat assessment was performed concurrently with mussel surveys, using methodology of Barbour et al. 1999 for high gradient streams. Values represent a mean of estimates determined independently by three surveyors.

	Big River Mussel Survey Sites																		
Habitat parameter	1.3	8.2	10.3	14.4	20.2	20.8	28.3	30.5	50.9	62.7	65.7	75.5	79.6	87.7	90.1	96.7	102.7	113	129
Epifaunal substrate/ cover	15.0	14.0	10.0	10.7	17.0	17.0	16.3	15.3	12.7	13.3	12.7	7.7	14.3	14.3	7.5	15.7	7.3	12.0	16.7
Substrate embeddedness	17.3	14.5	14.0	12.3	13.7	14.0	15.3	15.7	11.7	15.3	9.3	5.3	12.0	12.0	8.5	8.3	4.7	12.0	13.7
Velocity/depth regime	14.3	17.0	15.3	15.3	17.3	19.0	15.7	17.0	14.7	18.0	16.7	12.7	16.7	18.7	14	15.7	16.0	15.7	16.3
Sediment deposition	17.7	14.0	8.7	13.0	8.3	13.5	16.7	14.7	9.3	8.7	9.3	8.0	13.0	10.7	7.5	8.7	6.3	10.7	16.0
Channel flow status	16.7	16.0	15.0	15.3	15.3	14.0	16.3	15.0	15.7	12.0	12.7	13.7	13.7	13.0	13	11.3	14.0	10.7	17.0
Channel alteration	16.7	16.5	15.3	17.7	14.0	19.5	16.0	14.7	16.0	17.3	15.0	13.0	16.7	16.0	16	18.0	16.0	11.7	17.3
Frequency of riffles	14.0	12.0	12.7	12.0	16.0	16.0	16.7	16.3	7.0	15.7	15.7	7.7	18.0	16.0	10	17.7	12.0	14.7	16.3
Left bank stability	6.0	6.0	7.7	7.3	6.3	7.0	8.3	7.7	7.7	7.3	8.7	4.7	6.7	7.7	5	7.3	7.0	8.7	9.0
Right bank stability	6.3	5.0	6.7	6.0	6.7	5.0	7.3	8.0	8.3	7.7	5.0	7.3	7.3	5.3	5.5	8.3	8.3	7.7	8.7
Left bank vegetation	7.3	6.5	7.0	7.3	7.7	4.5	8.7	6.0	7.7	8.0	8.0	6.0	7.7	8.0	4	6.3	7.0	8.0	9.0
Right bank vegetation	8.3	4.0	6.0	4.7	6.7	4.5	7.0	7.3	8.3	8.7	4.3	7.0	7.7	6.3	5	9.7	7.3	7.7	8.7
Left bank riparian zone width	4.3	8.0	7.3	6.3	4.3	4.5	8.7	4.3	5.3	8.0	9.0	5.3	8.0	7.7	5	4.7	6.3	6.7	9.3
Right bank riparian zone width	6.3	4.5	5.3	4.0	4.0	4.5	3.3	6.3	9.0	9.0	4.3	5.3	6.7	4.3	4.5	9.3	7.0	5.7	7.7
Total habitat score	150.2	138.0	131.0	131.9	137.3	143.0	156.3	148.3	133.3	149.0	130.7	103.7	148.3	140.0	105.5	141.0	119.3	131.7	165.7

Table 8. Physical habitat scores for two mussel reference survey sites in the Meramec and Bourbeuse rivers in 2008. Habitat assessment was performed concurrently with mussel surveys, using methodology of Barbour et al. 1999 for high gradient streams. Values represent a mean of estimates determined independently by three surveyors.

Habitat parameter	Meramec River Pacific Palisades	Bourbeuse River Reference Site
Epifaunal substrate/cover	14.7	14.0
Embeddedness	15.0	12.0
Velocity/depth regime	15.3	15.7
Sediment deposition	15.7	13.0
Channel flow status	17.7	16.0
Channel alteration	16.0	15.0
Frequency of riffles	15.3	9.3
Left bank stability	7.7	6.7
Right bank stability	8.0	5.0
Left bank vegetation	7.3	8.3
Right bank vegetation	8.7	8.7
Left bank riparian zone width	8.0	8.0
Right bank riparian zone width	9.0	6.0
Total habitat score	158.3	137.7

Table 9. Rank correlation coefficients (r) for associations between sediment metal concentrations and scores for habitat characteristics at mussel survey sites in the Big River. Values in bold text indicate significant correlations ($p<0.05$). [CPUE=catch per unit effort.]

Variable	Number of live mussel species	Live mussel density (CPUE)
Lead in bulk (<2 mm) sediments	**-0.686**	**-0.654**
Zinc in bulk (<2 mm) sediments	**-0.824**	**-0.766**
Cadmium in bulk (<2 mm) sediments	**-0.689**	**-0.603**
Lead in fine (<0.25 mm) sediments	**-0.754**	**-0.718**
Zinc in fine (<0.25 mm) sediments	**-0.526**	**-0.757**
Cadmium in fine (<0.25 mm) sediments	**-0.732**	**-0.647**
Total habitat score	0.286	0.417
Epifaunal substrate/cover	0.178	0.334
Embeddedness	**0.467**	**0.557**
Velocity/depth regime	-0.185	-0.208
Sediment deposition	**0.572**	**0.628**
Channel flow status	**0.714**	**0.830**
Channel alteration	0.058	-0.006
Frequency of riffles	-0.273	-0.141
Left bank stability	-0.049	-0.073
Right bank stability	-0.211	-0.076
Left bank vegetation	0.081	0.101
Right bank vegetation	0.081	0.161
Left bank riparian zone width	0.094	0.034
Right bank riparian zone width	0.099	0.098

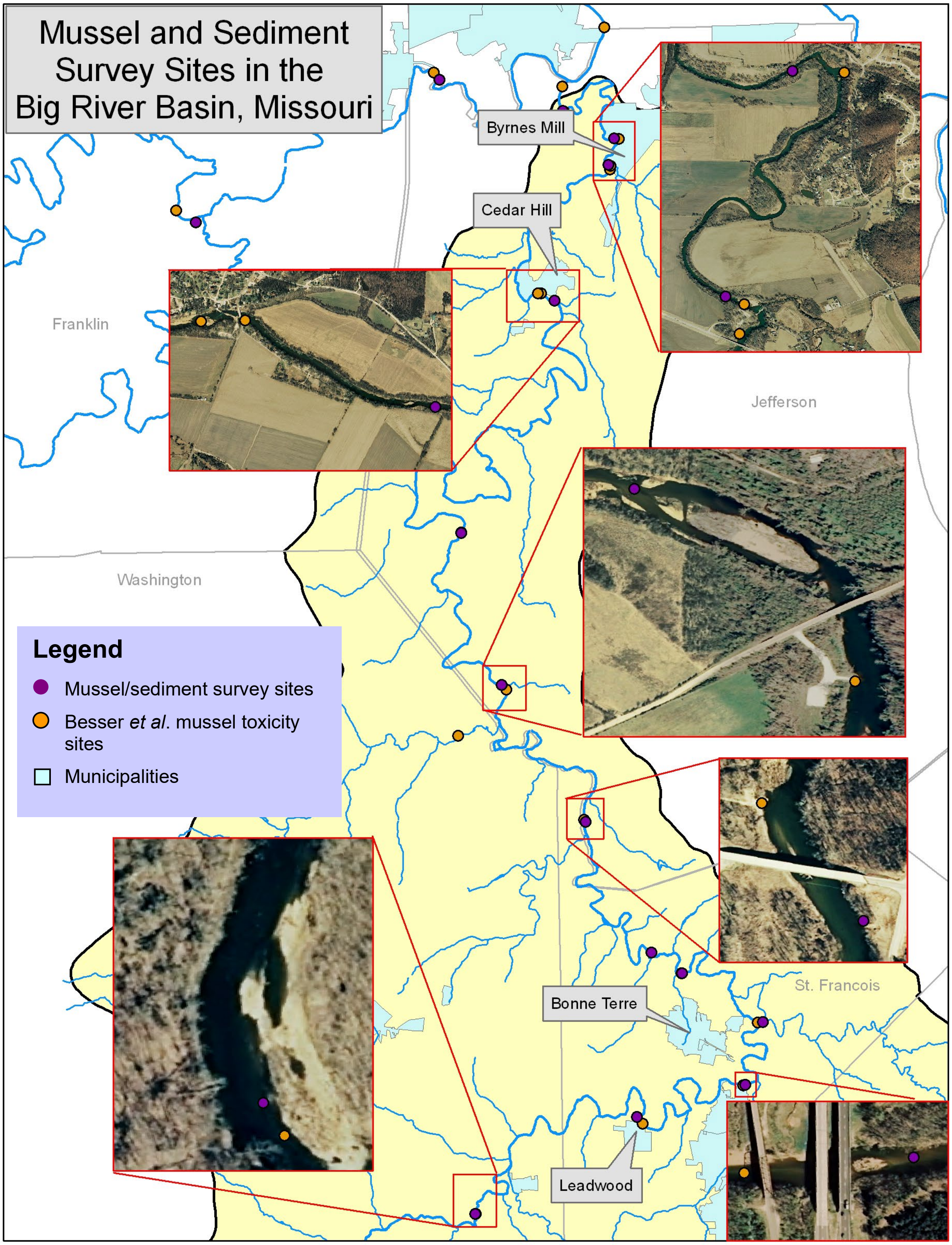


Figure 1. 2008 sediment and mussel survey sites and Besser et al. (2009) mussel toxicity sites in the Big, Bourbeuse, and Meramec rivers.

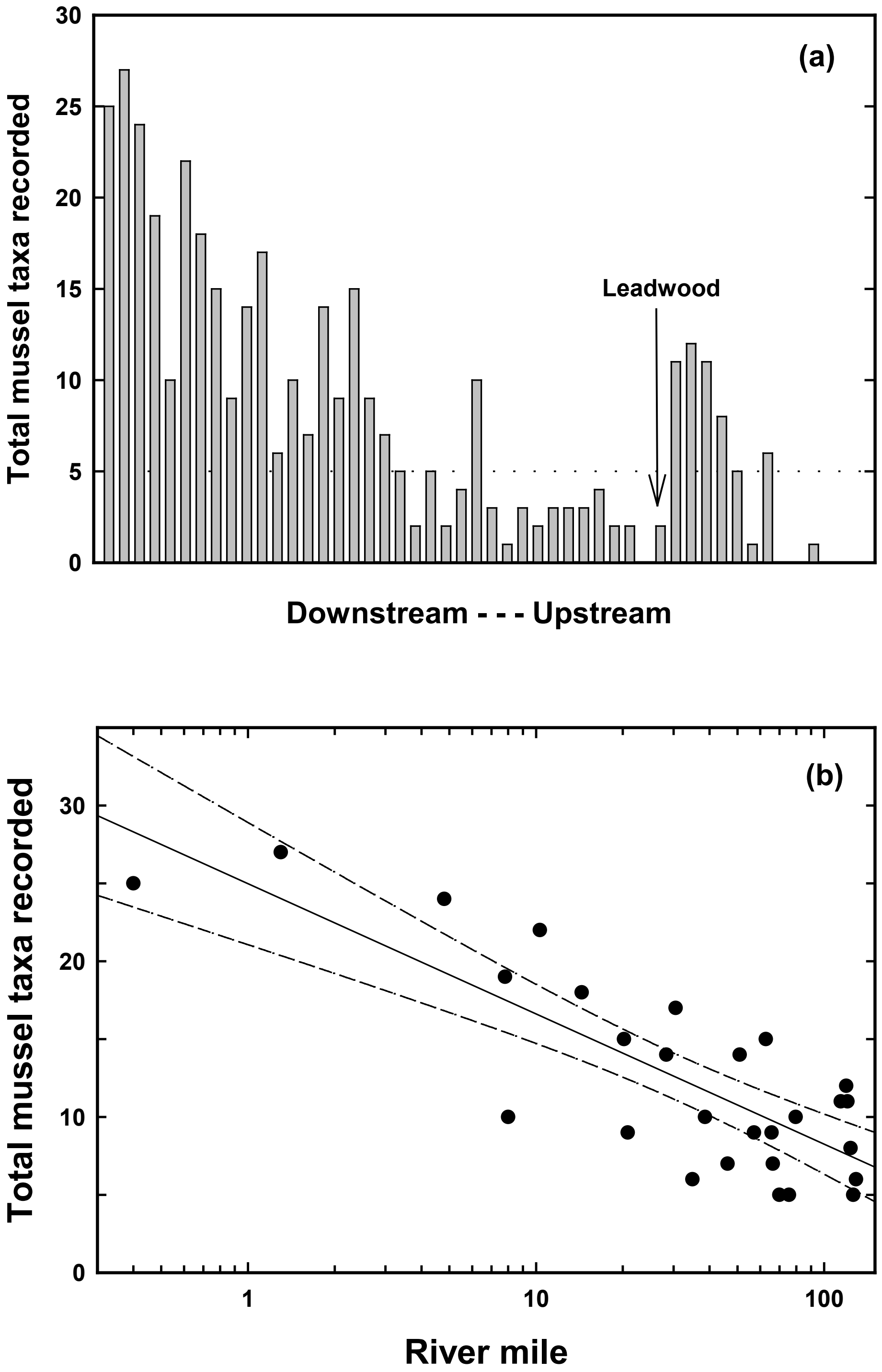


Figure 2. Determination of a 'reference envelope' for mussel species richness in the Big River: (a) Total number of mussel species documented at 50 sites on the Big River by surveys conducted between 1979 and 2008, with sites plotted in downstream-upstream order and arrow indicating upsteam extent of mining; (b) Regression of species richness vs. river mile (log scale), excluding sites with less than five species.

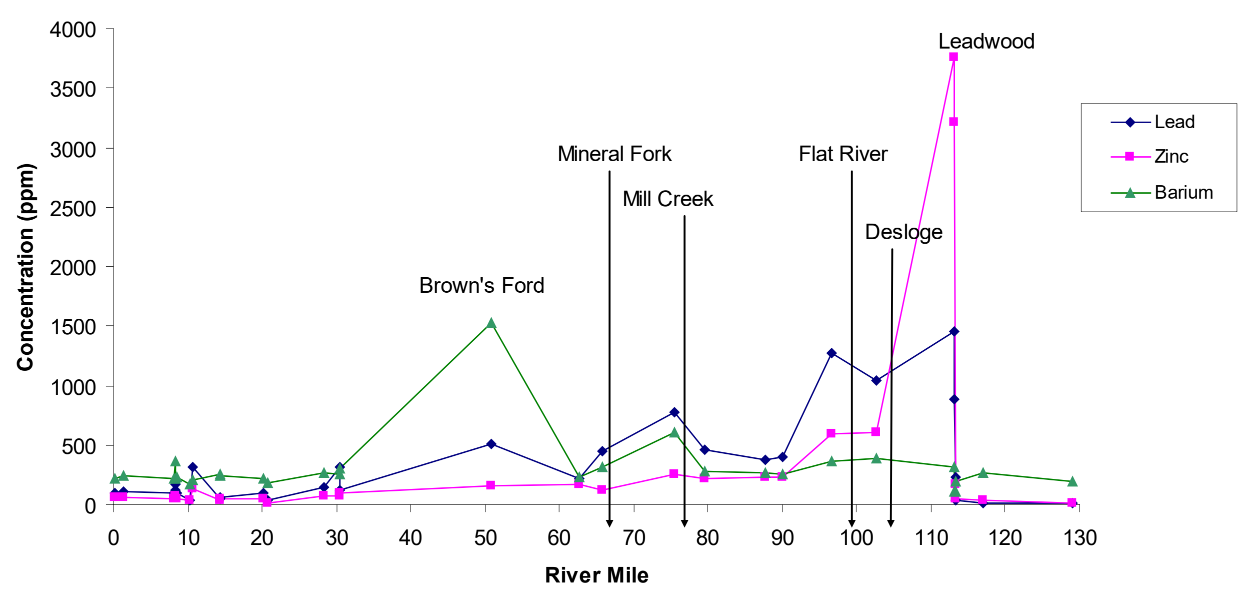


Figure 3. 2008 concentrations of Pb, Zn, and Ba as determined by XRF in bulk Big River Sediments by river mile. River miles increase with distance upstream.

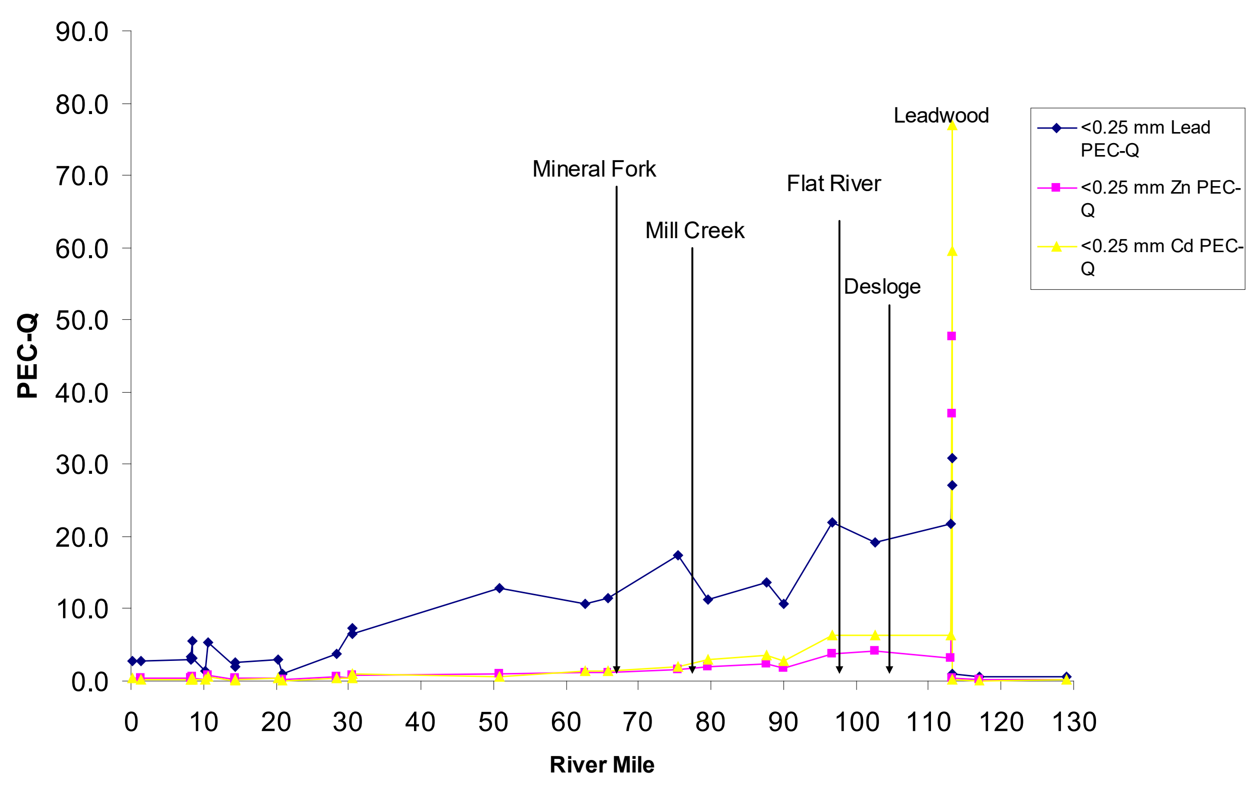


Figure 4. 2008 Probable Effects Quotients of Pb, Zn, and Ba in <0.25 mm Big River Sediments by river mile. River miles increase with distance upstream.

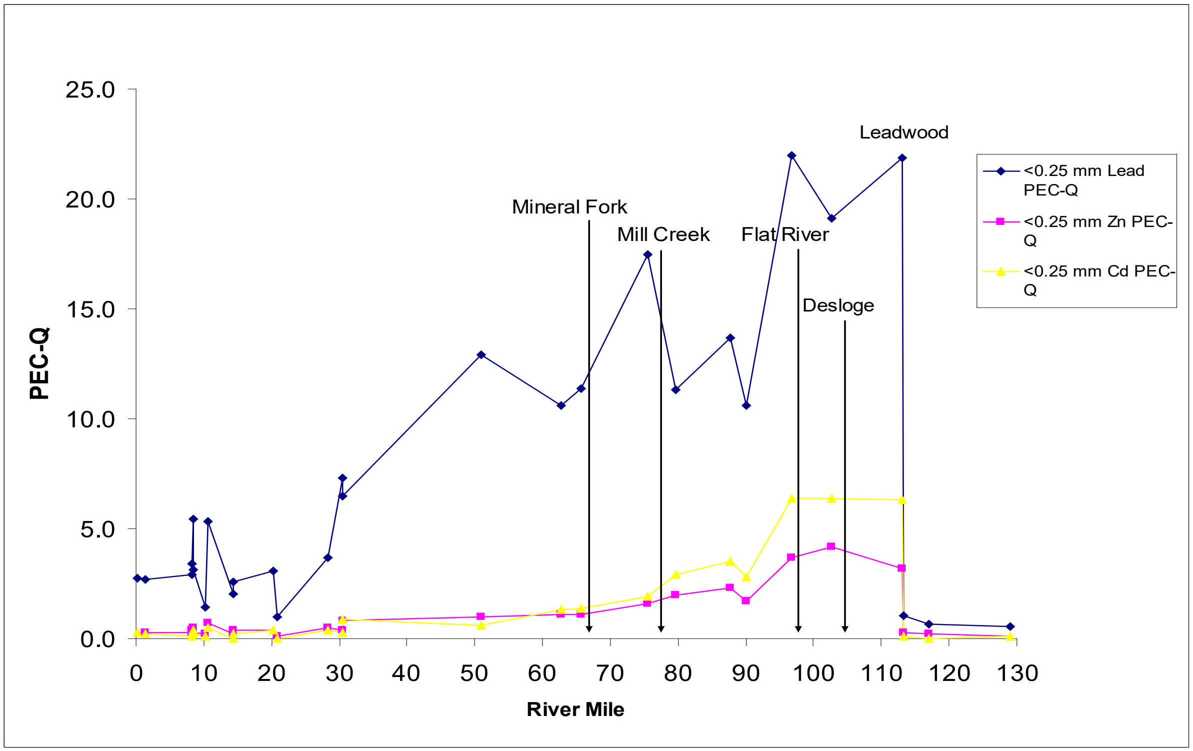


Figure 5. Big 2008 Probable Effects Quotients of Pb, Zn, and Ba in <0.25 mm Big River Sediments without Eaton Branch influenced samples. River miles increase with distance upstream.

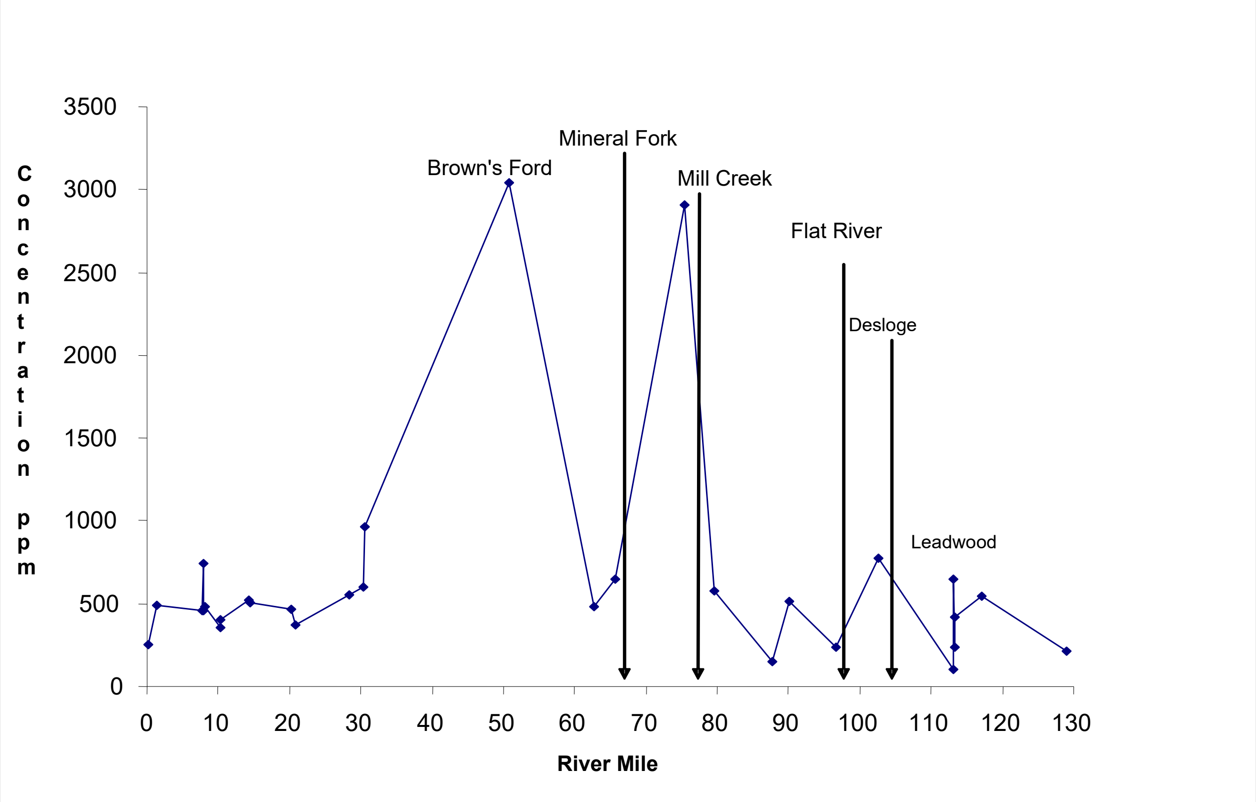


Figure 6. 2008 concentrations of Ba as determined by XRF in <0.25 mm Big River Sediments by river mile. River miles increase with distance upstream.

