

The Dynamics of Metals From Past and Present
Mining Activities in the Big and Black River
Watersheds, Southeastern Missouri

by

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INTRODUCTION

The Big River, a tributary of the Meramec River in southeastern Missouri, drains an area known as the "Old Lead Belt". This area, formerly the world's leading producer of lead, is no longer actively mined; the last mine in the Old Lead Belt closed in 1972. However, other areas of the watershed downstream of the Old Lead Belt are presently mined for barite (tiff). Tailings from the abandoned Pb mines were deposited in massive heaps throughout the region and remain the most prominent features of the landscape in the vicinity of Bonne Terre, Desloge, Leadwood, Elvins, and Flat River. These tailings have been identified as a potentially significant environmental hazard because of their high concentrations of toxic metals. The problem, and the area, recently received some notoriety when the Missouri Department of Conservation made public the results of its survey of Pb residues in Big River fishes (Czarneski 1980) and, a short time later, issued a press release cautioning local residents against eating some fishes because of high Pb residues.

In 1977, a severe thunderstorm resulted in the collapse of an unmaintained tailings deposit situated along the Big River upstream of Desloge, which resulted in some 50,000 yds³ of Pb-, Cd-, and Zn-rich tailings being washed into the river (Novak and Hasselwander 1980, Whitley 1980). Less catastrophic, but nonetheless significant, inputs continue to occur as a result of erosion at this site and at other unmaintained tailings piles in the region (Kramer 1976, N. Gale, personal communication). Barite tailings structures have also failed,

with resulting inputs of Ba-rich sediments into Big River tributaries downstream of the Old Lead Belt (Hocutt et al. 1978). The M.S. thesis by Kramer (1976 unpublished) contains a thorough review of the area's geology, geomorphology, and mining history; it, along with the USGS-State of Missouri (1967) survey of mineral resources and the recent article by Whitley (1980) should be consulted for further background information.

The U.S. Army Corps of Engineers, St. Louis District, has proposed the construction of Pine Ford Lake, a multi-purpose storage reservoir, on the mid-to-lower reaches of the Big River. Because the impoundment would be situated downstream of both the Old Lead Belt tailings and the active open-pit barite mines in the middle portions of the watershed, concerns have been voiced regarding the fate of the potentially toxic metals present in the watershed. Partly in response to these concerns, the present study was designed to evaluate the magnitude of the trace metals problem in the Big River watershed under present conditions, and to provide preliminary data with which to assess the impacts of the proposed reservoir on trace metal dynamics. Clearwater Lake, a multi-purpose impoundment on the Black River near Piedmont, Mo., which is operated by the Corp's Little Rock District, was selected for inclusion in this study because limnological conditions there are similar to those that would likely occur in the proposed Pine Ford Lake. Many tributaries of the Black River upstream of Clearwater Lake drain Missouri's "New Lead Belt", where Pb mining presently occurs (Gale et al. 1976).

The present study was intended to yield a great deal of basic information in an extremely limited timespan on the transport, dynamics,

fate and, to a lesser extent, biological effects, of potentially toxic metals emanating from past and present mining operations in the Big and Black River watersheds. The study, which began in the Spring of 1980, was designed and conducted from an applied, operational perspective and was intended to be neither all-inclusive nor completely quantitative; rather, it has the following limited objectives: (1) to survey the present extent of contamination by metals in the Big and Black River watersheds in an attempt to determine if, where, and to what degree the metals are accumulating; (2) to evaluate metals transport in the two watersheds and arrive at a simple mass balance; (3) to determine, to the extent possible, the chemical forms of the metals in the active sediments and how these forms might be altered under conditions typical of a reservoir environment; (4) to determine the availability of metals to the biota at different locations, and then relate this apparent biological availability to the chemical forms present; and (5) to determine whether or not selected aquatic organisms show symptoms indicative of chronic exposure to elevated Pb levels.

METHODS OF STUDY

Study Area

The study area (Fig. 1) included an 80-mi (128-km) section of the Big River and a 40-mi (64-km) section of the Black River. Samples were collected at five locations in the Big River Basin: at an upstream "control" site near Irondale, where there has been no active mining since 1921; at three "affected" sites located 5 mi (8 km, Desloge), 37 mi (59 km, Washington State Park) and 60 mi (96 km, Brown's Ford) downstream of the Desloge tailings pond dam break; and at a location on Mineral Fork, a major tributary that joins the Big River downstream of Washington State Park. Collection sites in the Black River Basin were located at a flowing water site upstream of Clearwater Lake near Annapolis, at a flowing water site approximately 1.0 mi (1.6 km) downstream of Clearwater Dam, and in the Black River Arm of Clearwater Lake. Other pertinent data for these sites are contained in Table 1.

Field Studies

A trace metal survey of the biota of the Big River and Black River study areas was completed in Summer 1980. Longear sunfish (Lepomis megalotis), black and golden redhorse