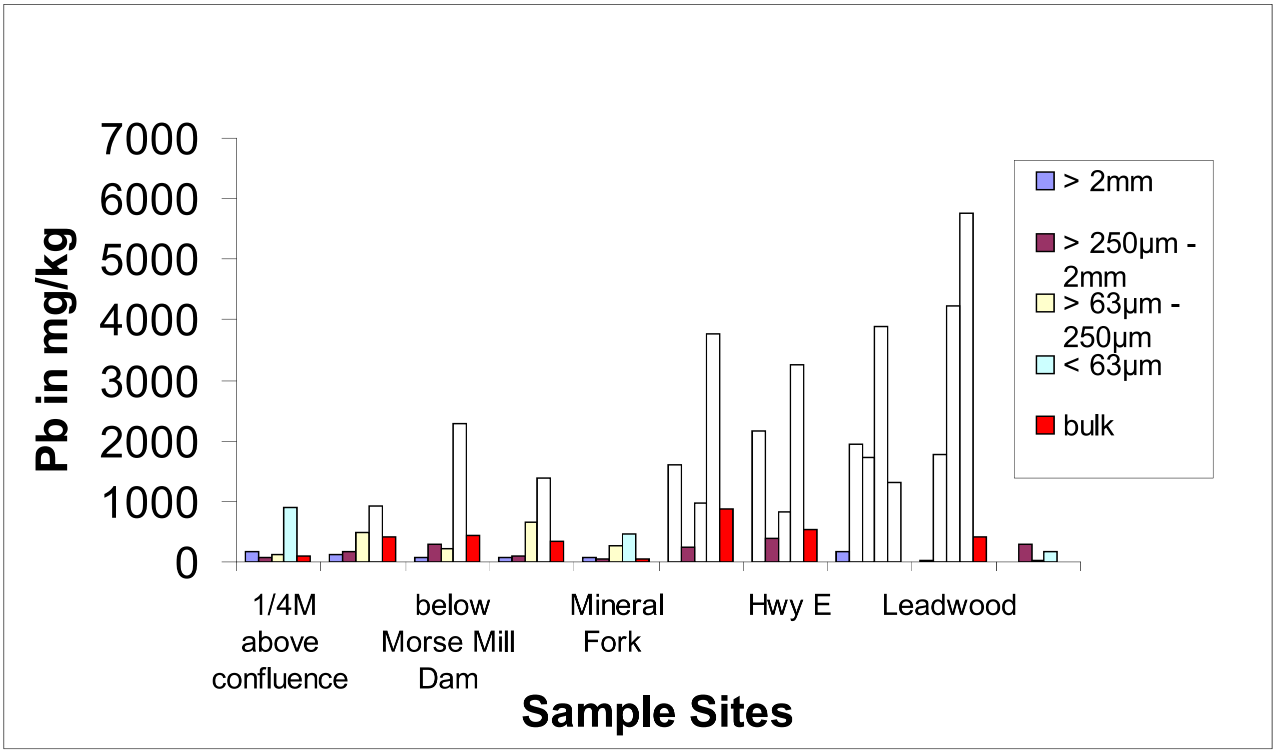


Figure 7. 2008 concentrations of Pb in Big River Sediments as determined by ICP-MS by river mile. Sediments were sieved to 4 separate size fractions and analyzed for metals. River miles increase with distance upstream.

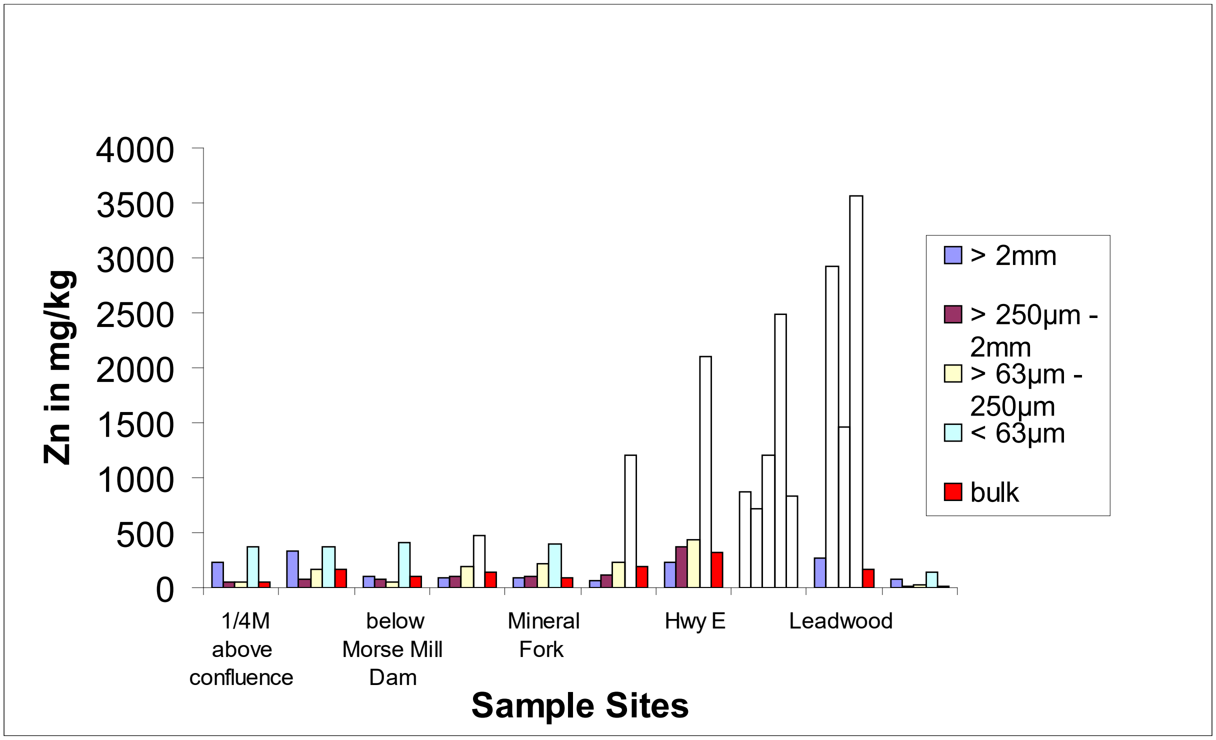


Figure 8. 2008 concentrations of Zn in Big River Sediments as determined by ICP-MS by river mile. Sediments were sieved to 4 separate size fractions and analyzed for metals. River miles increase with distance upstream.

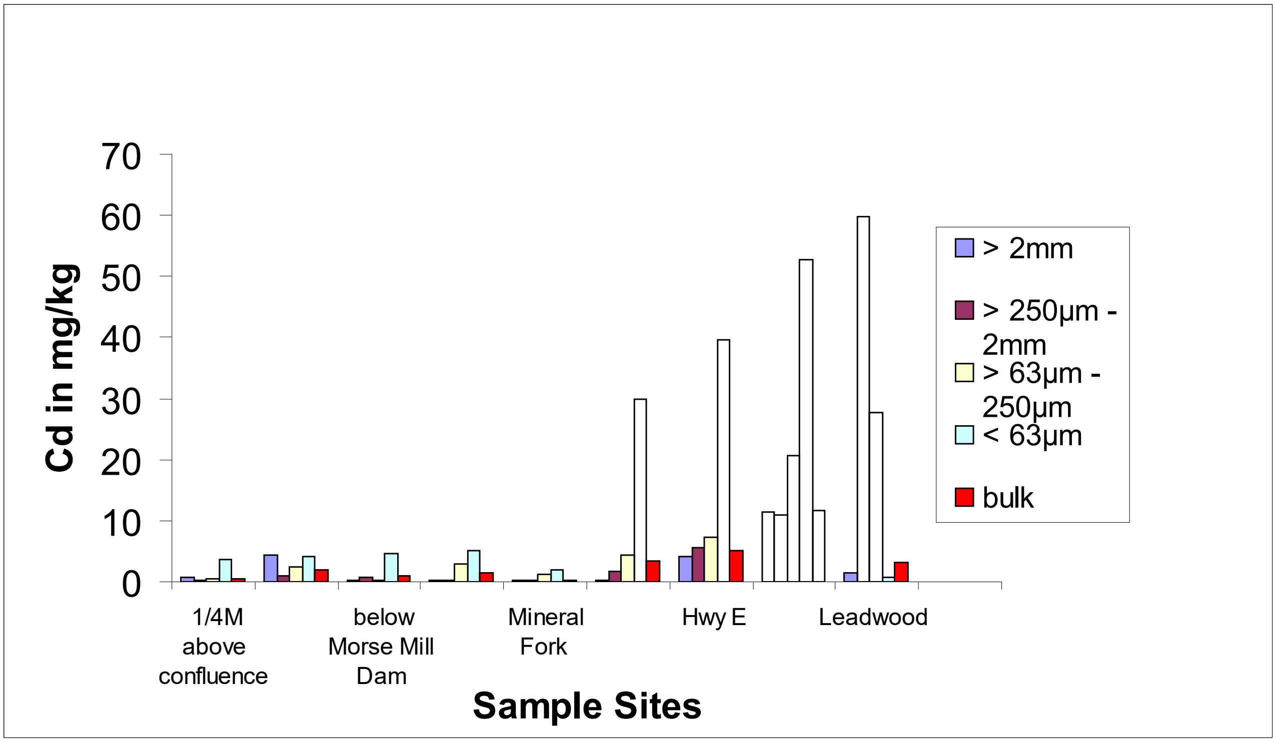


Figure 9. 2008 concentrations of Cd in Big River Sediments as determined by ICP-MS by river mile. Sediments were sieved to 4 separate size fractions and analyzed for metals. River miles increase with distance upstream.

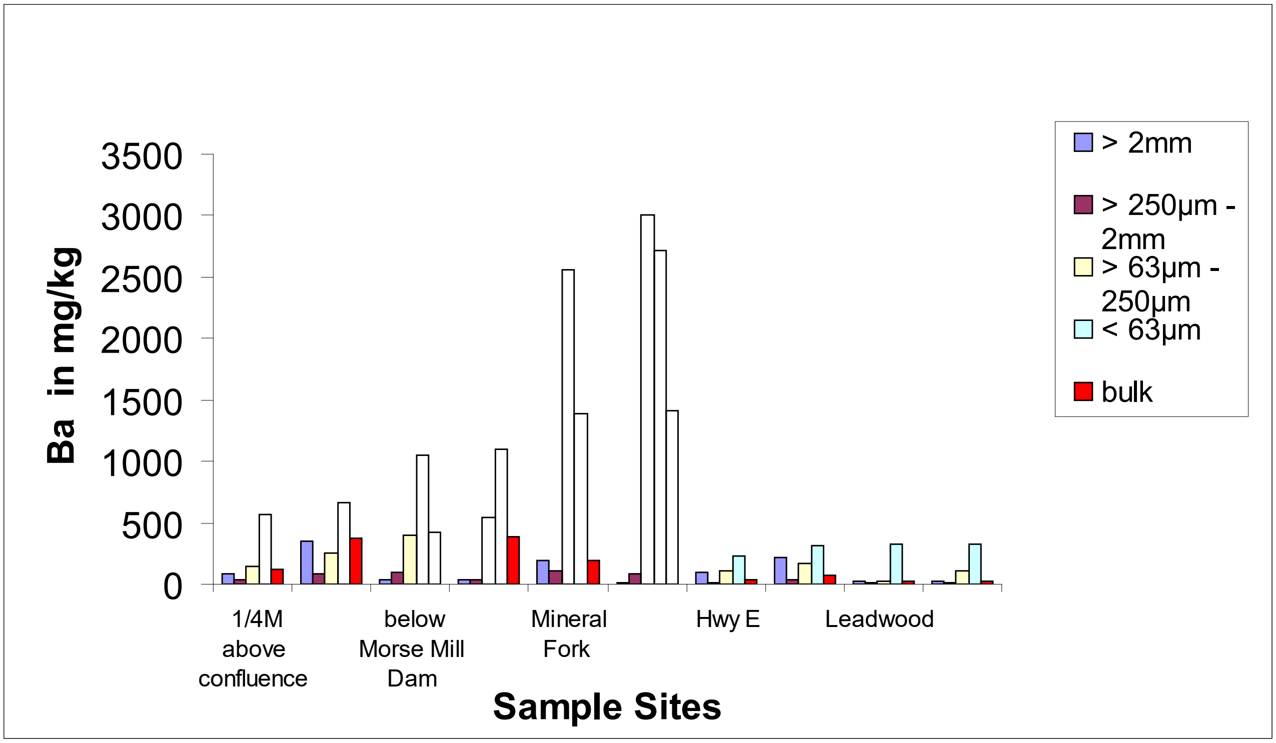


Figure 10. 2008 concentrations of Ba in Big River Sediments as determined by ICP-MS by river mile. Sediments were sieved to 4 separate size fractions and analyzed for metals. River miles increase with distance upstream.

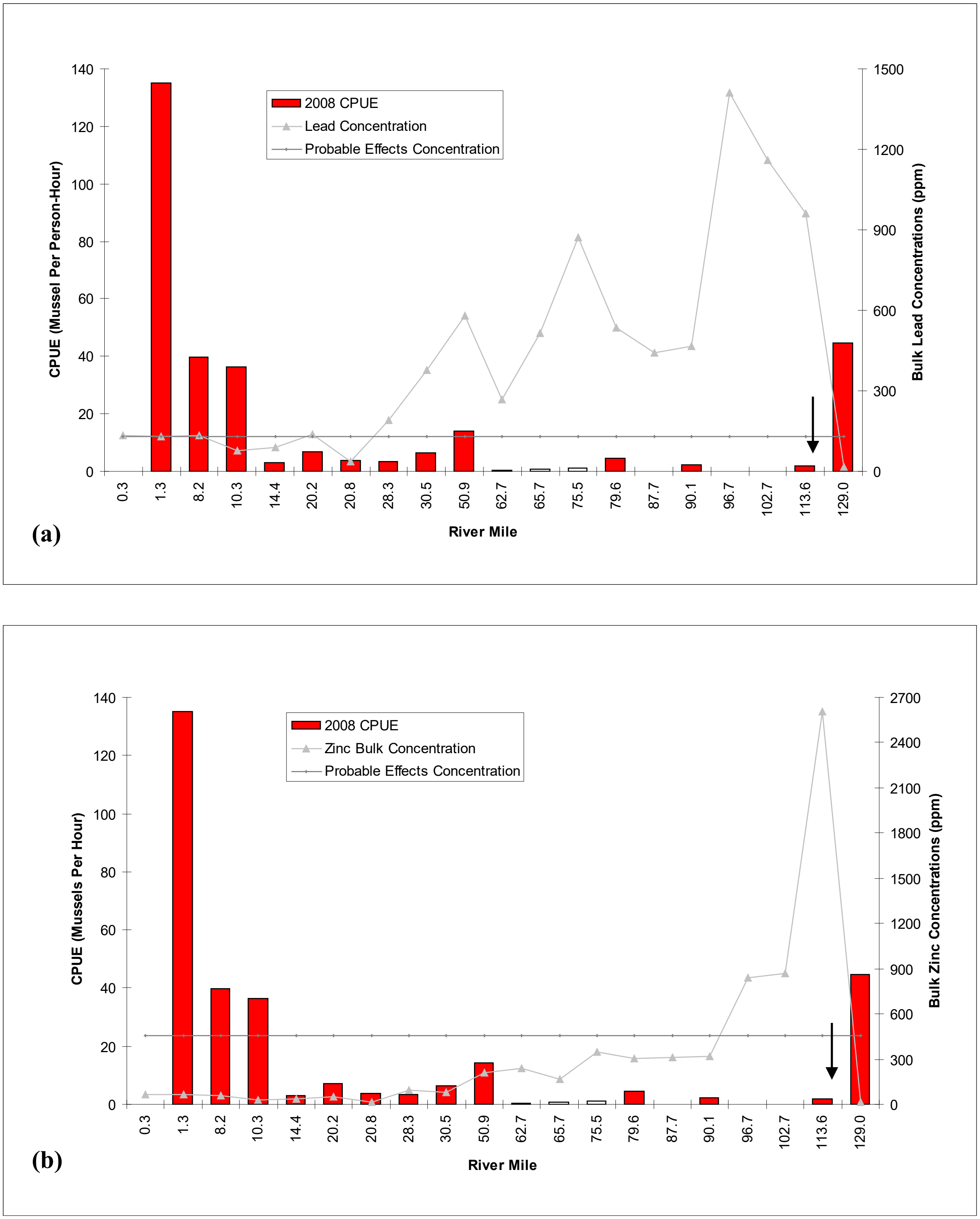


Figure 11. Catch per unit effort (CPUE) of mussels and bulk lead (a) and zinc (b) concentration at 2008 timed survey sites in the Big River. Arrow indicates upstream extent of mining. River miles increase with distance upstream.

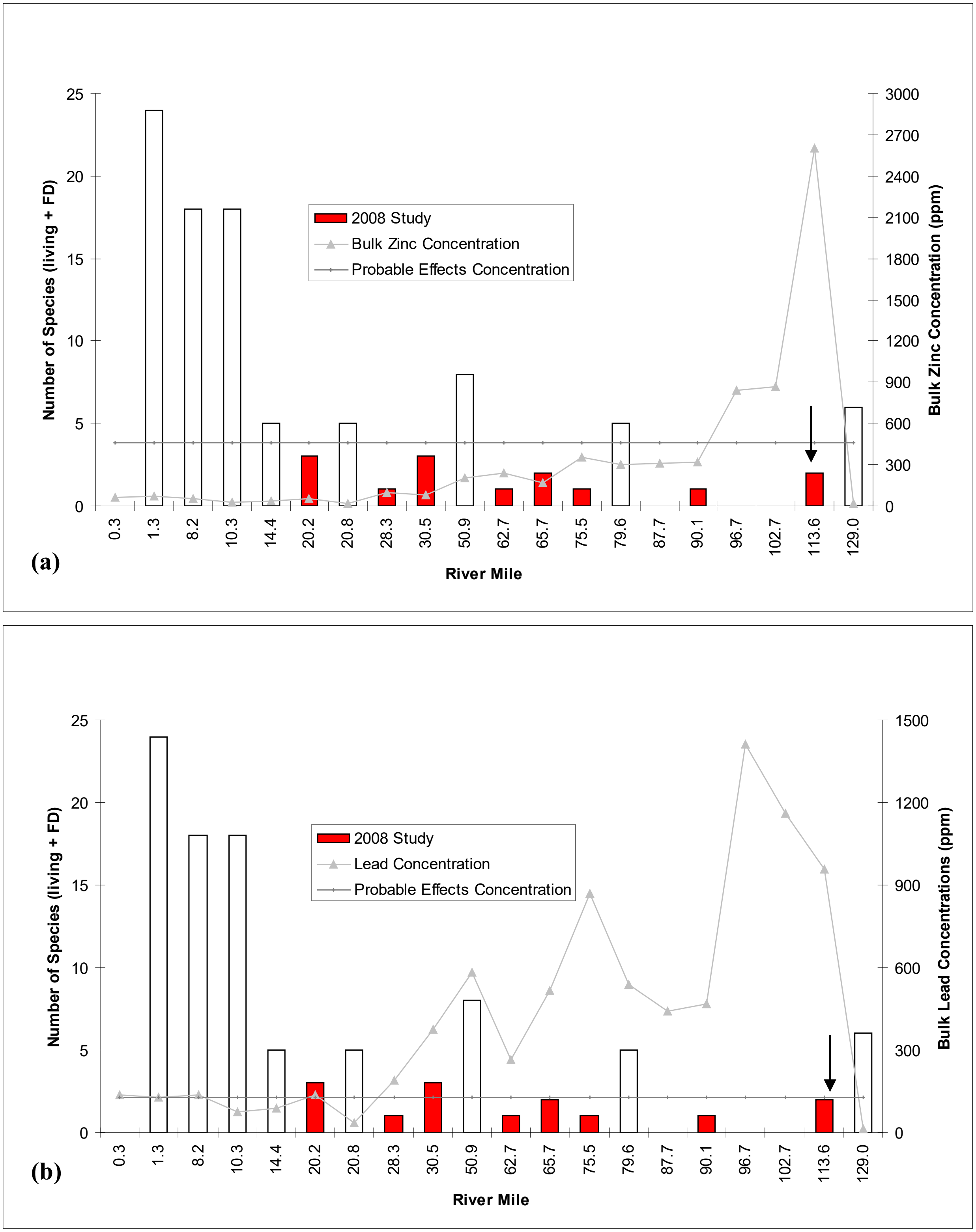


Figure 12. Mussel species richness and bulk lead (a) and zinc (b) concentration at 2008 timed survey sites in the Big River. Arrow indicates upstream extent of mining. River miles increase with distance upstream.

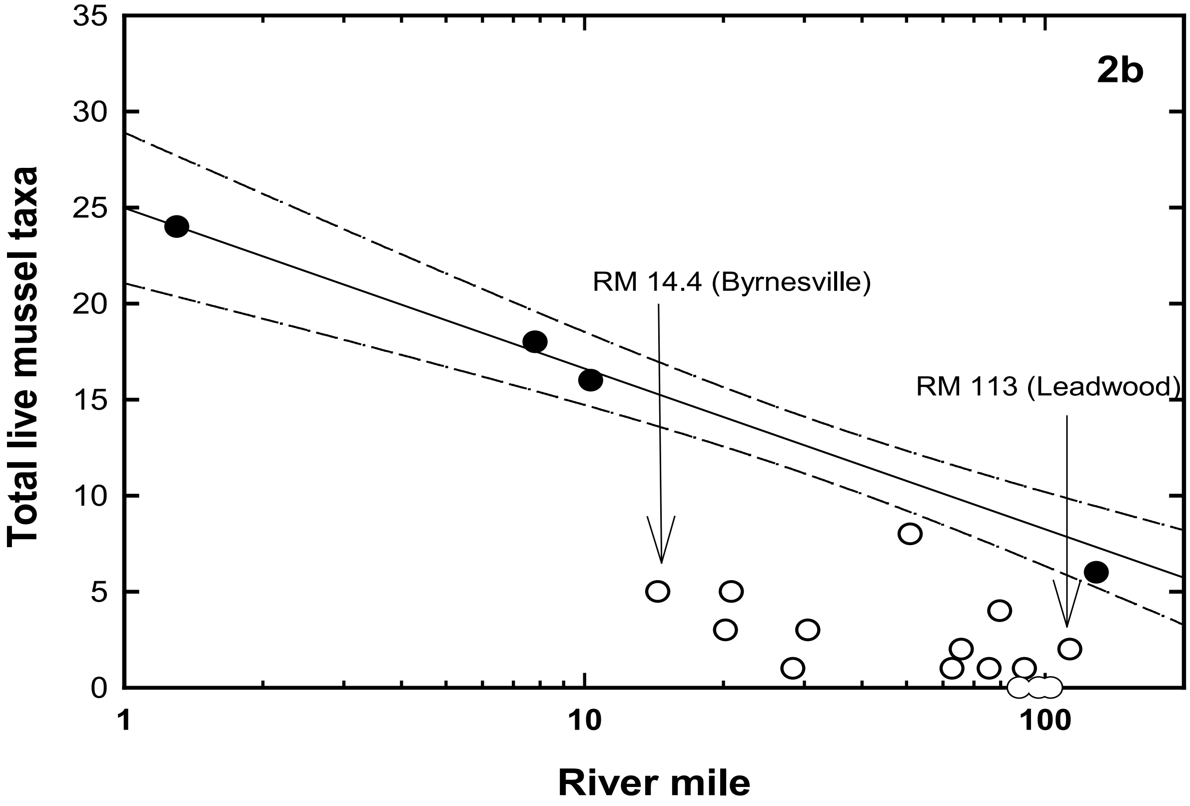


Figure 13. Comparison of live mussel species collected from Big River sites in 2008 to reference envelope based on regression of historic species-richness data (solid line). Sites with species richness below the 95% confidence band (hollow symbols) were classified as impacted sites.

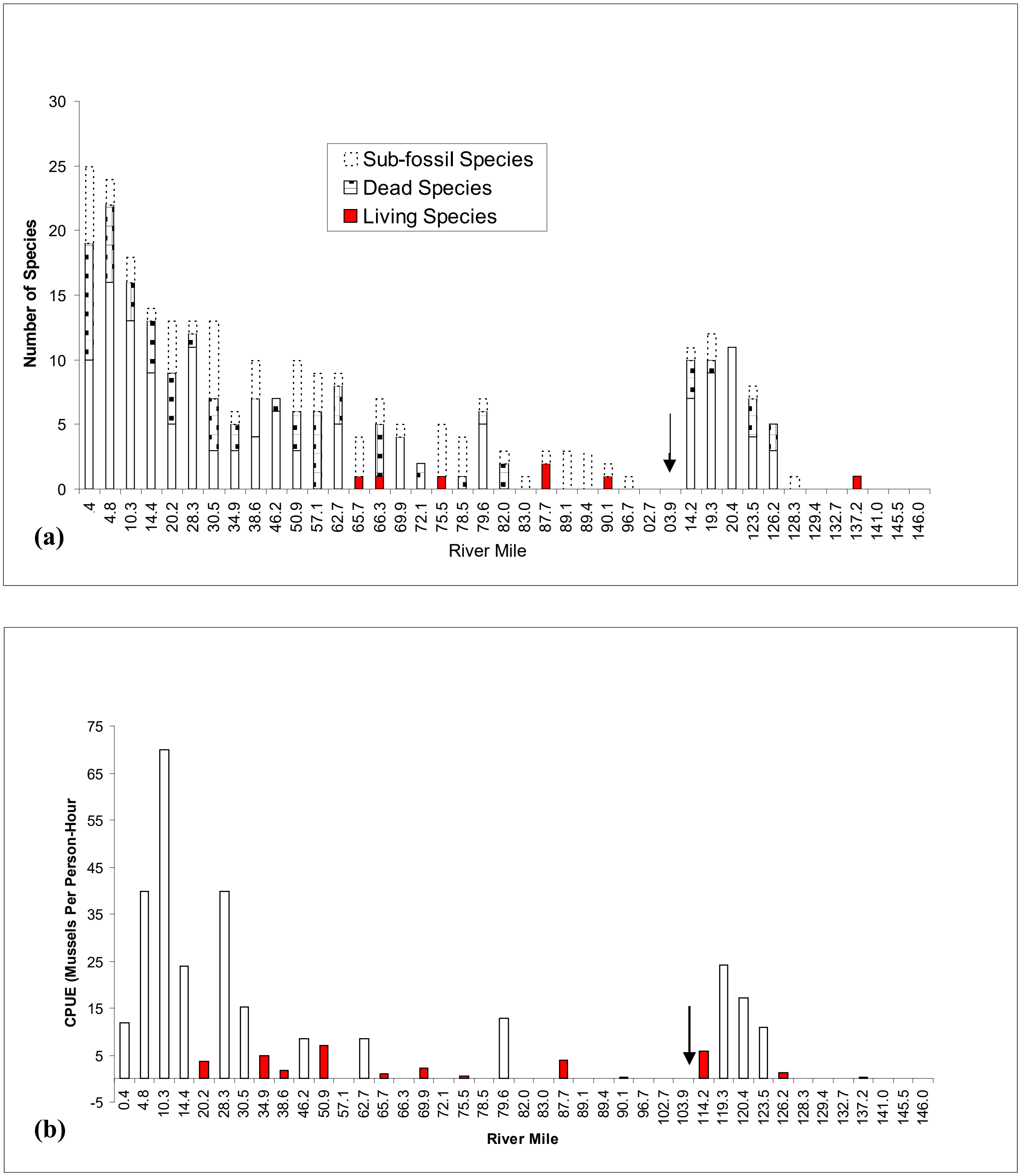


Figure 14. Mussel species richness (a) and catch per unit effort (b) in the Big River in 1979. Arrow indicates upstream extent of mining. River miles increase with distance upstream.

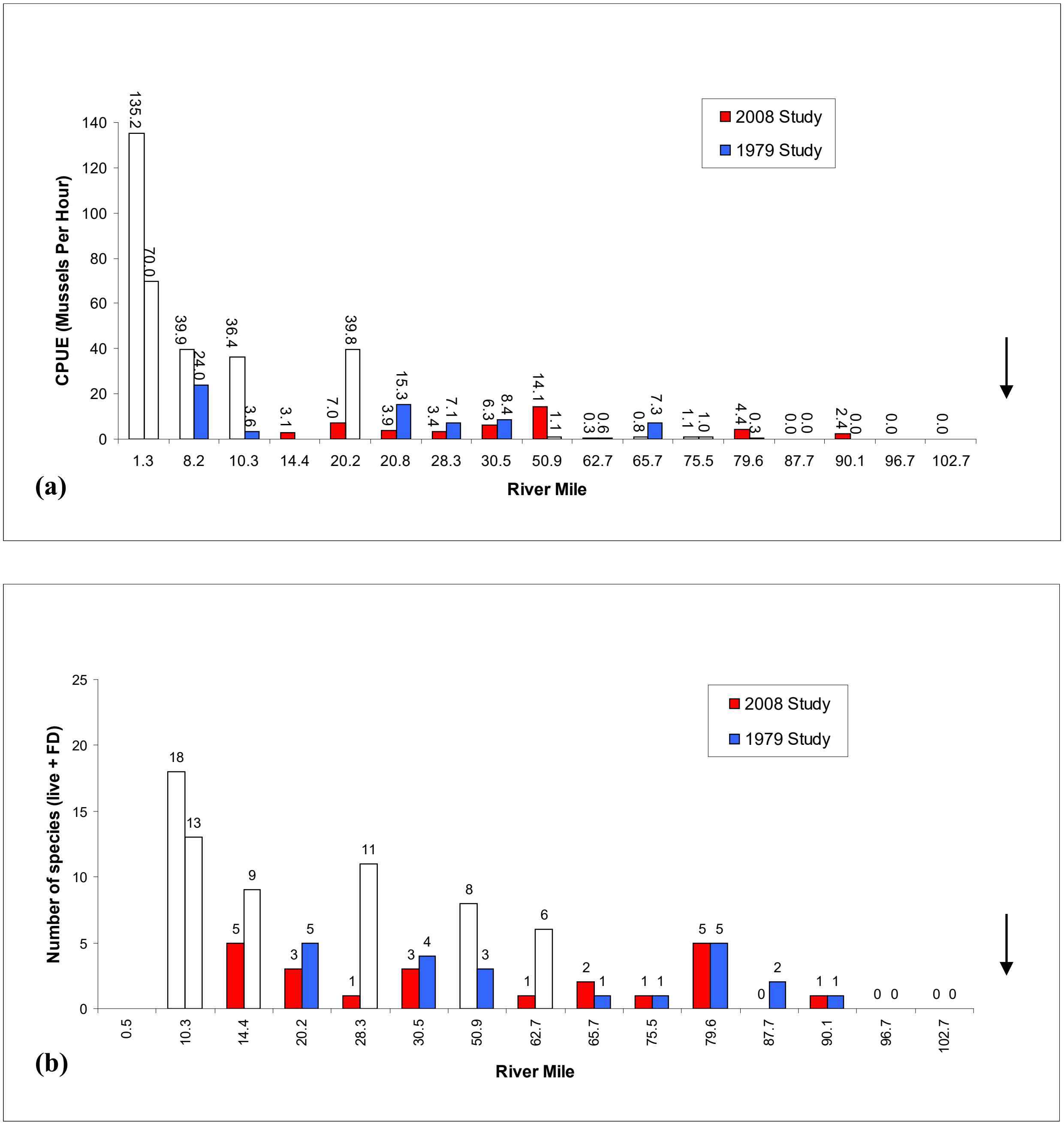
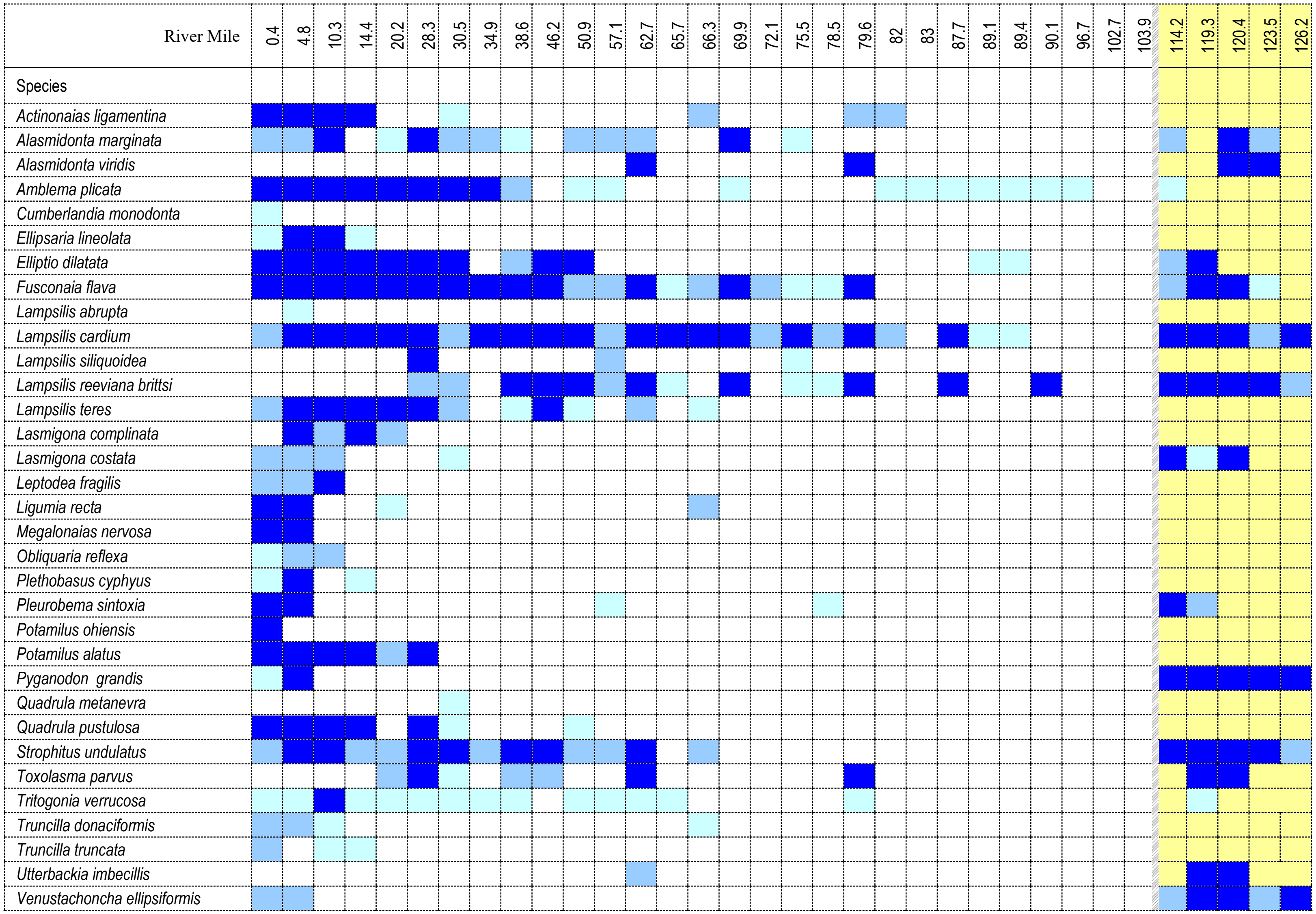
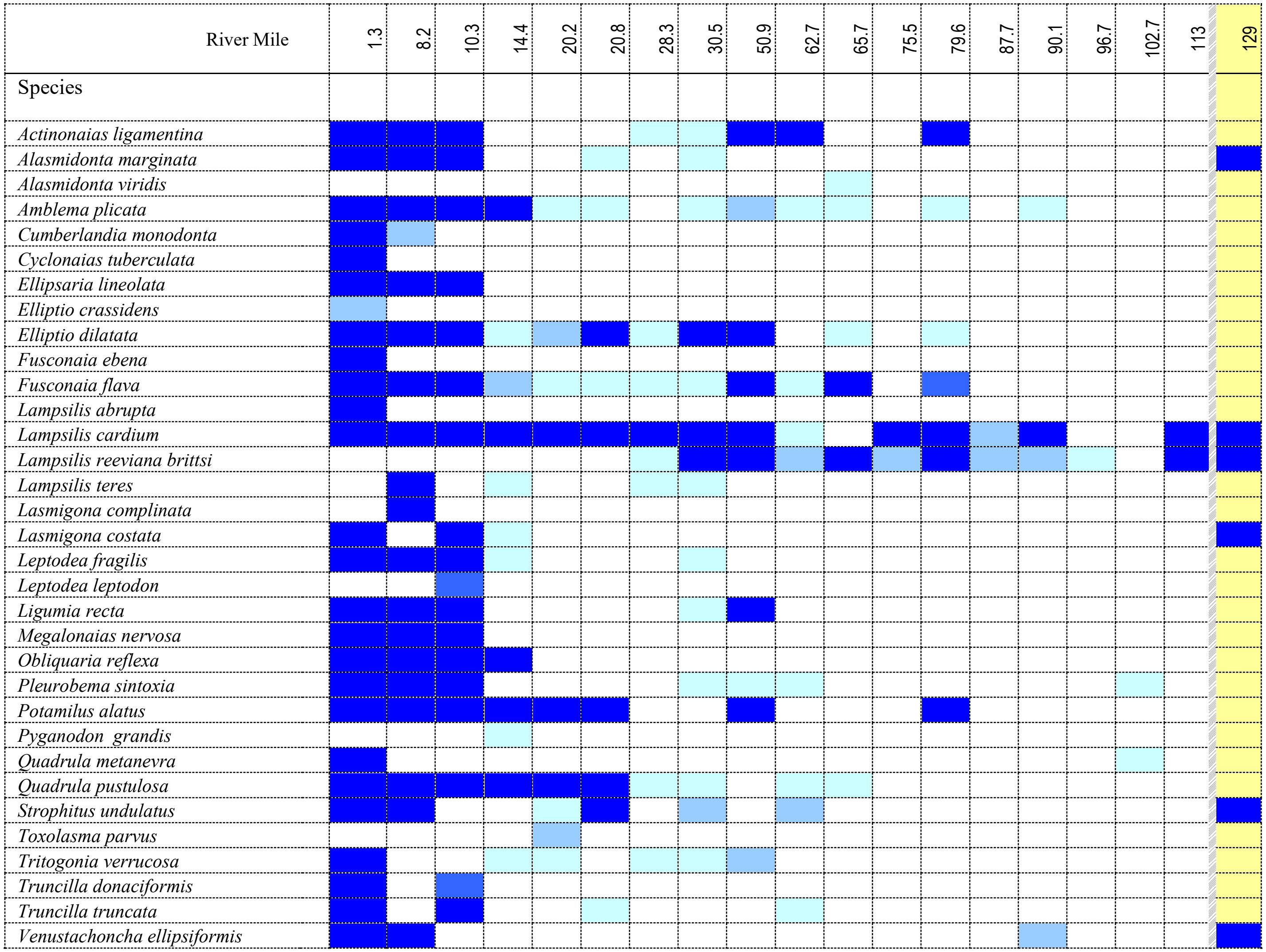


Figure 15. Comparison of 1979 (Buchanan 1979b) and current study of (a) catch per unit effort (mussels per person hour) and (b) number of living species for common survey reaches. Arrow indicates upstream extent of mining. River miles increase with distance upstream.



River Mile	0.4	4.8	10.3	14.4	20.2	28.3	30.5	34.9	38.6	46.2	50.9	57.1	62.7	65.7	66.3	69.9	72.1	75.5	78.5	79.6	82	83	87.7	89.1	89.4	90.1	96.7	102.7	103.9	114.2	119.3	120.4	123.5	126.2
Species																																		
Actinonaias ligamentina	■	■	■	■			░								▨					▨	▨													
Alasmidonta marginata	▨	▨	■		░	■	▨	▨	░		▨	▨	▨			■		░												▨		■	▨	
Alasmidonta viridis													■							■												■	■	
Amblema plicata	■	■	■	■	■	■	■	■	▨		░	░				░					░	░	░	░	░	░	░			░				
Cumberlandia monodonta	░																																	
Ellipsaria lineolata	░	■	■	░																														
Elliptio dilatata	■	■	■	■	■	■	■		▨	■	■													░	░					▨	■			
Fusconaia flava	■	■	■	■	■	■	■	■	■	■	▨	▨	■	░	▨	■	▨	░	░	■										▨	■	■	░	
Lampsilis abrupta		░																																
Lampsilis cardium	▨	■	■	■	■	■	▨	■	■	■	■	▨	■	■	■	■	▨	■	▨	■	▨		■	░	░					■	■	■	▨	■
Lampsilis siliquoidea						■						▨						░																
Lampsilis reeviana brittsi						▨	▨		■	■	■	▨	■	░		■		░	░	■			■			■				■	■	■	■	▨
Lampsilis teres	▨	■	■	■	■	■	▨		░	■	░		▨		░																			
Lasmigona complinata		■	▨	■	▨																													
Lasmigona costata	▨	▨	▨				░																							■	░	■		
Leptodea fragilis	▨	▨	■																															
Ligumia recta	■	■			░										▨																			
Megalonaias nervosa	■	■																																
Obliquaria reflexa	░	▨	▨																															
Plethobasus cyphyus	░	■		░																														
Pleurobema sintoxia	■	■										░							░											■	▨			
Potamilus ohiensis	■																																	
Potamilus alatus	■	■	■	■	▨	■																												
Pyganodon grandis	░	■																												■	■	■	■	■
Quadrula metanevra							░																											
Quadrula pustulosa	■	■	■	■		■	░				░																							
Strophitus undulatus	▨	■	■	▨	▨	■	■	▨	■	■	▨	▨	■		▨															■	■	■	■	▨
Toxolasma parvus					▨	■	░		▨	▨			■							■											■	■		
Tritogonia verrucosa	░	░	■	░	░	░	░	░	░		░	░	░	░						░											░			
Truncilla donaciformis	▨	▨	░												░																			
Truncilla truncata	▨		░	░																														
Utterbackia imbecillis													▨																		■	■		
Venustachoncha ellipsiformis	▨	▨																												▨	■	■	▨	■

Figure 16. Species presence at sites surveyed in 1979 in the Big River (Buchanan 1979b). Dark blue = collected live, light blue = weathered dead shell, pale blue = subfossil shell. Columns highlighted in yellow indicate reaches upstream of mining impacts.



River Mile	1.3	8.2	10.3	14.4	20.2	20.8	28.3	30.5	50.9	62.7	65.7	75.5	79.6	87.7	90.1	96.7	102.7	113	129
Species																			
Actinonaias ligamentina	■	■	■				░	░	■	■			■						
Alasmidonta marginata	■	■	■			░		░											■
Alasmidonta viridis											░								
Amblema plicata	■	■	■	■	░	░		░	▦	░	░		░		░				
Cumberlandia monodonta	■	▦																	
Cyclonaias tuberculata	■																		
Ellipsaria lineolata	■	■	■																
Elliptio crassidens	▦																		
Elliptio dilatata	■	■	■	░	▦	■	░	■	■		░		░						
Fusconaia ebena	■																		
Fusconaia flava	■	■	■	▦	░	░	░	░	■	░	■		■						
Lampsilis abrupta	■																		
Lampsilis cardium	■	■	■	■	■	■	■	■	■	░		■	■	▦	■			■	■
Lampsilis reeviana brittsi							░	■	■	▦	■	▦	■	▦	▦	░		■	■
Lampsilis teres		■		░			░	░											
Lasmigona complinata		■																	
Lasmigona costata	■		■	░															■
Leptodea fragilis	■	■	■	░				░											
Leptodea leptodon			■																
Ligumia recta	■	■	■					░	■										
Megalonaias nervosa	■	■	■																
Obliquaria reflexa	■	■	■	■															
Pleurobema sintoxia	■	■	■					░	░	░							░		
Potamilus alatus	■	■	■	■	■	■			■				■						
Pyganodon grandis				░															
Quadrula metanevra	■																░		
Quadrula pustulosa	■	■	■	■	■	■	░	░		░	░								
Strophitus undulatus	■	■			░	■		▦		▦									■
Toxolasma parvus					▦														
Tritogonia verrucosa	■			░	░		░	░	▦										
Truncilla donaciformis	■		■																
Truncilla truncata	■		■			░				░									
Venustachoncha ellipsiformis	■	■													▦				■

Figure 17. Species presence at sites surveyed during the present study (2008) in the Big River. Dark blue = collected live, light blue = weathered dead shell, pale blue = subfossil shell. Columns highlighted in yellow indicate reaches upstream of mining impact

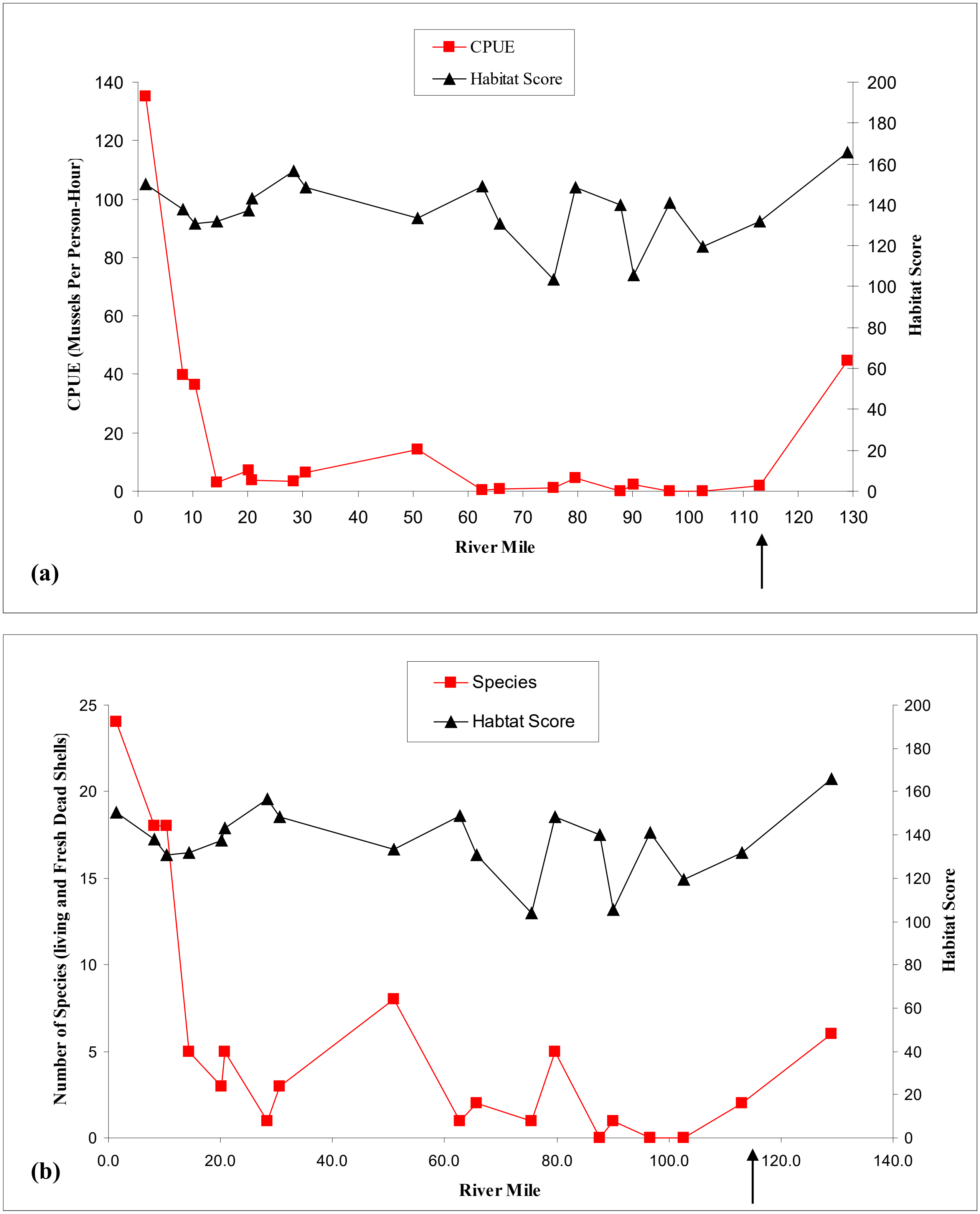


Figure 18. Mussel catch per unit effort (a) and species richness (b) versus habitat scores at 2008 timed survey sites in the Big River. Highest possible habitat score is 180. Arrow indicates upstream extent of mining. River miles increase with distance upstream.

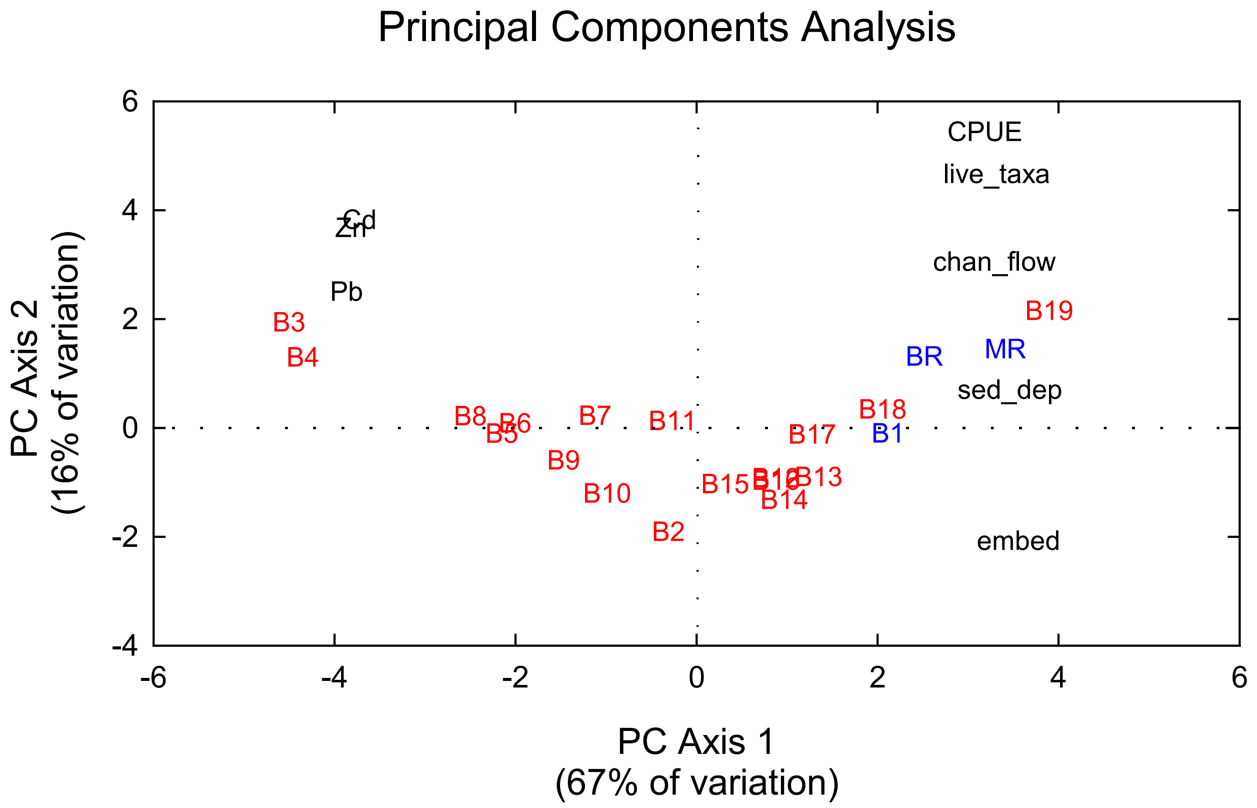


Figure 19. Summary of principal components analysis of correlations among mussel communities, metal concentrations in fine (<0.25 mm) sediments, and selected habitat characteristics determined in 2008. Site codes (blue text=reference sites, red text=sites downstream of mining) are plotted vs. the first two principal components axes, which explain 83% of total variation in the data set. Variable codes (black text) indicate the association of variable with the PC axes (eigenvectors). [BR=Bourbeuse River; MR=Meramec River; B1-B19=Big River Sites, numbered from upstream-downstream order. Habitat variables are described in Appendix A.

APPENDIX A

Description of habitat parameters used to assess habitat conditions in the 2008 mussel survey on the Big River taken from the rapid bioassessment protocol established by Barbour et al.

Parameters to be evaluated in sampling reach:

1

EPIFAUNAL SUBSTRATE/AVAILABLE COVER

high and low gradient streams

Includes the relative quantity and variety of natural structures in the stream, such as cobble (riffles), large rocks, fallen trees, logs and branches, and undercut banks, available as refugia, feeding, or sites for spawning and nursery functions of aquatic macrofauna. A wide variety and/or abundance of submerged structures in the stream provides macroinvertebrates and fish with a large number of niches, thus increasing habitat diversity. As variety and abundance of cover decreases, habitat structure becomes monotonous, diversity decreases, and the potential for recovery following disturbance decreases. Riffles and runs are critical for maintaining a variety and abundance of insects in most high-gradient streams and serving as spawning and feeding refugia for certain fish. The extent and quality of the riffle is an important factor in the support of a healthy biological condition in high-gradient streams. Riffles and runs offer a diversity of habitat through variety of particle size, and, in many small high-gradient streams, will provide the most stable habitat. Snags and submerged logs are among the most productive habitat structure for macroinvertebrate colonization and fish refugia in low-gradient streams. However, "new fall" will not yet be suitable for colonization.

Selected References

Wesche et al. 1985, Pearsons et al. 1992, Gorman 1988, Rankin 1991, Barbour and Stribling 1991, Plafkin et al. 1989, Platts et al. 1983, Osborne et al. 1991, Benke et al. 1984, Wallace et al. 1996, Ball 1982, MacDonald et al. 1991, Reice 1980, Clements 1987, Hawkins et al. 1982, Beechie and Sibley 1997.

Habitat Parameter	**Condition Category**			
	Optimal	**Suboptimal**	**Marginal**	**Poor**
1. Epifaunal Substrate/ Available Cover **(high and low gradient)**	Greater than 70% (50% for low gradient streams) of substrate favorable for epifaunal colonization and fish cover; mix of snags, submerged logs, undercut banks, cobble or other stable habitat and at stage to allow full colonization potential (i.e., logs/snags that are not new fall and not transient).	40-70% (30-50% for low gradient streams) mix of stable habitat; well-suited for full colonization potential; adequate habitat for maintenance of populations; presence of additional substrate in the form of newfall, but not yet prepared for colonization (may rate at high end of scale).	20-40% (10-30% for low gradient streams) mix of stable habitat; habitat availability less than desirable; substrate frequently disturbed or removed.	Less than 20% (10% for low gradient streams) stable habitat; lack of habitat is obvious; substrate unstable or lacking.
SCORE	20 19 18 17 16	15 14 13 12 11	10 9 8 7 6	5 4 3 2 1 0

1a. Epifaunal Substrate/Available Cover—High Gradient

Optimal Range

Poor Range

1b. Epifaunal Substrate/Available Cover—Low Gradient

Optimal Range *(Mary Kay Corazalla, U. of Minn.)*

Poor Range

2a EMBEDDEDNESS

high gradient streams

Refers to the extent to which rocks (gravel, cobble, and boulders) and snags are covered or sunken into the silt, sand, or mud of the stream bottom. Generally, as rocks become embedded, the surface area available to macroinvertebrates and fish (shelter, spawning, and egg incubation) is decreased. Embeddedness is a result of large-scale sediment movement and deposition, and is a parameter evaluated in the riffles and runs of high-gradient streams. The rating of this parameter may be variable depending on where the observations are taken. To avoid confusion with sediment deposition (another habitat parameter), observations of embeddedness should be taken in the upstream and central portions of riffles and cobble substrate areas.

Selected References

Ball 1982, Osborne et al. 1991, Barbour and Stribling 1991, Platts et al. 1983, MacDonald et al. 1991, Rankin 1991, Reice 1980, Clements 1987, Benke et al. 1984, Hawkins et al. 1982, Burton and Harvey 1990.

Habitat Parameter	Condition Category			
	Optimal	Suboptimal	Marginal	Poor
2.a Embeddedness **(high gradient)**	Gravel, cobble, and boulder particles are 0-25% surrounded by fine sediment. Layering of cobble provides diversity of niche space.	Gravel, cobble, and boulder particles are 25-50% surrounded by fine sediment.	Gravel, cobble, and boulder particles are 50-75% surrounded by fine sediment.	Gravel, cobble, and boulder particles are more than 75% surrounded by fine sediment.
SCORE	20 19 18 17 16	15 14 13 12 11	10 9 8 7 6	5 4 3 2 1 0

2a. Embeddedness—High Gradient

Optimal Range *(William Taft, MI DNR)*

Poor Range *(William Taft, MI DNR)*

2b POOL SUBSTRATE CHARACTERIZATION

low gradient streams

Evaluates the type and condition of bottom substrates found in pools. Firmer sediment types (e.g., gravel, sand) and rooted aquatic plants support a wider variety of organisms than a pool substrate dominated by mud or bedrock and no plants. In addition, a stream that has a uniform substrate in its pools will support far fewer types of organisms than a stream that has a variety of substrate types.

Selected References

Beschta and Platts 1986, U.S. EPA 1983.

Habitat Parameter	Condition Category			
	Optimal	Suboptimal	Marginal	Poor
2b. Pool Substrate Characterization **(low gradient)**	Mixture of substrate materials, with gravel and firm sand prevalent; root mats and submerged vegetation common.	Mixture of soft sand, mud, or clay; mud may be dominant; some root mats and submerged vegetation present.	All mud or clay or sand bottom; little or no root mat; no submerged vegetation.	Hard-pan clay or bedrock; no root mat or submerged vegetation.
SCORE	20 19 18 17 16	15 14 13 12 11	10 9 8 7 6	5 4 3 2 1 0

2b. Pool Substrate Characterization—Low Gradient

Optimal Range

(Mary Kay Corazalla, U. of Minn.)

Poor Range

3a VELOCITY/DEPTH COMBINATIONS

high gradient streams

Patterns of velocity and depth are included for high-gradient streams under this parameter as an important feature of habitat diversity. The best streams in most high-gradient regions will have all 4 patterns present: (1) slow-deep, (2) slow-shallow, (3) fast-deep, and (4) fast-shallow. The general guidelines are 0.5 m depth to separate shallow from deep, and 0.3 m/sec to separate fast from slow. The occurrence of these 4 patterns relates to the stream's ability to provide and maintain a stable aquatic environment.

Selected References

Ball 1982, Brown and Brussock 1991, Gore and Judy 1981, Oswood and Barber 1982.

Habitat Parameter	Condition Category			
	Optimal	**Suboptimal**	**Marginal**	**Poor**
3a. Velocity/ Depth Regimes **(high gradient)**	All 4 velocity/depth regimes present (slow-deep, slow-shallow, fast-deep, fast-shallow). (slow is <0.3 m/s, deep is >0.5 m)	Only 3 of the 4 regimes present (if fast-shallow is missing, score lower than if missing other regimes).	Only 2 of the 4 habitat regimes present (if fast-shallow or slow-shallow are missing, score low).	Dominated by 1 velocity/ depth regime (usually slow-deep).
SCORE	20 19 18 17 16	15 14 13 12 11	10 9 8 7 6	5 4 3 2 1 0

3a. Velocity/Depth Regimes—High Gradient

Optimal Range *(Mary Kay Corazalla, U. of Minn.)*
(arrows emphasize different velocity/depth regimes)

Poor Range *(William Taft, MI DNR)*

3b POOL VARIABILITY

low gradient streams

Rates the overall mixture of pool types found in streams, according to size and depth. The 4 basic types of pools are large-shallow, large-deep, small-shallow, and small-deep. A stream with many pool types will support a wide variety of aquatic species. Rivers with low sinuosity (few bends) and monotonous pool characteristics do not have sufficient quantities and types of habitat to support a diverse aquatic community. General guidelines are any pool dimension (i.e., length, width, oblique) greater than half the cross-section of the stream for separating large from small and 1 m depth separating shallow and deep.

Selected References

Beschta and Platts 1986, USEPA 1983.

Habitat Parameter	Condition Category			
	Optimal	**Suboptimal**	**Marginal**	**Poor**
3b. Pool Variability **(low gradient)**	Even mix of large-shallow, large-deep, small-shallow, small-deep pools present.	Majority of pools large-deep; very few shallow.	Shallow pools much more prevalent than deep pools.	Majority of pools small-shallow or pools absent.
SCORE	20 19 18 17 16	15 14 13 12 11	10 9 8 7 6	5 4 3 2 1 0

3b. Pool Variability—Low Gradient

Optimal Range *(Peggy Morgan, FL DEP)*

Poor Range *(William Taft, MI DNR)*

4 SEDIMENT DEPOSITION

high and low gradient streams Measures the amount of sediment that has accumulated in pools and the changes that have occurred to the stream bottom as a result of deposition. Deposition occurs from large-scale movement of sediment. Sediment deposition may cause the formation of islands, point bars (areas of increased deposition usually at the beginning of a meander that increase in size as the channel is diverted toward the outer bank) or shoals, or result in the filling of runs and pools. Usually deposition is evident in areas that are obstructed by natural or manmade debris and areas where the stream flow decreases, such as bends. High levels of sediment deposition are symptoms of an unstable and continually changing environment that becomes unsuitable for many organisms.

Selected References MacDonald et al. 1991, Platts et al. 1983, Ball 1982, Armour et al. 1991, Barbour and Stribling 1991, Rosgen 1985.

Habitat Parameter	**Condition Category**			
	Optimal	**Suboptimal**	**Marginal**	**Poor**
4. Sediment Deposition **(high and low gradient)**	Little or no enlargement of islands or point bars and less than 5% (<20% for low-gradient streams) of the bottom affected by sediment deposition.	Some new increase in bar formation, mostly from gravel, sand or fine sediment; 5-30% (20-50% for low-gradient) of the bottom affected; slight deposition in pools.	Moderate deposition of new gravel, sand or fine sediment on old and new bars; 30-50% (50-80% for low-gradient) of the bottom affected; sediment deposits at obstructions, constrictions, and bends; moderate deposition of pools prevalent.	Heavy deposits of fine material, increased bar development; more than 50% (80% for low-gradient) of the bottom changing frequently; pools almost absent due to substantial sediment deposition.
SCORE	20 19 18 17 16	15 14 13 12 11	10 9 8 7 6	5 4 3 2 1 0

4a. Sediment Deposition—High Gradient

Optimal Range

Poor Range
(arrow pointing to sediment deposition)

4b. Sediment Deposition—Low Gradient

Optimal Range

Poor Range
(arrows pointing to sediment deposition)

5 CHANNEL FLOW STATUS

high and low gradient streams

The degree to which the channel is filled with water. The flow status will change as the channel enlarges (e.g., aggrading stream beds with actively widening channels) or as flow decreases as a result of dams and other obstructions, diversions for irrigation, or drought. When water does not cover much of the streambed, the amount of suitable substrate for aquatic organisms is limited. In high-gradient streams, riffles and cobble substrate are exposed; in low-gradient streams, the decrease in water level exposes logs and snags, thereby reducing the areas of good habitat. Channel flow is especially useful for interpreting biological condition under abnormal or lowered flow conditions. This parameter becomes important when more than one biological index period is used for surveys or the timing of sampling is inconsistent among sites or annual periodicity.

Selected References

Rankin 1991, Rosgen 1985, Hupp and Simon 1986, MacDonald et al. 1991, Ball 1982, Hicks et al. 1991.

Habitat Parameter	**Condition Category**			
	Optimal	**Suboptimal**	**Marginal**	**Poor**
5. Channel Flow Status **(high and low gradient)**	Water reaches base of both lower banks, and minimal amount of channel substrate is exposed.	Water fills >75% of the available channel; or <25% of channel substrate is exposed.	Water fills 25-75% of the available channel, and/or riffle substrates are mostly exposed.	Very little water in channel and mostly present as standing pools.
SCORE	20 19 18 17 16	15 14 13 12 11	10 9 8 7 6	5 4 3 2 1 0

5a. Channel Flow Status—High Gradient

Optimal Range

Poor Range
(arrow showing that water is not reaching both banks; leaving much of channel uncovered)

5b. Channel Flow Status—Low Gradient

Optimal Range

Poor Range *(James Stahl, IN DEM)*

Parameters to be evaluated broader than sampling reach:

6 CHANNEL ALTERATION

high and low gradient streams

Is a measure of large-scale changes in the shape of the stream channel. Many streams in urban and agricultural areas have been straightened, deepened, or diverted into concrete channels, often for flood control or irrigation purposes. Such streams have far fewer natural habitats for fish, macroinvertebrates, and plants than do naturally meandering streams. Channel alteration is present when artificial embankments, riprap, and other forms of artificial bank stabilization or structures are present; when the stream is very straight for significant distances; when dams and bridges are present; and when other such changes have occurred. Scouring is often associated with channel alteration.

Selected References

Barbour and Stribling 1991, Simon 1989a, b, Simon and Hupp 1987, Hupp and Simon 1986, Hupp 1992, Rosgen 1985, Rankin 1991, MacDonald et al. 1991.

Habitat Parameter	Condition Category			
	Optimal	**Suboptimal**	**Marginal**	**Poor**
6. Channel Alteration **(high and low gradient)**	Channelization or dredging absent or minimal; stream with normal pattern.	Some channelization present, usually in areas of bridge abutments; evidence of past channelization, i.e., dredging, (greater than past 20 yr) may be present, but recent channelization is not present.	Channelization may be extensive; embankments or shoring structures present on both banks; and 40 to 80% of stream reach channelized and disrupted.	Banks shored with gabion or cement; over 80% of the stream reach channelized and disrupted. Instream habitat greatly altered or removed entirely.
SCORE	20 19 18 17 16	15 14 13 12 11	10 9 8 7 6	5 4 3 2 1 0

6a. Channel Alteration—High Gradient


Optimal Range


Poor Range
(arrows emphasizing large-scale channel alterations)

6b. Channel Alteration—Low Gradient


Optimal Range


Poor Range

(John Maxted, DE DNREC)

7a

FREQUENCY OF RIFFLES (OR BENDS)

high gradient streams

Is a way to measure the sequence of riffles and thus the heterogeneity occurring in a stream. Riffles are a source of high-quality habitat and diverse fauna, therefore, an increased frequency of occurrence greatly enhances the diversity of the stream community. For high gradient streams where distinct riffles are uncommon, a run/bend ratio can be used as a measure of meandering or sinuosity (see 7b). A high degree of sinuosity provides for diverse habitat and fauna, and the stream is better able to handle surges when the stream fluctuates as a result of storms. The absorption of this energy by bends protects the stream from excessive erosion and flooding and provides refugia for benthic invertebrates and fish during storm events. To gain an appreciation of this parameter in some streams, a longer segment or reach than that designated for sampling should be incorporated into the evaluation. In some situations, this parameter may be rated from viewing accurate topographical maps. The "sequencing" pattern of the stream morphology is important in rating this parameter. In headwaters, riffles are usually continuous and the presence of cascades or boulders provides a form of sinuosity and enhances the structure of the stream. A stable channel is one that does not exhibit progressive changes in slope, shape, or dimensions, although short-term variations may occur during floods (Gordon et al. 1992).

Selected References

Hupp and Simon 1991, Brussock and Brown 1991, Platts et al. 1983, Rankin 1991, Rosgen 1985, 1994, 1996, Osborne and Hendricks 1983, Hughes and Omernik 1983, Cushman 1985, Bain and Boltz 1989, Gislason 1985, Hawkins et al. 1982, Statzner et al. 1988.

Habitat Parameter	**Condition Category**			
	Optimal	**Suboptimal**	**Marginal**	**Poor**
7a. Frequency of Riffles (or bends) **(high gradient)**	Occurrence of riffles relatively frequent; ratio of distance between riffles divided by width of the stream <7:1 (generally 5 to 7); variety of habitat is key. In streams where riffles are continuous, placement of boulders or other large, natural obstruction is important.	Occurrence of riffles infrequent; distance between riffles divided by the width of the stream is between 7 to 15.	Occasional riffle or bend; bottom contours provide some habitat; distance between riffles divided by the width of the stream is between 15 to 25.	Generally all flat water or shallow riffles; poor habitat; distance between riffles divided by the width of the stream is a ratio of >25.
SCORE	20 19 18 17 16	15 14 13 12 11	10 9 8 7 6	5 4 3 2 1 0

7a. Frequency of Riffles (or bends)—High Gradient

Optimal Range
(arrows showing frequency of riffles and bends)

Poor Range

7b CHANNEL SINUOSITY

low gradient streams

Evaluates the meandering or sinuosity of the stream. A high degree of sinuosity provides for diverse habitat and fauna, and the stream is better able to handle surges when the stream fluctuates as a result of storms. The absorption of this energy by bends protects the stream from excessive erosion and flooding and provides refugia for benthic invertebrates and fish during storm events. To gain an appreciation of this parameter in low gradient streams, a longer segment or reach than that designated for sampling may be incorporated into the evaluation. In some situations, this parameter may be rated from viewing accurate topographical maps. The "sequencing" pattern of the stream morphology is important in rating this parameter. In "oxbow" streams of coastal areas and deltas, meanders are highly exaggerated and transient. Natural conditions in these streams are shifting channels and bends, and alteration is usually in the form of flow regulation and diversion. A stable channel is one that does not exhibit progressive changes in slope, shape, or dimensions, although short-term variations may occur during floods (Gordon et al. 1992).

Selected References

Hupp and Simon 1991, Brussock and Brown 1991, Platts et al. 1983, Rankin 1991, Rosgen 1985, 1994, 1996, Osborne and Hendricks 1983, Hughes and Omernik 1983, Cushman 1985, Bain and Boltz 1989, Gislason 1985, Hawkins et al. 1982, Statzner et al. 1988.

Habitat Parameter	Condition Category			
	Optimal	Suboptimal	Marginal	Poor
7b. Channel Sinuosity **(low gradient)**	The bends in the stream increase the stream length 3 to 4 times longer than if it was in a straight line. (Note - channel braiding is considered normal in coastal plains and other low-lying areas. This parameter is not easily rated in these areas.)	The bends in the stream increase the stream length 2 to 3 times longer than if it was in a straight line.	The bends in the stream increase the stream length 1 to 2 times longer than if it was in a straight line.	Channel straight; waterway has been channelized for a long distance.
SCORE	20 19 18 17 16	15 14 13 12 11	10 9 8 7 6	5 4 3 2 1 0

7b. Channel Sinuosity—Low Gradient

Optimal Range

Poor Range

8 BANK STABILITY (condition of banks)

high and low gradient streams

Measures whether the stream banks are eroded (or have the potential for erosion). Steep banks are more likely to collapse and suffer from erosion than are gently sloping banks, and are therefore considered to be unstable. Signs of erosion include crumbling, unvegetated banks, exposed tree roots, and exposed soil. Eroded banks indicate a problem of sediment movement and deposition, and suggest a scarcity of cover and organic input to streams. Each bank is evaluated separately and the cumulative score (right and left) is used for this parameter.

Selected References

Ball 1982, MacDonald et al. 1991, Armour et al. 1991, Barbour and Stribling 1991, Hupp and Simon 1986, 1991, Simon 1989a, Hupp 1992, Hicks et al. 1991, Osborne et al. 1991, Rosgen 1994, 1996.

Habitat Parameter	Condition Category			
	Optimal	**Suboptimal**	**Marginal**	**Poor**
8. Bank Stability (score each bank) **Note: determine left or right side by facing downstream** **(high and low gradient)**	Banks stable; evidence of erosion or bank failure absent or minimal; little potential for future problems. <5% of bank affected.	Moderately stable; infrequent, small areas of erosion mostly healed over. 5-30% of bank in reach has areas of erosion.	Moderately unstable; 30-60% of bank in reach has areas of erosion; high erosion potential during floods.	Unstable; many eroded areas; "raw" areas frequent along straight sections and bends; obvious bank sloughing; 60-100% of bank has erosional scars.
SCORE ___ (LB)	Left Bank 10 9	8 7 6	5 4 3	2 1 0
SCORE (RB)	Right Bank 10 9	8 7 6	5 4 3	2 1 0

8a. Bank Stability (condition of banks)—High Gradient

Optimal Range
(arrow pointing to stable streambanks)

Poor Range *(MD Save Our Streams)*
(arrow highlighting unstable streambanks)

8b. Bank Stability (condition of banks)—Low Gradient

Optimal Range *(Peggy Morgan, FL DEP)*

Poor Range
(arrow highlighting unstable streambanks)

9 BANK VEGETATIVE PROTECTION

high and low gradient streams

Measures the amount of vegetative protection afforded to the stream bank and the near-stream portion of the riparian zone. The root systems of plants growing on stream banks help hold soil in place, thereby reducing the amount of erosion that is likely to occur. This parameter supplies information on the ability of the bank to resist erosion as well as some additional information on the uptake of nutrients by the plants, the control of instream scouring, and stream shading. Banks that have full, natural plant growth are better for fish and macroinvertebrates than are banks without vegetative protection or those shored up with concrete or riprap. This parameter is made more effective by defining the native vegetation for the region and stream type (i.e., shrubs, trees, etc.). In some regions, the introduction of exotics has virtually replaced all native vegetation. The value of exotic vegetation to the quality of the habitat structure and contribution to the stream ecosystem must be considered in this parameter. In areas of high grazing pressure from livestock or where residential and urban development activities disrupt the riparian zone, the growth of a natural plant community is impeded and can extend to the bank vegetative protection zone. Each bank is evaluated separately and the cumulative score (right and left) is used for this parameter.

Selected References

Platts et al. 1983, Hupp and Simon 1986, 1991, Simon and Hupp 1987, Ball 1982, Osborne et al. 1991, Rankin 1991, Barbour and Stribling 1991, MacDonald et al. 1991, Armour et al. 1991, Myers and Swanson 1991, Bauer and Burton 1993.

Habitat Parameter	Condition Category										
	Optimal		Suboptimal			Marginal			Poor		
9. Vegetative Protection (score each bank) **Note: determine left or right side by facing downstream.** **(high and low gradient)**	More than 90% of the streambank surfaces and immediate riparian zones covered by native vegetation, including trees, understory shrubs, or nonwoody macrophytes; vegetative disruption through grazing or mowing minimal or not evident; almost all plants allowed to grow naturally.		70-90% of the streambank surfaces covered by native vegetation, but one class of plants is not well-represented; disruption evident but not affecting full plant growth potential to any great extent; more than one-half of the potential plant stubble height remaining.			50-70% of the streambank surfaces covered by vegetation; disruption obvious; patches of bare soil or closely cropped vegetation common; less than one-half of the potential plant stubble height remaining.			Less than 50% of the streambank surfaces covered by vegetation; disruption of streambank vegetation is very high; vegetation has been removed to 5 centimeters or less in average stubble height.		
SCORE ___ (LB)	Left Bank 10	9	8	7	6	5	4	3	2	1	0
SCORE (RB)	Right Bank 10	9	8	7	6	5	4	3	2	1	0

9a. Bank Vegetative Protection—High Gradient

Optimal Range
(arrow pointing to streambank with high level of vegetative cover)

Poor Range
(arrow pointing to streambank with almost no vegetative cover)

9b. Bank Vegetative Protection—Low Gradient

Optimal Range *(Peggy Morgan, FL DEP)*

Poor Range *(MD Save Our Streams)*
(arrow pointing to channelized streambank with no vegetative cover)

10

RIPARIAN VEGETATIVE ZONE WIDTH

high and low gradient streams

Measures the width of natural vegetation from the edge of the stream bank out through the riparian zone. The vegetative zone serves as a buffer to pollutants entering a stream from runoff, controls erosion, and provides habitat and nutrient input into the stream. A relatively undisturbed riparian zone supports a robust stream system; narrow riparian zones occur when roads, parking lots, fields, lawns, bare soil, rocks, or buildings are near the stream bank. Residential developments, urban centers, golf courses, and rangeland are the common causes of anthropogenic degradation of the riparian zone. Conversely, the presence of "old field" (i.e., a previously developed field not currently in use), paths, and walkways in an otherwise undisturbed riparian zone may be judged to be inconsequential to altering the riparian zone and may be given relatively high scores. For variable size streams, the specified width of a desirable riparian zone may also be variable and may be best determined by some multiple of stream width (e.g., 4 x wetted stream width). Each bank is evaluated separately and the cumulative score (right and left) is used for this parameter.

Selected References

Barton et al. 1985, Naiman et al. 1993, Hupp 1992, Gregory et al. 1991, Platts et al. 1983, Rankin 1991, Barbour and Stribling 1991, Bauer and Burton 1993.

Habitat Parameter	**Condition Category**			
	Optimal	**Suboptimal**	**Marginal**	**Poor**
10. Riparian Vegetative Zone Width (score each bank riparian zone) **(high and low gradient)**	Width of riparian zone >18 meters; human activities (i.e., parking lots, roadbeds, clear-cuts, lawns, or crops) have not impacted zone.	Width of riparian zone 12-18 meters; human activities have impacted zone only minimally.	Width of riparian zone 6-12 meters; human activities have impacted zone a great deal.	Width of riparian zone <6 meters: little or no riparian vegetation due to human activities.
SCORE ___ (LB)	Left Bank 10 9	8 7 6	5 4 3	2 1 0
SCORE (RB)	Right Bank 10 9	8 7 6	5 4 3	2 1 0

10a. Riparian Vegetative Zone Width—High Gradient

Optimal Range
(arrow pointing out an undisturbed riparian zone)

Poor Range
(arrow pointing out lack of riparian zone)

10b. Riparian Vegetative Zone Width—Low Gradient

Optimal Range
(arrow emphasizing an undisturbed riparian zone)

Poor Range *(MD Save Our Streams)*
(arrow emphasizing lack of riparian zone)

APPENDIX B

Table 1. Concentrations of elements in a continuing calibration blank (CCB) and independent calibration verification standard (ICVS) ran every 10 samples throughout the sediment analysis. Results expressed as ng/mL.

Set 1

BID[a]	Element	CCB[b]	ICVS	% Rec (ICVS)[c]	BID[a]	Element	CCB[b]	ICVS	% Rec (ICVS)[c]
01/07/09	Cu	0.00096	15.0	100	01/07/09	Cu	0.00117	14.7	98
Run #1	Zn	0.00406	205	102	Run #6	Zn	0.00309	202	101
	Cd	0.00017	4.04	101		Cd	0.00169	3.91	98
	Ba	0.00050	40.3	101		Ba	0.00195	41.1	103
	Pb	0.00347	15.0	100		Pb	0.00302	14.6	97
01/07/09	Cu	0.00020	14.7	98	01/07/09	Cu	-0.00120	14.3	95
Run #2	Zn	-0.00448	202	101	Run #7	Zn	0.00135	199	99
	Cd	0.00076	3.99	100		Cd	0.00040	3.86	96
	Ba	-0.00176	40.0	100		Ba	-0.00074	40.3	101
	Pb	0.00401	15.0	100		Pb	0.00224	14.4	96
01/07/09	Cu	-0.00151	14.4	96	01/07/09	Cu	-0.00207	13.7	92
Run #3	Zn	0.00233	201	100	Run #8	Zn	-0.00034	193	96
	Cd	-0.00029	4.01	100		Cd	0.00045	3.86	97
	Ba	-0.00285	40.5	101		Ba	-0.00127	39.6	99
	Pb	0.00406	14.8	99		Pb	0.00475	14.3	95
01/07/09	Cu	0.00101	14.2	95	01/07/09	Cu	0.00001	13.8	92
Run #4	Zn	0.00319	199	100	Run #9	Zn	0.00019	195	97
	Cd	0.00141	3.95	99		Cd	0.00139	3.91	98
	Ba	0.00022	41.5	104		Ba	-0.00172	40.5	101
	Pb	0.00396	14.8	99		Pb	0.00473	14.4	96
01/07/09	Cu	-0.00058	14.4	96	01/07/09	Cu	-0.00075	14.7	98
Run #5	Zn	0.00557	199	99	Run #10	Zn	-0.00406	202	101

Table 1. Continued

	Cd	0.00060	3.98	99		Cd	0.00041	4.00	100
	Ba	0.00145	41.2	103		Ba	-0.00183	40.1	100
	Pb	0.00343	14.7	98		Pb	-0.00059	14.7	98

Set 1					**Set 2**				
BID[a]	Element	CCB[b]	ICVS	% Rec (ICVS)[c]	BID[a]	Element	CCB[b]	ICVS	% Rec (ICVS)[c]
01/07/09	Cu	0.00053	14.9	99		Cu	0.00032	14.4	96
Run #11	Zn	0.01208	202	101	Run #1	Zn	0.00806	198	99
	Cd	0.00037	4.03	101		Cd	-0.00021	3.99	100
	Ba	-0.00166	40.1	100		Ba	0.00124	39.5	99
	Pb	0.00038	14.7	98		Pb	0.00182	14.6	97
01/07/09	Cu	0.00121	14.6	97		Cu	-0.00397	14.2	94
Run #12	Zn	0.00831	198	99	Run #2	Zn	-0.00533	200	100
	Cd	0.00039	4.00	100		Cd	0.00006	4.06	101
	Ba	-0.00110	39.5	99		Ba	-0.00201	39.5	99
	Pb	0.00106	14.7	98		Pb	-0.00203	14.6	97
01/07/09	Cu	0.00005	14.3	95		Cu	-0.00046	14.6	98
Run #13	Zn	0.00741	195.	98	Run #3	Zn	-0.00460	197	98
	Cd	-0.00029	3.92	98		Cd	-0.00090	4.03	101
	Ba	0.00096	38.9	97		Ba	0.00092	41.3	103
	Pb	0.00223	14.4	96		Pb	-0.00120	14.4	96
01/07/09	Cu	-0.00130	15.3	102		Cu	-0.00226	14.1	94
Run #14	Zn	0.00743	202	101	Run #4	Zn	-0.00090	192	96
	Cd	-0.00008	3.89	97		Cd	-0.00013	3.89	97
	Ba	-0.00088	38.6	97		Ba	-0.00068	40.0	100
	Pb	-0.00049	14.4	96		Pb	-0.00202	14.4	96
01/07/09	Cu	0.00052	14.3	95		Cu	-0.00219	14.4	96
Run #15	Zn	0.00868	194	97	Run #5	Zn	-0.00276	191	95
	Cd	0.00161	3.87	97		Cd	-0.00065	3.85	96
	Ba	-0.00032	38.5	96		Ba	0.00218	40.8	102
	Pb	0.00020	14.4	96		Pb	-0.00101	14.2	95

Table 1. Continued

Set 2

BID[a]	Element	CCB[b]	ICVS	% Rec (ICVS)[c]
	Cu	-0.00157	14.0	94
Run #6	Zn	0.00186	189	95
	Cd	0.00000	3.86	97
	Ba	0.00435	39.5	99
	Pb	0.00048	14.1	94
	Cu	-0.00144	14.4	96
Run #7	Zn	-0.00109	187	94
	Cd	-0.00072	3.81	95
	Ba	0.00017	40.8	102
	Pb	-0.00024	14.1	94
	Cu	-0.00343	13.8	92
Run #8	Zn	-0.00346	188	94
	Cd	-0.00041	3.84	96
	Ba	0.00155	39.2	98
	Pb	-0.00178	14.0	93
	Cu	0.00044	13.9	93
Run #9	Zn	0.00227	190	95
	Cd	-0.00035	3.87	97
	Ba	0.00228	39.2	98
	Pb	-0.00175	14.1	94
	Cu	-0.00206	14.1	94
Run #10	Zn	-0.00120	191	95
	Cd	-0.00004	3.87	97
	Ba	0.00143	39.5	99
	Pb	-0.00179	14.3	95

[a] BID = Block Initiation Date: a date assigned to each member of a group of samples that will identify the sample as a member of the group or "block."

[b] acceptance criteria for CCB is +/- 3 X IDL for each element.

[c] acceptance criteria for ICVS = +/- 10% (90% - 110%); ICVS = 15ppb for Cu and Pb; 200ppb for Zn; 4ppb for Cd; 40ppb for Ba.

Table 2. Recoveries of elements from reference solutions used as laboratory control samples in the ICP-MS quantitative analysis of Big River sediment samples.

BID	Analysis Date	Reference Material	Element	Actual Conc.	Meas. Conc.	% Rec[a]	ISOP	Oper. Init.
01/07/09	02/05/09	NIST 1643e[b]	Cu	22.76 +/- 0.31	22.2	99	P.241	VDM/TWM
01/07/09	02/05/09	Spex ICS -1[c]	Zn	50 +/- 5	52.1	100	P.241	VDM/TWM
01/07/09	02/05/09	NIST 1643e[b]	Cd	6.568 +/- 0.073	6.36	98	P.241	VDM/TWM
01/07/09	02/05/09	Spex ICS -1[c]	Ba	50+/- 5	51.5	100	P.241	VDM/TWM
01/07/09	02/05/09	NIST 1643e[b]	Pb	19.63 +/- 0.21	18.7	96	P.241	VDM/TWM
01/26/09	02/10/09	NIST 1643e[b]	Cu	22.76 +/- 0.31	23.2	99	P.241	VDM/TWM
01/26/09	02/10/09	Spex ICS -1[c]	Zn	50 +/- 5	53.1	100	P.241	VDM/TWM
01/26/09	02/10/09	NIST 1643e[b]	Cd	6.568 +/- 0.073	6.54	100	P.241	VDM/TWM
01/26/09	02/10/09	Spex ICS -1[c]	Ba	50+/- 5	53.6	100	P.241	VDM/TWM
01/26/09	02/10/09	NIST 1643e[b]	Pb	19.63 +/- 0.21	18.9	97	P.241	VDM/TWM
02/17/09	02/26/09	NIST 1643e[b]	Cu	22.76 +/- 0.31	22.4	100	P.241	VDM/TWM
02/17/09	02/26/09	Spex ICS -1[c]	Zn	50 +/- 5	51.6	100	P.241	VDM/TWM
02/17/09	02/26/09	NIST 1643e[b]	Cd	6.568 +/- 0.073	6.42	99	P.241	VDM/TWM
02/17/09	02/26/09	Spex ICS -1[c]	Ba	50+/- 5	51.5	100	P.241	VDM/TWM
02/17/09	02/26/09	NIST 1643e[b]	Pb	19.63 +/- 0.21	18.8	97	P.241	VDM/TWM

[a] %Rec = 100% if within range, otherwise calculated based on upper or lower limit of range.

[b] NIST 1643e = National Institute of Standards and Technology Standard Reference Material Trace Elements in Water 1643e. Concentration results expressed as ng/mL. Solution used as laboratory control sample.

[c] Spex ICS-1 = SPEX ClaritasPPT Instrument Check Standard 1; Cat No. CL-ICS-1; Spec Certiprep, Metuchen, NJ; Solution used as laboratory control sample.

Table 3. Recoveries of Cu, Zn, Cd, Ba, and Pb in sediment reference materials.

Measured concentrations using total recoverable digestion; reported concentrations based on complete dissolution.

NRCC PACS-1[a]

BID	Element	Reported Conc (µg/g dry wgt)	Measured Conc	% Recovery[b]
01/07/09	Cu	452 ± 16	397	91
01/07/09	Zn	824 ± 22	774	97
01/07/09	Cd	2.38 ± 0.2	2.30	97
01/07/09	Ba	---	348	---
01/07/09	Pb	404 ± 20	349	91

[a] National Research Council Canada CRM PACS-1: marine sediment.

[b] %Rec = 100% if within range, otherwise calculated based on upper or lower limit of range.

NIST 2704[c]

BID	Element	Reported Conc (µg/g dry wgt)	Measured Conc	% Recovery[d]
01/07/09	Cu	98.6 ± 5	88.9	95
01/07/09	Zn	438 ± 12	426	100
01/07/09	Cd	3.45 ±0.22	3.39	100
01/07/09	Ba	414 ± 12	141	35
01/07/09	Pb	161 ± 17	151	100
02/10/09	Cu	98.6 ± 5	86.3	95
02/10/09	Zn	438 ± 12	380	89
02/10/09	Cd	3.45 ± 0.22	4.96	135
02/10/09	Ba	414 ± 12	133	33
02/10/09	Pb	161 ± 17	151	100

[c] National Institute of Standards and Technology SRM 2704: Buffalo River sediment.

[d] %Rec = 100% if within range, otherwise calculated based on upper or lower limit of range.

Table 3. Continued

Measured concentrations using total recoverable digestion; reported concentrations based on complete dissolution.

NIST 2710[a] BID	Element	Reported Conc (µg/g dry wgt)	Measured Conc	% Rec[b]	**IAEA SL-1**[a] BID	Element	Reported Conc (µg/g dry wgt)	Measured Conc	% Rec[b]
01/26/09	Cu	2950 ± 130	2570	91	01/26/09	Cu	30 ± 5.6	28.4	100
01/26/09	Zn	6952 ± 91	5590	81	01/26/09	Zn	223 ± 10	200	90
01/26/09	Cd	21.8 ± 0.2	19.3	89	01/26/09	Cd	0.26 ± 0.05	0.24	100
01/26/09	Ba	707 ± 51	342	52	01/26/09	Ba	639 ± 53	449	77
01/26/09	Pb	5532 ± 80	4660	85	01/26/09	Pb	37.7 ± 7.4	36.2	100

[a] National Institute of Standards and Technology SRM 2710: Montana soil.

[b] %Rec = 100% if within range, otherwise calculated based on upper or lower limit of range.

[a] International Atomic Energy Agency SRM SL-1: lake sediment.

[b] %Rec = 100% if within range, otherwise calculated based on upper or lower limit of range.

NIST 2709[c] BID	Element	Reported Conc (µg/g dry wgt)	Measured Conc	% Rec[d]
01/26/09	Cu	34.6 ± 0.7	30.4	90
01/26/09	Zn	106 ± 3	92.2	90
01/26/09	Cd	0.38 ± 0.01	0.34	92
01/26/09	Ba	968 ± 40	416	45
01/26/09	Pb	18.9 ± 0.5	13.2	72

[c] National Institute of Standards and Technology SRM 2709: San Joaquin soil.

[d] %Rec = 100% if within range, otherwise calculated based on upper or lower limit of range.

Table 4. Percent relative standard deviation from triplicate preparation and analysis of Big River sediment samples for Cu, Zn, Cd, Ba, and Pb.

BID[a]	Ele.	Sample	Rep 1	Rep 2	Rep 3	Mean	Units	SD[b]	%RSD[c]	PSOP[d]	Prep. Init.	ISOP[e]	Oper. Init.
01/07/09	Cu	44243	35.7	34.9	34.3	35.0	µg/g	0.68	2.0	P.510h	VDM	P.241	VDM/TWM
01/07/09	Zn	44243	3573	3669	3705	3649	µg/g	68.3	1.9	P.510h	VDM	P.241	VDM/TWM
01/07/09	Cd	44243	52.7	53.3	54.5	53.5	µg/g	0.93	1.7	P.510h	VDM	P.241	VDM/TWM
01/07/09	Ba	44243	325	325	305	318	µg/g	11.6	3.6	P.510h	VDM	P.241	VDM/TWM
01/07/09	Pb	44243	5770	5619	5657	5682	µg/g	78.6	1.4	P.510h	VDM	P.241	VDM/TWM
01/07/09	Cu	44569	45.9	43.7	44.0	44.5	µg/g	1.19	2.7	P.510h	VDM	P.241	VDM/TWM
01/07/09	Zn	44569	415	399	398	404	µg/g	9.46	2.3	P.510h	VDM	P.241	VDM/TWM
01/07/09	Cd	44569	4.58	4.54	4.48	4.53	µg/g	0.05	1.2	P.510h	VDM	P.241	VDM/TWM
01/07/09	Ba	44569	1051	1037	1096	1061	µg/g	31.1	2.9	P.510h	VDM	P.241	VDM/TWM
01/07/09	Pb	44569	2276	2173	2235	2228	µg/g	52.1	2.3	P.510h	VDM	P.241	VDM/TWM
01/26/09	Cu	43727	0.47	0.43	0.48	0.46	µg/g	0.027	5.9	P.510h	VDM	P.241	VDM/TWM
01/26/09	Zn	43727	3.43	2.74	2.70	2.96	µg/g	0.41	14	P.510h	VDM	P.241	VDM/TWM
01/26/09	Cd	43727	0.011	0.011	0.017	0.013	µg/g	0.004	30	P.510h	VDM	P.241	VDM/TWM
01/26/09	Ba	43727	12.3	13.7	12.1	12.7	µg/g	0.87	6.9	P.510h	VDM	P.241	VDM/TWM
01/26/09	Pb	43727	1.29	1.38	1.25	1.31	µg/g	0.068	5.2	P.510h	VDM	P.241	VDM/TWM
02/17/09	Cu	43726	2.07	2.01	2.06	2.05	µg/g	0.033	1.6	P.510h	VDM	P.241	VDM/TWM
02/17/09	Zn	43726	15.3	12.7	16.2	14.8	µg/g	1.82	12	P.510h	VDM	P.241	VDM/TWM
02/17/09	Cd	43726	< 0.20	< 0.20	< 0.20	---[f]	µg/g	---[f]	---[f]	P.510h	VDM	P.241	VDM/TWM
02/17/09	Ba	43726	17.5	15.9	15.2	16.2	µg/g	1.18	7.3	P.510h	VDM	P.241	VDM/TWM
02/17/09	Pb	43726	9.61	10.6	8.66	9.61	µg/g	0.96	10	P.510h	VDM	P.241	VDM/TWM

[a] BID = Block Initiation Date: a date assigned to each member of a group of samples that will identify the sample as a member of the group or "block."

[b] SD = standard deviation.

[c] %RSD = percent relative standard deviation, calculated as SD/Mean X 100.

[d] PSOP = standard operating procedure used for chemical preparation of sample.

[e] ISOP = standard operating procedure used for instrumental analysis of sample.

[f] %RSD invalid due to one or more of replicates being < method detection limit.

Table 4. Continued

BID[a]	Ele.	Sample	Rep 1	Rep 2	Rep 3	Mean	Units	SD[b]	%RSD[c]	PSOP[d]	Prep. Init.	ISOP[e]	Oper. Init.
02/17/09	Cu	44244	1.82	2.12	4.52	2.82	µg/g	1.48	52	P.510h	VDM	P.241	VDM/TWM
02/17/09	Zn	44244	9.35	18.5	30.8	19.6	µg/g	10.8	55	P.510h	VDM	P.241	VDM/TWM
02/17/09	Cd	44244	< 0.20	< 0.20	< 0.20	---[f]	µg/g	---[f]	---[f]	P.510h	VDM	P.241	VDM/TWM
02/17/09	Ba	44244	12.2	14.3	18.4	15.0	µg/g	3.15	21	P.510h	VDM	P.241	VDM/TWM
02/17/09	Pb	44244	21.6	8.65	25.4	18.6	µg/g	8.78	47	P.510h	VDM	P.241	VDM/TWM
02/17/09	Cu	44246	5.07	10.2	5.20	6.82	µg/g	2.93	43	P.510h	VDM	P.241	VDM/TWM
02/17/09	Zn	44246	36.4	30.5	27.6	31.5	µg/g	4.48	14	P.510h	VDM	P.241	VDM/TWM
02/17/09	Cd	44246	0.52	< 0.20	< 0.20	---[f]	µg/g	---[f]	---[f]	P.510h	VDM	P.241	VDM/TWM
02/17/09	Ba	44246	66.8	76.1	52.4	65.1	µg/g	11.9	18	P.510h	VDM	P.241	VDM/TWM
02/17/09	Pb	44246	30.2	31.4	31.0	30.9	µg/g	0.61	2.0	P.510h	VDM	P.241	VDM/TWM
02/17/09	Cu	45168	1.58	2.16	2.13	1.96	µg/g	0.33	17	P.510h	VDM	P.241	VDM/TWM
02/17/09	Zn	45168	112	75.6	68.8	85.5	µg/g	23.2	27	P.510h	VDM	P.241	VDM/TWM
02/17/09	Cd	45168	0.44	0.50	0.23	0.39	µg/g	0.14	36	P.510h	VDM	P.241	VDM/TWM
02/17/09	Ba	45168	24.7	12.4	12.4	16.5	µg/g	7.10	43	P.510h	VDM	P.241	VDM/TWM
02/17/09	Pb	45168	119	117	165	134	µg/g	27.2	20	P.510h	VDM	P.241	VDM/TWM

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[a] BID = Block Initiation Date: a date assigned to each member of a group of samples that will identify the sample as member of group or "block."

[b] SD = standard deviation.

[c] %RSD = percent relative standard deviation, calculated as SD/Mean X 100.

[d] PSOP = standard operating procedure used for chemical preparation of sample.

[e] ISOP = standard operating procedure used for instrumental analysis of sample.

[f] %RSD invalid due to one or more of replicates being < method detection limit.

[e] ISOP = standard operating procedure used for instrumental analysis of sample.

Table 5. Relative percent difference for duplicate sieving, digestion, and analysis of Big R. sediments by ICP-MS.

BID[a]	Duplicate Type	Sample	Fraction	Element	Dup 1	Dup 2	Diff[b]	Mean	RPD[c]	ISOP[d]	Oper. Init.
01/07/09	sieve duplicate	44228, 44231	> 250µm - 2mm	Cu	16.5	4.5	12.0	10.5	115	P.241	VDM/TWM
01/07/09	sieve duplicate	44228, 44231	> 250µm - 2mm	Zn	377	217	160	297	54	P.241	VDM/TWM
01/07/09	sieve duplicate	44228, 44231	> 250µm - 2mm	Cd	5.55	3.55	2.00	4.55	44	P.241	VDM/TWM
01/07/09	sieve duplicate	44228, 44231	> 250µm - 2mm	Ba	17.1	13.7	3.40	15.4	22	P.241	VDM/TWM
01/07/09	sieve duplicate	44228, 44231	> 250µm - 2mm	Pb	397	296	101	347	29	P.241	VDM/TWM
01/07/09	sieve duplicate	44229, 44232	> 63µm - 250µm	Cu	31.2	52.5	21.3	41.9	51	P.241	VDM/TWM
01/07/09	sieve duplicate	44229, 44232	> 63µm - 250µm	Zn	436	704	268	570	47	P.241	VDM/TWM
01/07/09	sieve duplicate	44229, 44232	> 63µm - 250µm	Cd	7.30	10.5	3.20	8.90	36	P.241	VDM/TWM
01/07/09	sieve duplicate	44229, 44232	> 63µm - 250µm	Ba	110	113	3.00	112	2.7	P.241	VDM/TWM
01/07/09	sieve duplicate	44229, 44232	> 63µm - 250µm	Pb	833	749	84.0	791	11	P.241	VDM/TWM
01/07/09	sieve duplicate	44230,44233	< 63µm	Cu	110	113	3.00	112	2.7	P.241	VDM/TWM
01/07/09	sieve duplicate	44230,44233	< 63µm	Zn	2100	2360	260	2230	12	P.241	VDM/TWM
01/07/09	sieve duplicate	44230,44233	< 63µm	Cd	29.9	32.7	2.80	31.3	8.9	P.241	VDM/TWM
01/07/09	sieve duplicate	44230,44233	< 63µm	Ba	228	261	33.0	245	13	P.241	VDM/TWM
01/07/09	sieve duplicate	44230,44233	< 63µm	Pb	3260	3850	590	3555	17	P.241	VDM/TWM
01/07/09	sieve duplicate	44235,44238	> 250µm - 2mm	Cu	30.4	10.0	20.4	20.2	101	P.241	VDM/TWM
01/07/09	sieve duplicate	44235,44238	> 250µm - 2mm	Zn	722	483	239	603	40	P.241	VDM/TWM
01/07/09	sieve duplicate	44235,44238	> 250µm - 2mm	Cd	11.0	6.55	4.45	8.78	51	P.241	VDM/TWM
01/07/09	sieve duplicate	44235,44238	> 250µm - 2mm	Ba	40.2	31.0	9.20	35.6	26	P.241	VDM/TWM
01/07/09	sieve duplicate	44235,44238	> 250µm - 2mm	Pb	1940	2190	250	2065	12	P.241	VDM/TWM
01/07/09	sieve duplicate	44236, 44239	> 63µm - 250µm	Cu	52.2	47.4	4.80	49.8	9.6	P.241	VDM/TWM
01/07/09	sieve duplicate	44236, 44239	> 63µm - 250µm	Zn	1210	1370	160	1290	12	P.241	VDM/TWM
01/07/09	sieve duplicate	44236, 44239	> 63µm - 250µm	Cd	20.7	23.9	3.20	22.3	14	P.241	VDM/TWM
01/07/09	sieve duplicate	44236, 44239	> 63µm - 250µm	Ba	165	162	3.00	164.	1.8	P.241	VDM/TWM
01/07/09	sieve duplicate	44236, 44239	> 63µm - 250µm	Pb	1730	1770	40.0	1750	2.3	P.241	VDM/TWM
01/07/09	sieve duplicate	44564,44565	< 63µm	Cu	39.0	42.7	3.70	40.9	9.1	P.241	VDM/TWM
01/07/09	sieve duplicate	44564,44565	< 63µm	Zn	470	502	32.0	486	6.6	P.241	VDM/TWM
01/07/09	sieve duplicate	44564,44565	< 63µm	Cd	5.18	5.63	0.45	5.41	8.3	P.241	VDM/TWM
01/07/09	sieve duplicate	44564,44565	< 63µm	Ba	1100	1140	40.0	1120	3.6	P.241	VDM/TWM
01/07/09	sieve duplicate	44564,44565	< 63µm	Pb	1390	1380	10	1390	0.7	P.241	VDM/TWM
01/26/09	Method	44226	< 63µm	Cu	31.0	30.3	0.68	30.6	2.2	P.241	VDM/TWM
01/26/09	Method	44226	< 63µm	Zn	343	340	3.15	341	0.9	P.241	VDM/TWM

Table 5. Continued

01/26/09	Method	44226	< 63µm	Cd	3.91	3.80	0.12	3.85	3.1	P.241	VDM/TWM
01/26/09	Method	44226	< 63µm	Ba	633	622	11.4	628	1.8	P.241	VDM/TWM
01/26/09	Method	44226	< 63µm	Pb	843	844	1.27	843	0.2	P.241	VDM/TWM
01/26/09	Method	44236	> 63µm - 250µm	Cu	44.2	63.1	19.0	53.6	35	P.241	VDM/TWM
01/26/09	Method	44236	> 63µm - 250µm	Zn	1080	1140	60.0	1110	5.4	P.241	VDM/TWM
01/26/09	Method	44236	> 63µm - 250µm	Cd	19.4	19.7	0.33	19.6	1.7	P.241	VDM/TWM
01/26/09	Method	44236	> 63µm - 250µm	Ba	136	158	21.9	147	15	P.241	VDM/TWM
01/26/09	Method	44236	> 63µm - 250µm	Pb	2530	1830	700	2180	32	P.241	VDM/TWM
01/26/09	Method	44564	< 63µm	Cu	38.4	36.4	1.94	37.4	5.2	P.241	VDM/TWM
01/26/09	Method	44564	< 63µm	Zn	436	422	14	429	3.2	P.241	VDM/TWM
01/26/09	Method	44564	< 63µm	Cd	4.78	4.67	0.11	4.73	2.3	P.241	VDM/TWM
01/26/09	Method	44564	< 63µm	Ba	1090	1050	40.0	1070	3.7	P.241	VDM/TWM
01/26/09	Method	44564	< 63µm	Pb	1300	1250	50.3	1280	3.9	P.241	VDM/TWM

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[a] BID = Block Initiation Date: a date assigned to each member of a group of samples that will identify the sample as a member of the group or "block."

[b] Diff = Dup 1 - Dup 2.

[c] RPD = relative percent difference, calculated as Diff/Mean X 100; acceptance criteria +/- 10%.

[d] ISOP = standard operating procedure used for instrumental analysis of sample (SOP P.241).

Table 6. Relative percent difference for duplicate analysis of Big R. sediment digestates by ICP-MS.

BID[a]	Duplicate Type	Matrix	Element	Dup 1	Dup 2	Diff[b]	Mean	RPD[c]	ISOP[d]	Oper. Init.
01/07/09	44220 - Analytical	sediment	Cu	19.4	19.4	0.07	19.4	0.3	P.241	VDM/TWM
01/07/09	44220 - Analytical	sediment	Zn	150	152	2.34	151	1.5	P.241	VDM/TWM
01/07/09	44220 - Analytical	sediment	Cd	5.72	5.83	0.11	5.77	1.9	P.241	VDM/TWM
01/07/09	44220 - Analytical	sediment	Ba	59.7	60.5	0.82	60.1	1.4	P.241	VDM/TWM
01/07/09	44220 - Analytical	sediment	Pb	38.9	39.2	0.34	39.0	0.9	P.241	VDM/TWM
01/07/09	44221 - Analytical	sediment	Cu	18.9	19.0	0.12	19.0	0.6	P.241	VDM/TWM
01/07/09	44221 - Analytical	sediment	Zn	145	146	0.45	145	0.3	P.241	VDM/TWM
01/07/09	44221 - Analytical	sediment	Cd	5.67	5.73	0.06	5.70	1.0	P.241	VDM/TWM
01/07/09	44221 - Analytical	sediment	Ba	82.5	82.7	0.20	82.6	0.2	P.241	VDM/TWM
01/07/09	44221 - Analytical	sediment	Pb	49.8	49.5	0.33	49.7	0.7	P.241	VDM/TWM
01/07/09	44224 - Analytical	sediment	Cu	20.8	20.9	0.07	20.8	0.3	P.241	VDM/TWM
01/07/09	44224 - Analytical	sediment	Zn	156	157	1.02	156	0.7	P.241	VDM/TWM
01/07/09	44224 - Analytical	sediment	Cd	6.04	6.07	0.03	6.06	0.4	P.241	VDM/TWM
01/07/09	44224 - Analytical	sediment	Ba	68.0	69.0	0.97	68.5	1.4	P.241	VDM/TWM
01/07/09	44224 - Analytical	sediment	Pb	64.1	64.4	0.32	64.3	0.5	P.241	VDM/TWM
01/26/09	43726 - Analytical	sediment	Cu	19.8	19.6	0.25	19.7	1.3	P.241	VDM/TWM
01/26/09	43726 - Analytical	sediment	Zn	142	140	1.72	141	1.2	P.241	VDM/TWM
01/26/09	43726 - Analytical	sediment	Cd	5.83	5.75	0.09	5.79	1.5	P.241	VDM/TWM
01/26/09	43726 - Analytical	sediment	Ba	54.1	53.6	0.54	53.9	1.0	P.241	VDM/TWM
01/26/09	43726 - Analytical	sediment	Pb	23.0	22.8	0.25	22.9	1.1	P.241	VDM/TWM
01/26/09	43727 - Analytical	sediment	Cu	19.1	19.0	0.13	19.0	0.7	P.241	VDM/TWM
01/26/09	43727 - Analytical	sediment	Zn	137	137	0.08	137	0.1	P.241	VDM/TWM
01/26/09	43727 - Analytical	sediment	Cd	5.71	5.73	0.02	5.72	0.4	P.241	VDM/TWM
01/26/09	43727 - Analytical	sediment	Ba	51.0	51.6	0.55	51.3	1.1	P.241	VDM/TWM
01/26/09	43727 - Analytical	sediment	Pb	20.0	20.0	0.02	20.0	0.1	P.241	VDM/TWM
02/17/09	43726 - Analytical	sediment	Cu	19.5	19.5	0.035	19.5	0.2	P.241	VDM/TWM
02/17/09	43726 - Analytical	sediment	Zn	142	143	0.43	143	0.3	P.241	VDM/TWM
02/17/09	43726 - Analytical	sediment	Cd	5.81	5.79	0.019	5.80	0.3	P.241	VDM/TWM
02/17/09	43726 - Analytical	sediment	Ba	50.7	51.0	0.34	50.9	0.7	P.241	VDM/TWM
02/17/09	43726 - Analytical	sediment	Pb	22.1	22.0		22.1	0.3	P.241	VDM/TWM

Table 6. Continued

02/17/09	44244 - Analytical	sediment	Cu	19.3	19.2	0.069	19.3	0.4	P.241	VDM/TWM
02/17/09	44244 - Analytical	sediment	Zn	139	139	0.44	139	0.3	P.241	VDM/TWM
02/17/09	44244 - Analytical	sediment	Cd	5.70	5.71	0.017	5.70	0.3	P.241	VDM/TWM
02/17/09	44244 - Analytical	sediment	Ba	49.3	49.1	0.17	49.2	0.4	P.241	VDM/TWM
02/17/09	44244 - Analytical	sediment	Pb	25.0	25.0	0.056	25.0	0.2	P.241	VDM/TWM

[a]BID = Block Initiation Date: a date assigned to each member of a group of samples that will identify the sample as a member of the group or "block."

[b]Diff = Dup 1 - Dup 2; digestates spiked with mid-range standard prior to analysis.

[c]RPD = relative percent difference, calculated as Diff/Mean X 100; acceptance criteria +/- 10%.

[d]ISOP = standard operating procedure used for instrumental analysis of sample (SOP P.241).

Table 7. Percent recoveries of elements in pre-digestion spikes of Big River sediment samples.

BID[a]	Ele.	Spk Type	Analysis Units	Spk Amt.[b] µg	Wgt. (g)	Effective[c] Conc.	Unspked.[d] Conc.	Spk/ Unspiked	Unspiked SD	Spk/ Bkgd SD	Spiked[e] Conc.	% Rec.[f]	ISOP	Oper. Init.
01/26/09	Cu	43727 - Method	µg/g	0.1	0.250	0.40	0.46	0.9	0.027	15	1.03	143	P.241	VDM/TWM
01/26/09	Zn	43727 - Method	µg/g	50.0	0.250	200	2.96	68	0.41	484	195	96	P.241	VDM/TWM
01/26/09	Cd	43727 - Method	µg/g	1.0	0.250	4.00	0.013	307	0.004	1040	3.89	97	P.241	VDM/TWM
01/26/09	Ba	43727 - Method	µg/g	100	0.250	400	12.7	31	0.87	460	399	97	P.241	VDM/TWM
01/26/09	Pb	43727 - Method	µg/g	10.0	0.250	40.0	1.31	31	0.068	586	41.2	100	P.241	VDM/TWM
01/26/09	Cu	43727 - Method	µg/g	1.0	0.250	4.00	0.46	8.8	0.027	150	4.13	92	P.241	VDM/TWM
01/26/09	Zn	43727 - Method	µg/g	500	0.250	2000	2.96	676	0.41	4840	1877	94	P.241	VDM/TWM
01/26/09	Cd	43727 - Method	µg/g	10.0	0.250	40.0	0.013	3070	0.004	10400	38.4	96	P.241	VDM/TWM
01/26/09	Ba	43727 - Method	µg/g	500	0.250	2000	12.7	157	0.87	2300	1841	91	P.241	VDM/TWM
01/26/09	Pb	43727 - Method	µg/g	100	0.250	400	1.31	305	0.068	5860	373	93	P.241	VDM/TWM
02/17/09	Cu	43726 - Method	µg/g	1.0	0.258	3.88	2.05	1.9	0.033	118	5.75	96	P.241	VDM/TWM
02/17/09	Zn	43726 - Method	µg/g	50.0	0.258	194	14.8	13	1.82	107	191	91	P.241	VDM/TWM
02/17/09	Cd	43726 - Method	µg/g	1.0	0.258	3.88	0.007	587	0.005	721	4.12	106	P.241	VDM/TWM
02/17/09	Ba	43726 - Method	µg/g	50.0	0.258	194	16.2	12	1.18	164	206	98	P.241	VDM/TWM
02/17/09	Pb	43726 - Method	µg/g	10.0	0.258	38.8	9.61	4.0	0.96	40	47.3	97	P.241	VDM/TWM

Table 7. Continued

02/17/09	Cu	43726 - Method	µg/g	1.0	0.257	3.89	2.05	1.9	0.033	119	6.40	112	P.241	VDM/TWM
02/17/09	Zn	43726 - Method	µg/g	50.0	0.257	195	14.8	13	1.82	107	197	94	P.241	VDM/TWM
02/17/09	Cd	43726 - Method	µg/g	1.0	0.257	3.89	0.007	589	0.005	724	3.92	101	P.241	VDM/TWM
02/17/09	Ba	43726 - Method	µg/g	50.0	0.257	195	16.2	12	1.18	165	208	98	P.241	VDM/TWM
02/17/09	Pb	43726 - Method	µg/g	10.0	0.257	38.9	9.61	4.0	0.96	41	50.1	104	P.241	VDM/TWM
02/17/09	Cu	44244 - Method	µg/g	1.0	0.255	3.92	2.82	1.4	1.48	2.7	---g	---g	P.241	VDM/TWM
02/17/09	Zn	44244 - Method	µg/g	50.0	0.255	196	19.6	10	10.7	18	215	100	P.241	VDM/TWM
02/17/09	Cd	44244 - Method	µg/g	1.0	0.255	3.92	0.019	211	0.049	80	4.11	104	P.241	VDM/TWM
02/17/09	Ba	44244 - Method	µg/g	50.0	0.255	196	14.9	13	3.16	62	216	102	P.241	VDM/TWM
02/17/09	Pb	44244 - Method	µg/g	10.0	0.255	39.2	18.6	2.1	8.79	4.5	---g	---g	P.241	VDM/TWM
02/17/09	Cu	44244 - Method	µg/g	1.0	0.256	3.91	2.82	1.4	1.48	2.6	---g	---g	P.241	VDM/TWM
02/17/09	Zn	44244 - Method	µg/g	50.0	0.256	195	19.6	10	10.7	18	198	91	P.241	VDM/TWM
02/17/09	Cd	44244 - Method	µg/g	1.0	0.256	3.91	0.019	210	0.049	80	3.87	99	P.241	VDM/TWM
02/17/09	Ba	44244 - Method	µg/g	50.0	0.256	195	14.9	13	3.16	62	207	98	P.241	VDM/TWM
02/17/09	Pb	44244 - Method	µg/g	10.0	0.256	39.1	18.6	2.1	8.79	4.4	---g	---g	P.241	VDM/TWM
02/17/09	Cu	44246 - Method	µg/g	1.0	0.253	3.95	6.81	0.6	2.90	1.4	---g	---g	P.241	VDM/TWM
02/17/09	Zn	44246 - Method	µg/g	50.0	0.253	198	31.5	6.3	4.51	44	219	95	P.241	VDM/TWM
02/17/09	Cd	44246 - Method	µg/g	1.0	0.253	3.95	0.22	18	0.27	15	4.19	100	P.241	VDM/TWM

Table 7. Continued

02/17/09	Ba	44246 - Method	µg/g	50.0	0.253	198	65.1	3.0	11.9	17	258	98	P.241	VDM/TWM
02/17/09	Pb	44246 - Method	µg/g	10.0	0.253	39.5	30.9	1.3	0.61	65	74.3	110	P.241	VDM/TWM
02/17/09	Cu	44246 - Method	µg/g	1.0	0.251	3.98	6.81	0.6	2.90	1.4	---g	---g	P.241	VDM/TWM
02/17/09	Zn	44246 - Method	µg/g	50.0	0.251	199	31.5	6.3	4.51	44	217	93	P.241	VDM/TWM
02/17/09	Cd	44246 - Method	µg/g	1.0	0.251	3.98	0.22	18	0.27	15	4.20	100	P.241	VDM/TWM
02/17/09	Ba	44246 - Method	µg/g	50.0	0.251	199	65.1	3.1	11.9	17	287	111	P.241	VDM/TWM
02/17/09	Pb	44246 - Method	µg/g	10.0	0.251	39.8	30.9	1.3	0.61	66	75.6	112	P.241	VDM/TWM
02/17/09	Cu	45168 - Method	µg/g	1.0	0.259	3.86	1.96	2.0	0.33	11.8	8.31	164	P.241	VDM/TWM
02/17/09	Zn	45168 - Method	µg/g	50.0	0.259	193	85.6	2.3	23.4	8.3	322	122	P.241	VDM/TWM
02/17/09	Cd	45168 - Method	µg/g	1.0	0.259	3.86	0.39	10	0.14	27	4.91	117	P.241	VDM/TWM
02/17/09	Ba	45168 - Method	µg/g	50.0	0.259	193	16.5	12	7.10	27	225	108	P.241	VDM/TWM
02/17/09	Pb	45168 - Method	µg/g	10.0	0.259	38.6	134	0.3	27.2	1.4	---g	---g	P.241	VDM/TWM
02/17/09	Cu	45168 - Method	µg/g	1.0	0.252	3.97	1.96	2.0	0.33	12.1	11	221	P.241	VDM/TWM
02/17/09	Zn	45168 - Method	µg/g	50.0	0.252	198	85.6	2.3	23.4	8.5	---g	---g	P.241	VDM/TWM
02/17/09	Cd	45168 - Method	µg/g	1.0	0.252	3.97	0.39	10	0.14	28	4.86	113	P.241	VDM/TWM
02/17/09	Ba	45168 - Method	µg/g	50.0	0.252	198	16.5	12	7.10	28	235	110	P.241	VDM/TWM
02/17/09	Pb	45168 - Method	µg/g	10.0	0.252	39.7	134	0.3	27.2	1.5	---g	---g	P.241	VDM/TWM

Table 7. Continued

[a] BID = Block Initiation Date: a date assigned to each member of a group of samples that will identify the sample as a member of the group or "block."

[b] Spike Amt. µg = the absolute microgram (µg) amount of the spike which was added to a sample.

[c] Effective Conc. = the Spike Amt (µg) divided by the sample weight (g), units µg/g.

[d] Unspiked Conc. = the measured concentration of the sample prior to spiking, units µg/g.

[e] Spiked Conc. = the measured concentration of the spiked sample (spike + unspiked, units µg/g).

[f] % Rec. = percent recovery: [(Spiked Conc. - Unspiked Conc.)/Effective Conc. * 100]

[g] spike invalid due to spk/bkgd SD < 10.

Table 8. Percent recovery of elements spiked in Big River sediment digestates and analyzed by ICP-MS.

BID[a]	Ele.	Spk Type	Matrix	Analysis Units	Spk Amt.[b] µg	Vol. (mL)	Effective[c] Conc.	Bkgd.[d] Conc.	Spk/ Bkgd	Total[e] Conc.	% Rec.[f]	ISOP	Oper. Init.
01/07/09	Cu	44220 - Analytical	sediment	ng/mL	100	5	20.0	0.39	52	19.3	95	P.241	VDM/TWM
01/07/09	Zn	44220 - Analytical	sediment	ng/mL	750	5	150	13.6	11	150	91	P.241	VDM/TWM
01/07/09	Cd	44220 - Analytical	sediment	ng/mL	30	5	6.00	0.079	76	5.73	94	P.241	VDM/TWM
01/07/09	Ba	44220 - Analytical	sediment	ng/mL	250	5	50.0	10.0	5.0	59.6	99	P.241	VDM/TWM
01/07/09	Pb	44220 - Analytical	sediment	ng/mL	100	5	20.0	19.3	1.0	39.1	99	P.241	VDM/TWM
01/07/09	Cu	44221 - Analytical	sediment	ng/mL	100	5	20.0	1.10	18	19.2	91	P.241	VDM/TWM
01/07/09	Zn	44221 - Analytical	sediment	ng/mL	750	5	150	12.9	12	149	91	P.241	VDM/TWM
01/07/09	Cd	44221 - Analytical	sediment	ng/mL	30	5	6.00	0.13	45	5.88	96	P.241	VDM/TWM
01/07/09	Ba	44221 - Analytical	sediment	ng/mL	250	5	50.0	36.1	1.4	84.2	96	P.241	VDM/TWM
01/07/09	Pb	44221 - Analytical	sediment	ng/mL	100	5	20.0	30.6	0.7	50.7	100	P.241	VDM/TWM
01/07/09	Cu	44224 - Analytical	sediment	ng/mL	100	5	20.0	1.71	12	20.8	95	P.241	VDM/TWM
01/07/09	Zn	44224 - Analytical	sediment	ng/mL	750	5	150	18.4	8.1	155	91	P.241	VDM/TWM
01/07/09	Cd	44224 - Analytical	sediment	ng/mL	30	5	6.00	0.28	22	6.13	98	P.241	VDM/TWM
01/07/09	Ba	44224 - Analytical	sediment	ng/mL	250	5	50.0	21.9	2.3	68.8	94	P.241	VDM/TWM
01/07/09	Pb	44224 - Analytical	sediment	ng/mL	100	5	20.0	44.5	0.4	64.6	100	P.241	VDM/TWM
01/26/09	Cu	43726 - Analytical	sediment	ng/mL	100	5	20.0	0.63	32	19.6	95	P.241	VDM/TWM
01/26/09	Zn	43726 - Analytical	sediment	ng/mL	750	5	150	5.32	28	141	90	P.241	VDM/TWM
01/26/09	Cd	43726 - Analytical	sediment	ng/mL	30	5	6.00	0.014	432	5.76	96	P.241	VDM/TWM
01/26/09	Ba	43726 - Analytical	sediment	ng/mL	250	5	50.0	5.38	9.3	54.1	98	P.241	VDM/TWM
01/26/09	Pb	43726 - Analytical	sediment	ng/mL	100	5	20.0	3.04	6.6	22.7	98	P.241	VDM/TWM
01/26/09	Cu	43727 - Analytical	sediment	ng/mL	100	5	20.0	0.16	124	18.8	93	P.241	VDM/TWM
01/26/09	Zn	43727 - Analytical	sediment	ng/mL	750	5	150	2.19	68	135	89	P.241	VDM/TWM

Table 8. Continued

01/26/09	Cd	43727 - Analytical	sediment	ng/mL	30	5	6.00	0.011	550	5.70	95	P.241	VDM/TWM
01/26/09	Ba	43727 - Analytical	sediment	ng/mL	250	5	50.0	3.25	15	51.0	95	P.241	VDM/TWM
01/26/09	Pb	43727 - Analytical	sediment	ng/mL	100	5	20.0	0.37	54	20.0	98	P.241	VDM/TWM
02/17/09	Cu	43726 - Analytical	sediment	ng/mL	100	5	20.0	0.66	30	19.6	95	P.241	VDM/TWM
02/17/09	Zn	43726 - Analytical	sediment	ng/mL	750	5	150	4.60	33	143	92	P.241	VDM/TWM
02/17/09	Cd	43726 - Analytical	sediment	ng/mL	30	5	6.00	0.022	270	5.81	96	P.241	VDM/TWM
02/17/09	Ba	43726 - Analytical	sediment	ng/mL	250	5	50.0	4.54	11	50.9	93	P.241	VDM/TWM
02/17/09	Pb	43726 - Analytical	sediment	ng/mL	100	5	20.0	2.46	8.1	22.1	98	P.241	VDM/TWM
02/17/09	Cu	44244 - Analytical	sediment	ng/mL	100	5	20.0	0.65	31	19.1	92	P.241	VDM/TWM
02/17/09	Zn	44244 - Analytical	sediment	ng/mL	750	5	150	3.22	46.6	138	90	P.241	VDM/TWM
02/17/09	Cd	44244 - Analytical	sediment	ng/mL	30	5	6.00	0.020	307	5.66	94	P.241	VDM/TWM
02/17/09	Ba	44244 - Analytical	sediment	ng/mL	250	5	50.0	3.17	15.8	48.9	91	P.241	VDM/TWM
02/17/09	Pb	44244 - Analytical	sediment	ng/mL	100	5	20.0	5.70	3.5	25.3	98	P.241	VDM/TWM

[a] BID = Block Initiation Date: a date assigned to each member of a group of samples that will identify the sample as a member of the group or "block."

[b] Spike Amt. µg = the absolute microgram (µg) amount of the spike which was added to a sample.

[c] Effective Conc. = the Spike Amt (ng) divided by the sample volume (mL), units ng/mL.

[d] Unspiked Conc. = the measured concentration of the sample prior to spiking, units ng/mL.

[e] Spiked Conc. = the measured concentration of the spiked sample (spike + unspiked, units ng/mL).

[f] % Rec. = percent recovery: [(Spiked Conc. - Unspiked Conc.)/Effective Conc. * 100]

Table 9. Interference check of the Big River sediment matrix using dilution difference during ICP-MS quantitative analysis.

BID[a]	Run Date	Sample Used	Matrix	Element	Undiluted Sample	Diluted Sample[b]	Dil Conc X 5	Dil % Diff[c]
01/07/09	02/05/09	44220	sediment	Cu	19.2	4.06	20.3	5.6
01/07/09	02/05/09	44220	sediment	Zn	151	32.5	162	7.6
01/07/09	02/05/09	44220	sediment	Cd	5.80	1.22	6.08	4.7
01/07/09	02/05/09	44220	sediment	Ba	59.8	12.3	61.6	3.0
01/07/09	02/05/09	44220	sediment	Pb	39.1	8.14	40.7	4.1
01/07/09	02/05/09	44221	sediment	Cu	18.7	3.96	19.8	5.9
01/07/09	02/05/09	44221	sediment	Zn	145	31.2	156	7.5
01/07/09	02/05/09	44221	sediment	Cd	5.70	1.19	5.96	4.6
01/07/09	02/05/09	44221	sediment	Ba	82.4	16.9	84.7	2.8
01/07/09	02/05/09	44221	sediment	Pb	49.2	10.3	51.3	4.2
01/07/09	02/05/09	44224	sediment	Cu	20.9	4.44	22.2	6.2
01/07/09	02/05/09	44224	sediment	Zn	155	33.6	168	8.3
01/07/09	02/05/09	44224	sediment	Cd	6.11	1.28	6.40	4.6
01/07/09	02/05/09	44224	sediment	Ba	68.9	14.1	70.7	2.7
01/07/09	02/05/09	44224	sediment	Pb	64.8	13.4	66.8	3.0
01/26/09	02/10/09	43726	sediment	Cu	19.6	4.06	20.3	3.7
01/26/09	02/10/09	43726	sediment	Zn	142	30.4	152	7.0
01/26/09	02/10/09	43726	sediment	Cd	5.78	1.19	5.95	2.9
01/26/09	02/10/09	43726	sediment	Ba	53.7	11.0	54.8	2.1
01/26/09	02/10/09	43726	sediment	Pb	22.9	4.6	23.1	0.8
01/26/09	02/10/09	43727	sediment	Cu	18.9	4.06	20.3	7.3
01/26/09	02/10/09	43727	sediment	Zn	135	29.2	146	7.7
01/26/09	02/10/09	43727	sediment	Cd	5.73	1.20	6.02	5.0
01/26/09	02/10/09	43727	sediment	Ba	51.1	10.6	52.8	3.4
01/26/09	02/10/09	43727	sediment	Pb	20.0	4.1	20.6	2.9

Table 9. Continued

02/17/09	02/26/09	44244	sediment	Cu	19.5	4.10	20.5	5.0
02/17/09	02/26/09	44244	sediment	Zn	141	30.5	153	8.2
02/17/09	02/26/09	44244	sediment	Cd	5.83	1.25	6.25	7.1
02/17/09	02/26/09	44244	sediment	Ba	50.5	10.3	51.7	2.3
02/17/09	02/26/09	44244	sediment	Pb	25.5	5.2	26.0	2.1

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[a] BID = Block Initiation Date: a date assigned to each member of a group of samples that will identify the sample as a member of the group or "block."

[b] dilution factor = 5 (1+4); digestates spiked with mid-range standard prior to analysis.

[c] dilution % difference acceptance criteria = +/- 10%; concentrations exceeding +/- 10%. indicative of suspect interferent

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Table 10. Recovery of elements from an interference check solution[a] determined during quantitative ICP-MS analysis.

BID	Run Date	Element	Conc (ppb) actual	Conc (ppb) measured	Dilution Factor	% Recovery[b]
01/07/09	02/05/09	Cu	100	24.9	5	124
01/07/09	02/05/09	Zn	100	33.3	5	167
01/07/09	02/05/09	Cd	50	9.97	5	100
01/07/09	02/05/09	Pb[c]	20	22.9	5	115
01/26/09	02/10/09	Cu	100	24.1	5	120
01/26/09	02/10/09	Zn	100	29.8	5	149
01/26/09	02/10/09	Cd	50	10.3	5	103
01/26/09	02/10/09	Pb[c]	20	22.4	5	112
02/17/09	02/26/09	Cu	100	23.5	5	118
02/17/09	02/26/09	Zn	100	30.5	5	152
02/17/09	02/26/09	Cd	50	8.89	5	89
02/17/09	02/26/09	Pb[c]	20	22.4	5	112

[a] High Purity ICP-MS Solution AB in 2% nitric acid, Charleston, SC.; CAT # ICP-MS-ICS.

[b] Target recovery range 80% - 120%. Check solution contains extraordinarily high concentrations of several potentially interfering elements.

[c] Pb not present in interference check solution, but added (effective conc 10ppb) following dilution.

Table 11. Blank equivalent concentrations (BEC) of Cu, Zn, Cd, Ba, and Pb for procedural blank solutions digested and analyzed with Big River sediment samples.

BID[a]	Ele.	Matrix	Soln. Units	Soln 1 Conc.	Soln 2 Conc.	Soln 3 Conc.	Dil. Vol.	Mean Conc.[b]	Sample Wgt. (g)[c]	Mean BEC µg/g	BEC SD µg/g	PSOP	Prep. Init.	ISOP	Oper. Init.
01/07/09	Cu	Digestion Blk	ng/mL	0.060	0.041	0.010	100	0.037	0.250	0.015	0.010	P.510h	VDM	P.241	TWM
01/07/09	Zn	Digestion Blk	ng/mL	1.32	2.94	1.12	100	1.79	0.250	0.72	0.40	P.510h	VDM	P.241	TWM
01/07/09	Cd	Digestion Blk	ng/mL	0.019	0.017	0.035	100	0.02	0.250	0.009	0.004	P.510h	VDM	P.241	TWM
01/07/09	Ba	Digestion Blk	ng/mL	-0.009	-0.011	0.018	100	0.00	0.250	-0.0002	0.006	P.510h	VDM	P.241	TWM
01/07/09	Pb	Digestion Blk	ng/mL	-0.019	-0.024	0.014	100	-0.010	0.250	-0.004	0.008	P.510h	VDM	P.241	TWM
01/26/09	Cu	Digestion Blk	ng/mL	0.055	-0.006	0.27	100	0.105	0.250	0.042	0.057	P.510h	VDM	P.241	TWM
01/26/09	Zn	Digestion Blk	ng/mL	0.71	0.016	2.57	100	1.098	0.250	0.439	0.53	P.510h	VDM	P.241	TWM
01/26/09	Cd	Digestion Blk	ng/mL	0.000	0.001	0.011	100	0.00	0.250	0.00	0.002	P.510h	VDM	P.241	TWM
01/26/09	Ba	Digestion Blk	ng/mL	-0.013	0.026	-0.001	100	0.00	0.250	0.002	0.008	P.510h	VDM	P.241	TWM
01/26/09	Pb	Digestion Blk	ng/mL	-0.051	-0.035	-0.047	100	-0.044	0.250	-0.018	0.003	P.510h	VDM	P.241	TWM

[a] BID = Block Initiation Date: a date assigned to each member of a group of samples that will identify the sample as a member of the group or "block."

[b] Mean Conc. = the mean solution concentration of the procedural blanks for a block, n = 3; units ng/mL.

[c] Sample Wgt. = weight (g) used for BEC calculation.

Table 12. Method detection and quantitation limits for Cu, Zn, Cd, Ba, and Pb for analysis of Big R. sediments.

BID[a]	Ele.	Matrix	W/D/L[b]	Blk SD	Standard SD	IDL[c]	MDL[d]	MQL[e]	PSOP	Prep. Init.	ISOP	Inst. Init.	Units
01/07/09	Cu	sediment	D	0.010	0.004	0.014	0.033	0.11	P.510h	VDM	P.241	VDM/TWM	µg/g
01/07/09	Zn	sediment	D	0.40	0.028	1.78	1.20	3.96	P.510h	VDM	P.241	VDM/TWM	µg/g
01/07/09	Cd	sediment	D	0.004	0.000	0.002	0.012	0.040	P.510h	VDM	P.241	VDM/TWM	µg/g
01/07/09	Ba	sediment	D	0.006	0.003	0.005	0.021	0.069	P.510h	VDM	P.241	VDM/TWM	µg/g
01/07/09	Pb	sediment	D	0.008	0.002	0.002	0.025	0.083	P.510h	VDM	P.241	VDM/TWM	µg/g
01/26/09	Cu	sediment	D	0.057	0.002	0.014	0.17	0.56	P.510h	VDM	P.241	VDM/TWM	µg/g
01/26/09	Zn	sediment	D	0.53	0.007	1.78	1.60	5.28	P.510h	VDM	P.241	VDM/TWM	µg/g
01/26/09	Cd	sediment	D	0.002	0.001	0.002	0.008	0.026	P.510h	VDM	P.241	VDM/TWM	µg/g
01/26/09	Ba	sediment	D	0.008	0.009	0.005	0.036	0.12	P.510h	VDM	P.241	VDM/TWM	µg/g
01/26/09	Pb	sediment	D	0.003	0.001	0.002	0.011	0.036	P.510h	VDM	P.241	VDM/TWM	µg/g
02/17/09	Cu	sediment	D	0.008	0.003	0.014	0.024	0.079	P.510h	VDM	P.241	VDM/TWM	µg/g
02/17/09	Zn	sediment	D	0.93	0.009	1.78	2.79	9.21	P.510h	VDM	P.241	VDM/TWM	µg/g
02/17/09	Cd	sediment	D	0.068	0.001	0.002	0.20	0.66	P.510h	VDM	P.241	VDM/TWM	µg/g
02/17/09	Ba	sediment	D	0.002	0.005	0.005	0.018	0.059	P.510h	VDM	P.241	VDM/TWM	µg/g
02/17/09	Pb	sediment	D	0.001	0.002	0.002	0.006	0.020	P.510h	VDM	P.241	VDM/TWM	µg/g

[a] BID = Block Initiation Date: a date assigned to each member of a group of samples that will identify the sample as a member of the group or "block."

[b] W/D/L = state of starting sample: wet (W), dry (D), or liquid (L).

[c] IDL = instrument detection limit, unit ng/mL.

[d] MDL = method limit of detection, computed as $3 \text{ X } (SD_b^2 + SD_s^2)^{1/2}$ where SD_b = standard deviation of digestion blanks (n = 3) and SD_s = standard deviation of a low level standard diluted 100X (n = 3).

[e] MQL = 3.3 x MDL.

Table 13. XRF Calibration and Standards Data

Date of Analysis	Type	Units	Sample Location	Pb (ppm)	Zn (ppm)	Ba (ppm)	Cd (ppm)
9/10/2008	Standard	ppm	Calibrate Detector	PASS	PASS	PASS	PASS
9/10/2008	Standard	ppm	NIST High	PASS	PASS	PASS	PASS
9/10/2008	Standard	ppm	NIST Low	PASS	PASS	PASS	PASS
9/10/2008	Standard	ppm	NIST Med	PASS	PASS	PASS	PASS
9/10/2008	Standard	ppm	RCRA	PASS	PASS	PASS	PASS
9/10/2008	Standard	ppm	SiO2 Blank	PASS	PASS	PASS	PASS
10/6/2008	Standard	ppm	Calibrate Detector	PASS	PASS	PASS	PASS
10/6/2008	Standard	ppm	NIST High	PASS	PASS	PASS	PASS
10/6/2008	Standard	ppm	NIST Low	PASS	PASS	PASS	PASS
10/6/2008	Standard	ppm	NIST Med	PASS	PASS	PASS	PASS
10/6/2008	Standard	ppm	RCRA	PASS	PASS	PASS	PASS
10/6/2008	Standard	ppm	SiO2 Blank	PASS	PASS	PASS	PASS
10/20/2008	Standard	ppm	Calibrate Detector	PASS	PASS	PASS	PASS
10/20/2008	Standard	ppm	NIST High	PASS	PASS	PASS	PASS
10/20/2008	Standard	ppm	NIST Low	PASS	PASS	PASS	PASS
10/20/2008	Standard	ppm	NIST Med	PASS	PASS	PASS	PASS
10/20/2008	Standard	ppm	RCRA	PASS	PASS	PASS	PASS
10/20/2008	Standard	ppm	SiO2 Blank	PASS	PASS	PASS	PASS
10/31/2008	Standard	ppm	Calibrate Detector	PASS	PASS	PASS	PASS
10/31/2008	Standard	ppm	NIST High	PASS	PASS	PASS	PASS
10/31/2008	Standard	ppm	NIST Low	PASS	PASS	PASS	PASS
10/31/2008	Standard	ppm	NIST Med	PASS	PASS	PASS	PASS
10/31/2008	Standard	ppm	RCRA	PASS	PASS	PASS	PASS
10/31/2008	Standard	ppm	SiO2 Blank	PASS	PASS	PASS	PASS
11/5/2008	Standard	ppm	Calibrate Detector	PASS	PASS	PASS	PASS
11/5/2008	Standard	ppm	NIST High	PASS	PASS	PASS	PASS
11/5/2008	Standard	ppm	NIST Low	PASS	PASS	PASS	PASS
11/5/2008	Standard	ppm	NIST Med	PASS	PASS	PASS	PASS
11/5/2008	Standard	ppm	RCRA	PASS	PASS	PASS	PASS
11/5/2008	Standard	ppm	SiO2 Blank	PASS	PASS	PASS	PASS

APPENDIX C

Table 1. Metal Concentrations in Big River sediments collected in 2008 by River Mile

Site Name	River Mile	Lab Adjusted Bulk Pb	Lab Adjusted Bulk Zn	Lab or Estimated <2mm Cd	Adjusted <0.25 mm Pb	Adjusted <0.25 mm Zn	Lab or Estimated <0.25 mm Cd	ICP or Estimated <0.25 mm Ba
ID	129.0	15	17.0	0.043[b]	70.9[d]	64.6[d]	0.295[a]	215[a]
LG	117.8	17	37.0	0.00[a]	82.7[a]	107[a]	0.01[a]	592[a]
LWR	113.4	36	48.0	0.00[a]	131[a]	134[a]	0.48[a]	388[a]
LWE	113.3	1354[a]	8922[a]	72.3[d]	3471[a]	21885[a]	383[a]	362[a]
LWE2	113.2	1545[a]	6905[a]	80.2[d]	3955[a]	16940[a]	296[a]	577[a]
LW	113.0	226[a]	164[a]	7.04[b]	2797[d]	1467[d]	31.2[b]	103[c]
LWI	113.0	1042[a]	3984[a]	66.8[a]	2680[a]	9781[a]	170[a]	357[a]
67D	102.7	1503[a]	1112[a]	20[d]	2439[d]	1924[d]	32.0[c]	830[a]
HK	96.7	2420[a]	740[a]	11.6[c]	2821[d]	1706[d]	32.0[c]	238[c]
67C	90.1	361[a]	320[a]	8.00[c]	1360[d]	801[d]	14.0[c]	508[a]
HE	87.7	531[a]	425[a]	6.01[b]	1756[d]	1077[d]	17.3[b]	152[c]
CL	79.6	554[a]	374[a]	5.43[a]	1444[a]	933[a]	14.5[a]	586[a]
SB	NA	164[a]	623[a]	9.66[a]	454[a]	1542[a]	25.3[a]	3177[a]
MC	NA	134[a]	531[a]	8.09[a]	378[a]	1316[a]	21.3[a]	3687[a]
CC	75.5	986[a]	437[a]	4.76[b]	2246[d]	728[d]	9.38[b]	2910[c]
WSP	65.7	559[a]	196[a]	2.40[a]	1455[a]	496[a]	6.85[a]	673[1a]
MFK	NA	115[a]	128[a]	0.4[c]	254[d]	355[d]	0.9[a]	982[a]
MFC	NA	118[a]	137[a]	0.2[c]	403[d]	322[d]	1.68[a]	1840[a]
MA	62.7	257[a]	532[a]	3.04[d]	1356[d]	492[d]	6.29[d]	423[a]
BF	50.9	749[a]	272[a]	2.00[c]	1656[d]	442[d]	3.00[a]	2872[a]
MMA	30.7	145[a]	96[a]	1.40[c]	829[d]	370[d]	4.61[a]	966[a]
MMB	30.5	330[a]	71[a]	1.06[c]	936[d]	188[d]	1.70[a]	604[a]
KR	28.3	172[a]	82[a]	0.46[a]	476[a]	216[a]	1.93[a]	516[a]

Table 1. Continued

BC	20.8	35	17	0.00^a	128^a	57.8^a	0.00^a	380^a
CHB	20.2	123^a	52^a	1.00^c	392^d	164^d	2.00^c	504^a
BVA	14.7	114^a	64^a	0.00^a	329^a	173^a	1.18^a	527^a
BVB	14.4	86^a	32^a	0.00^a	258^a	94^a	0.00^a	545^a
RBA	10.7	372^a	222^a	1.47^b	680^d	319^d	2.53^b	405^a
RBB	10.3	71^a	13^a	0.50^c	186^d	91^d	0.70^c	465^a
BMA	8.5	142^a	57^a	0.00^a	400^a	155^a	0.86^a	539^a
BME	8.4	186^a	66^a	2.00^c	698^d	217^d	2.00^c	518^a
BMB	8.3	156^a	61^a	0.11^a	435^a	166^a	1.05^a	535^a
BMB2	8.2	132^a	45^a	0.0^a	375^a	127^a	0.36^a	445^a
HW	1.3	148^a	67^a	0.60^c	345^d	155^d	1.00^c	503^a
CON	0.3	145^a	95^a	1.21^b	353^d	154^d	1.68^b	250^a
REFERENCE LOCATIONS								
Bref	NA	5	10	0.046^b	31^d	35^d	0.725^b	535^a
BU	NA	5	58	0.06^a	52.3^a	158^a	0.91^a	547^a
MPP	NA	7	10	0.02^c	38^d	50^d	0.02^c	291^a
MTB	NA	17	21	0.02^c	66^d	54^d	0.02^c	453^a

X^a = XRF Transformed data
X^b = Mean of two lab values
X^c = Single lab value
X^d = Mean of XRF transformed and lab data

Table 2. 2008 XRF Sediment Metal Concentrations in the Meramec River

Sample Location	River Mile	Pb (ppm)	Zn (ppm)	Ba (ppm)	Cd (ppm)
Meramec River (MR) at Pacific Palisades	46.25	<LOD (10)	<LOD (14)	154	<LOD
MR at Times Beach-1	32.50	17	22	199	<LOD
MR at Times Beach-2	32.00	21	34	219	<LOD
MR at Meramec Palisades	30.50	34	33	208	<LOD
MR at Meramec Palisades Duplicate	30.50	32	37	217	<LOD
MR at Jedburg High Water Island	29.50	122	71	253	<LOD
MR Above Jedburg Railroad Bridge	29.25	18	16	189	<LOD
MR Below Jedburg Railroad Bridge	29.00	12	16	205	<LOD
MR at Tyson Research Area	28.50	26	28	229	<LOD
MR at Pink Mucket City 97014	27.25	15	21	206	<LOD
MR Opposite from 97014	27.00	15	17	214	<LOD
MR Pool Below 97014	26.25	45	39	167	<LOD
MR at Three Islands	25.50	30	31	187	<LOD
MR Sunset Hills 97004	19.00	>LOD (10)	20	190	<LOD
MR Sunset Hills Pool 97004	18.50	33	39	248	<LOD

<LOD = Below Limit of Detection for the XRF instrument.

Table 3. 2007 XRF <0.25 mm Sediment Concentrations of Pb and Zn from the Big River

SAMPLE #	**LOCATION**	**Pb (ppm)**	**Zn (ppm)**	**Latitude**	**Longitude**	**Miles from Confluence w/ Meramec River**
FWS#10	Meramec River Below I-44 at Times Beach	**110**	**72**	N38.42015	W090.59005	**-2**
FWS#11	Big River/Meramec Confluence	**88**	**35**	N38.47171	W090.61828	**0**
FWS#12	Big River Above Confluence ~1/4 mile	**134**	**61**	N38.46902	W090.62376	**0.25**
FWS#15A	Big River adjacent to Hwy W above Eureka	**69**	**33**	NA	NA	**1.25**
FWS#14	1 mile below 1st mill dam Byrne's Mill	**98**	**34**	N38.456770	W090.592290	**7.5**
FWS#13	1st Mill Dam on Big River Byrne's mill	**382**	**135**	N38.43763	W090.58360	**8.5**
FWS#8	House Springs at Jefferson County Park	**69**	**27**	N38.42333	W090.59216	**10.25**
FWS#9A	Above Mill Dam House Springs	**244**	**91**	N38.42015	W090.59004	**10.5**
FWS#18	Byrnesville above Mill Dam	**46**	**22**	N38.309320	W090.63607	**14.6**
FWS#17A	Cedar Hill below Mill Dam	**54**	**23**	N38.34960	W090.644670	**21.3**
FWS#JSW1	Above Cedar Hill Mill Dam	**285**	**96**	NA	NA	**21.5**
FWS#JSW2	Below Morse Mill Dam Dec 2007	**259**	**85**	NA	NA	**31.7**
FWS#JSW3	Above Morse Mill Dam Dec 2007	**339**	**133**	NA	NA	**31.8**
FWS#JSW4	Brown's Ford Dec 2007	**399**	**137**	NA	NA	**50.1**
FWS#7	Mammoth Access to Big River	**258**	**101**	NA	NA	**60.8**
MDC#8	Big River Hwy CC at Blackwell	**229**	**110**	N38.04498	W090.621190	**71.3**
MDC#7	Hwy E St. Francois	**598**	**314**	N37.96594	W090.57419	**82.3**
FWS#4	Hwy 67 N of Bonne Terre	**405**	**501**	N37.954493	W090.55257	**84.3**
FWS#02	Big River, 70 Yds above Hwy k	**927**	**606**	N37.92686	W090.50106	**90.6**
FWS#01	Big River above Flat River, 300 m above old 67 bridge	**465**	**952**	N37.888990	W090.51211	**96.3**
FWS#3	Below Hwy 8 Above Leadwood	**22**	**24**	N37.86759	W090.63962	**111.4**
FWS#06	Above Irondale below Cedar Cr.	**17**	**<LOD**	NA	NA	**117.9**

<LOD = Below Limit of Detection for the XRF instrument.

Table 4. 2007 XRF Bulk Sediment Concentrations of Pb and Zn from the Big River

SAMPLE #	LOCATION	Pb (ppm)	Zn (ppm)	Latitude	Longitude	Miles from Confluence w/ Meramec River
FWS#10	Meramec River Below I-44 at Times Beach	**85**	**55**	N38.42015	W090.59005	**NA**
FWS#11	Big River/Meramec Confluence	**72**	**35**	N38.47171	W090.61828	**0**
FWS#12	Big River Above Confluence ~1/4 mile	**124**	**91**	N38.46902	W090.62376	**0.25**
FWS#15A	Big River adjacent to Hwy W above Eureka	**76**	**34**	NA	NA	**1.25**
FWS#14	1 mile below 1st mill dam Byrne's Mill	**82**	**44**	N38.456770	W090.592290	**7.5**
FWS#13	1st Mill Dam on Big River Byrne's mill	**242**	**126**	N38.43763	W090.58360	**8.5**
FWS#8	House Springs at Jefferson County Park	**84**	**42**	N38.42333	W090.59216	**10.25**
FWS#9A	Above Mill Dam House Springs	**327**	**123**	N38.42015	W090.59004	**10.5**
FWS#18	Byrnesville above Mill Dam	**68**	**42**	N38.309320	W090.63607	**14.6**
FWS#17A	Cedar Hill below Mill Dam	**113**	**70**	N38.34960	W090.644670	**21.3**
FWS#JSW1	Above Cedar Hill Mill Dam	**246**	**111**	NA	NA	**21.5**
FWS#JSW2	Below Morse Mill Dam Dec 2007	**224**	**84**	NA	NA	**31.7**
FWS#JSW3	Above Morse Mill Dam Dec 2007	**199**	**83**	NA	NA	**31.8**
FWS#JSW4	Brown's Ford Dec 2007	**358**	**135**	NA	NA	**50.1**
FWS#7	Mammoth Access to Big River	**672**	**403**	NA	NA	**60.8**
MDC#8	Big River Hwy CC at Blackwell	**280**	**131**	N38.04498	W090.621190	**71.3**
MDC#7	Hwy E St. Francois	**633**	**305**	N37.96594	W090.57419	**82.3**
FWS#4	Hwy 67 N of Bonne Terre	**495**	**376**	N37.954493	W090.55257	**84.3**
FWS#02	Big River, 70 Yds above Hwy k	**845**	**552**	N37.92686	W090.50106	**90.6**
FWS#01	Big River above Flat River, 300 m above old 67 bridge	**813**	**911**	N37.888990	W090.51211	**96.3**
FWS#3	Below Hwy 8 Above Leadwood	**20**	**32**	N37.86759	W090.63962	**111.4**
FWS#06	Above Irondale below Cedar Cr.	**15**	**18**	NA	NA	**117.9**

Table 5. Particle size distribution of sediments collected in 2008 at select sites in the Big River

Field/Lab ID	Fraction Name	Fraction Size	Fraction % of Whole
Big River above Irondale	Gravel	> 2mm	65.80
Big River above Irondale	Medium to Coarse Sand	> 250µm - 2mm	33.10
Big River above Irondale	Fine Sand	> 63µm - 250µm	0.57
Big River above Irondale	Silt and Clay	< 63µm	0.58
Big River at Leadwood MDC Access	Gravel	> 2mm	52.60
Big River at Leadwood MDC Access	Medium to Coarse Sand	> 250µm - 2mm	45.40
Big River at Leadwood MDC Access	Fine Sand	> 63µm - 250µm	1.48
Big River at Leadwood MDC Access	Silt and Clay	< 63µm	0.54
Big River at Hwy K	Gravel	> 2mm	76.70
Big River at Hwy K	Medium to Coarse Sand	> 250µm - 2mm	22.00
Big River at Hwy K	Fine Sand	> 63µm - 250µm	0.62
Big River at Hwy K	Silt and Clay	< 63µm	0.65
Big River at Hwy E	Gravel	> 2mm	32.90
Big River at Hwy E	Medium to Coarse Sand	> 250µm - 2mm	63.30
Big River at Hwy E	Fine Sand	> 63µm - 250µm	2.44
Big River at Hwy E	Silt and Clay	< 63µm	1.37
Big River at Hwy CC	Gravel	> 2mm	21.70
Big River at Hwy CC	Medium to Coarse Sand	> 250µm - 2mm	69.00
Big River at Hwy CC	Fine Sand	> 63µm - 250µm	6.26
Big River at Hwy CC	Silt and Clay	< 63µm	3.10
Mineral Fork above Big River confluence	Gravel	> 2mm	71.80
Mineral Fork above Big River confluence	Medium to Coarse Sand	> 250µm - 2mm	26.60
Mineral Fork above Big River confluence	Fine Sand	> 63µm - 250µm	0.62
Mineral Fork above Big River confluence	Silt and Clay	< 63µm	1.00
Big River above Morse Mill Dam	Gravel	> 2mm	80.60
Big River above Morse Mill Dam	Medium to Coarse Sand	> 250µm - 2mm	18.20
Big River above Morse Mill Dam	Fine Sand	> 63µm - 250µm	0.28
Big River above Morse Mill Dam	Silt and Clay	< 63µm	0.89
Big River below Morse Mill Dam	Gravel	> 2mm	5.40
Big River below Morse Mill Dam	Medium to Coarse Sand	> 250µm - 2mm	73.30
Big River below Morse Mill Dam	Fine Sand	> 63µm - 250µm	14.50
Big River below Morse Mill Dam	Silt and Clay	< 63µm	6.85
Big River above House Springs	Gravel	> 2mm	1.54
Big River above House Springs	Medium to Coarse Sand	> 250µm - 2mm	30.40
Big River above House Springs	Fine Sand	> 63µm - 250µm	42.60
Big River above House Springs	Silt and Clay	< 63µm	25.40
Big River 1/4M above confluence	Gravel	> 2mm	27.20
Big River 1/4M above confluence	Medium to Coarse Sand	> 250µm - 2mm	67.60
Big River 1/4M above confluence	Fine Sand	> 63µm - 250µm	3.91
Big River 1/4M above confluence	Silt and Clay	< 63µm	1.36

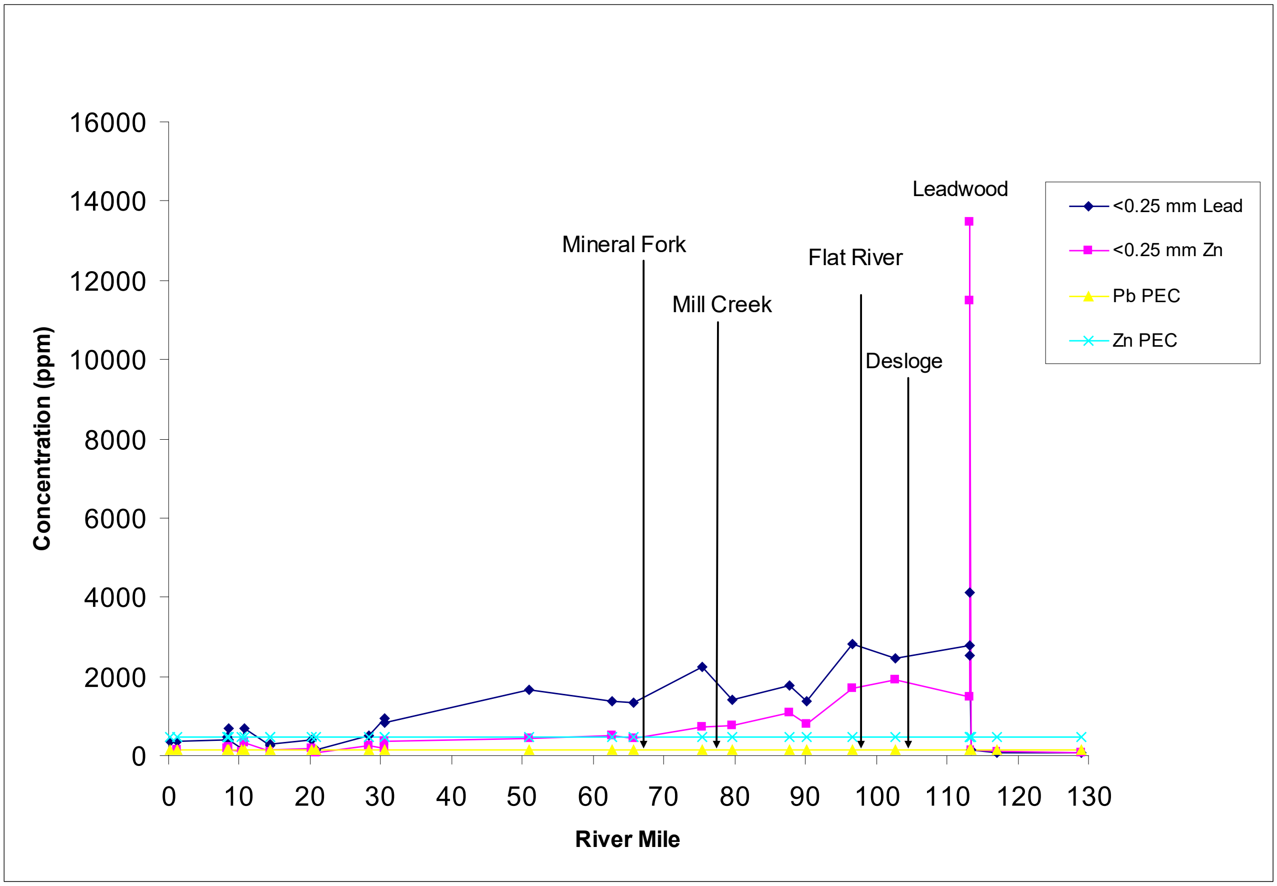

Figure 1. Pb and Zn in 2008 Big River sediments sieved to less than <0.25 mm as determined by XRF and compared to respective PECs.

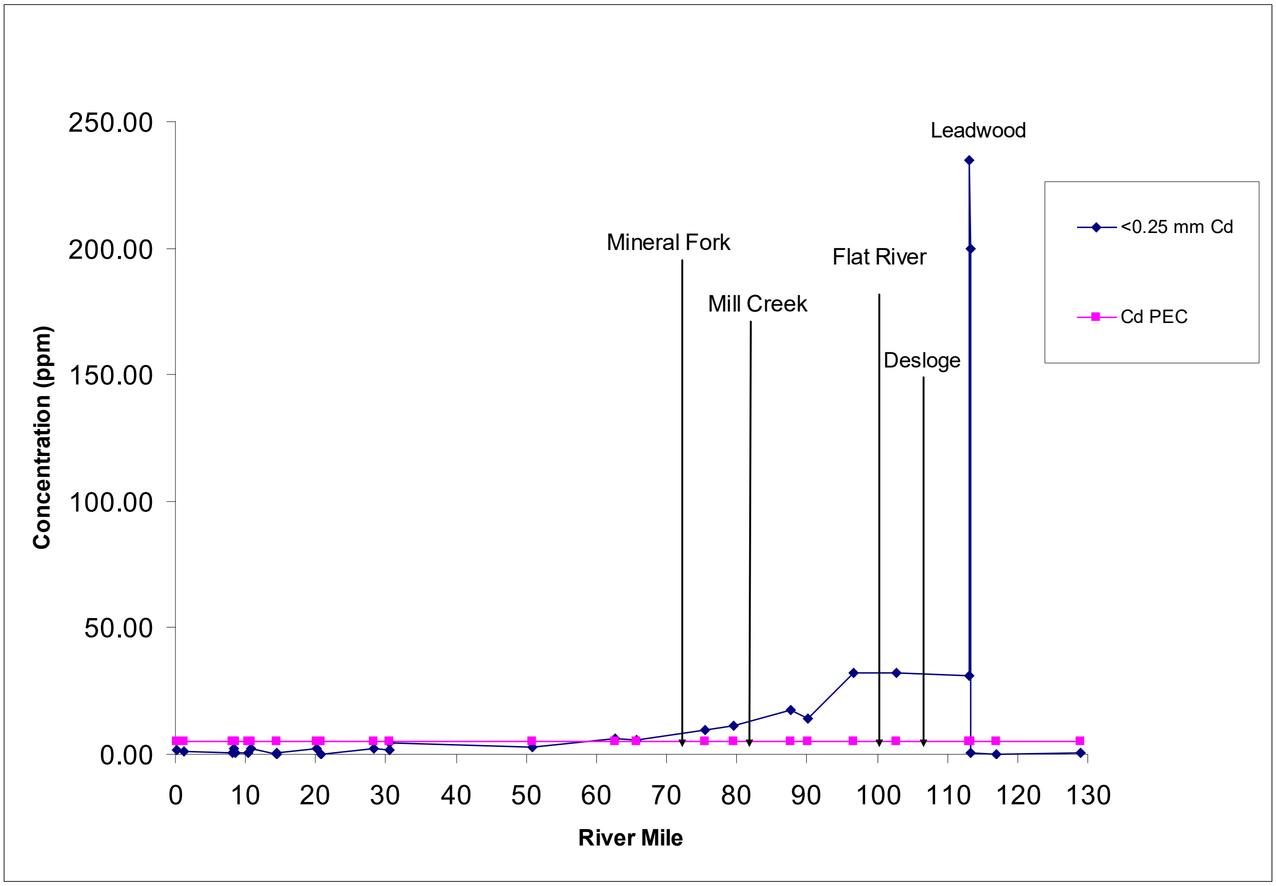

Figure 2. Estimated Cd in 2008 Big River sediments sieved to less than <0.25 mm as determined by XRF and ICP-MS compared to respective PECs.

APPENDIX D

Table 1. Unionid species and numbers found at sites sampled in the Big River between miles 1.3 and 75.5. "FD" = fresh dead shells, "WD" = weathered shells, and "SF" = subfossil shells, "P" = present, “R” = rare, "A" = abundant, “*” = on-shore collection of dead shell material.

Species	**River mile and site numbers**											
	1.3	8.2	10.3	14.4	20.2	20.8	28.3	30.5	50.9	62.7	65.7	75.5
Actinonaias ligamentina	921	11	15				SF	SF	4	1		
Alasmidonta marginata	17	2	1			SF		SF				
Alasmidonta viridis											SF	
Amblema plicata	25	20	105	1	SF	SF		SF	WD	SF	SF	
Cumberlandia monodonta	115	WD										
Cyclonaias tuberculata	10											
Ellipsaria lineolata	14	2	1									
Elliptio crassidens	SF											
Elliptio dilatata	306	2	6	SF	WD	2	SF	4	1		SF	
Fusconaia ebena	2											
Fusconaia flava	7	2	7	WD	SF	SF	SF	SF	6	SF	1	
Lampsilis abrupta	WD											
Lampsilis cardium	21	13	8	5	19	3	6	12	16	SF		2
Lampsilis siliquoidea												
Lampsilis reeviana brittsi							SF	3	2	WD	1	WD
Lampsilis teres		1		SF			SF	SF				
Lasmigona complinata		1										
Lasmigona costata	8		1	SF								
Leptodea fragilis	1	2	1	SF				SF				
Leptodea leptodon			FD									
Ligumia recta	29	12	2					SF	1			
Megalonaias nervosa	12	1	1									
Obliquaria reflexa	12	2	9	1								
Pleurobema sintoxia	62	1	1					SF	SF	SF		
Potamilus alatus	2	10	8	2	1	1			2			
Pyganodon grandis				SF								
Quadrula metanevra	3											
Quadrula pustulosa	16	6	12	1	1	2	SF	SF		SF	SF	
Strophitus undulatus	3	1			SF	3		WD		WD		

Table 1 cont'd. Unionid species and numbers found at sites sampled in the Big River between miles 1.3 and 75.5. "FD" = fresh dead shells, "WD" = weathered shells, and "SF" = subfossil shells, "P" = present, "R" = rare, "A" = abundant, "*" = on-shore collection of dead shell material.

Species	**River mile and site numbers**											
	1.3	8.2	10.3	14.4	20.2	20.8	28.3	30.5	50.9	62.7	65.7	75.5
Toxolasma parvus					WD							
Tritogonia verrucosa	4			SF	SF		SF	SF	WD			
Truncilla donaciformis	3		FD									
Truncilla truncata	6		4			SF				SF		
Venustachoncha ellipsiformis	23	4							1			
Corbicula fluminea	P	R	P	P	P	P	A	A	P	WD	A	P
Minutes search time	12.0	2.3	5.0	3.3	3.0	2.8	1.8	3.0	2.3	4.0	2.5	1.8
Number of live individuals	1622	93	182	10	21	11	6	19	33	1	2	2
CPUE (individuals/person hour)	135.2	39.9	36.4	3.1	7.0	3.9	3.4	6.3	14.1	0.3	0.8	1.1
Number of species live	24	18	16	5	3	5	1	3	8	1	2	1
Additional species dead	2	1	2	8	6	4	7	11	3	9	4	1
Total number of species	26	19	18	13	9	9	8	14	11	10	6	2

Table 1 con't. Unionid species and numbers found at sites sampled in the Big River between miles 79.6 and 129. "FD" = fresh dead shells, "WD" = weathered shells, and "SF" = subfossil shells, "P" = present, "R" = rare, "A" = abundant, "*" = on-shore collection of dead shell material.

Species	River mile and site numbers						
	79.6	87.7	90.1	96.7	102.7	113	129
Actinonaias ligamentina	1						
Alasmidonta marginata							1
Alasmidonta viridis							
Amblema plicata	SF		SF				
Cumberlandia monodonta							
Cyclonaias tuberculata							
Ellipsaria lineolata							
Elliptio crassidens							
Elliptio dilatata	SF						
Fusconaia ebena							
Fusconaia flava	FD						
Lampsilis abrupta							
Lampsilis cardium	3	WD	4			2	51
Lampsilis siliquoidea							
Lampsilis reeviana brittsi	5	WD	WD	SF		2	79
Lampsilis teres							
Lasmigona complinata							
Lasmigona costata							6
Leptodea fragilis							
Leptodea leptodon							
Ligumia recta							
Megalonaias nervosa							
Obliquaria reflexa							
Pleurobema sintoxia					SF		
Potamilus alatus	1						
Pyganodon grandis							
Quadrula metanevra					SF		
Quadrula pustulosa							
Strophitus undulatus							3

Table 1 cont'd. Unionid species and numbers found at sites sampled in the Big River between miles 79.6 and 129. "FD" = fresh dead shells, "WD" = weathered shells, and "SF" = subfossil shells, "P" = present, "R" = rare, "A" = abundant, "*" = on-shore collection of dead shell material.

Species	**River mile and site numbers**						
	79.6	87.7	90.1	96.7	102.7	113	129
Toxolasma parvus							
Tritogonia verrucosa							
Truncilla donaciformis							
Truncilla truncata							
Venustachoncha ellipsiformis			WD				38
Corbicula fluminea	A	P	P	SF		A	A
Minutes search time	2.3	2.7	1.7	2.0	1.3	2.3	4.0
Number of live individuals	10	0	4	0	0	4	178
CPUE (individuals/person hour)	4.4	0.0	2.4	0.0	0.0	1.7	44.5
Number of species live	4	0	1	0	0	2	6
Additional species dead	3	2	3	1	2	0	0
Total number of species	7	2	4	1	2	2	6

Table 2. Unionid species and numbers found at sites sampled in the Bourbeuse River and Meramec River reference sites. "FD" = fresh dead shells, "WD" = weathered shells, and "SF" = subfossil shells, "P" = present, “R” = rare, "A" = abundant, “*” = on-shore collection of dead shell material.

Species	Bourbeuse River Reference Site	Meramec River at Pacific Palisades
Actinonaias ligamentina	69	97
Alasmidonta marginata	13	11
Amblema plicata	121	122
Cumberlandia monodonta		SF
Cyclonaias tuberculata		1
Ellipsaria lineolata	4	21
Elliptio dilatata	3	
Fusconaia flava	38	7
Lampsilis abrupta		1
Lampsilis cardium	31	39
Lampsilis siliquoidea	1	
Lampsilis teres	1	WD
Lasmigona complinata	3	1
Lasmigona costata	1	
Leptodea fragilis	16	13
Leptodea leptodon	4	6
Ligumia recta		5
Megalonaias nervosa	3	3
Obliquaria reflexa	5	44
Plethobasus cyphyus	2	20
Pleurobema sintoxia	21	41
Potamilus alatus	21	12
Pyganodon grandis		1
Quadrula metanevra	1	64
Quadrula pustulosa	68	56
Quadrula quadrula		8
Strophitus undulatus	3	5
Toxolasma parvus	WD	
Tritogonia verrucosa	112	

Table 2 cont'd. Unionid species and numbers found at sites sampled in the Bourbeuse and Meramec river reference sites. "FD" = fresh dead shells, "WD" = weathered shells, and "SF" = subfossil shells, "P" = present, "R" = rare, "A" = abundant, "*" = on-shore collection of dead shell material.

Species	Bourbeuse River Reference Site	Meramec River at Pacific Palisades
Truncilla donaciformis	8	16
Truncilla truncata	24	13
Venustachoncha ellipsiformis	3	43
Corbicula fluminea	R	P
Minutes search time	450	480
Number of live individuals	576	650
CPUE (individuals/person hour)	76.8	81.25
Number of species live	26	25
Additional species dead	0	2
Total number of species	26	27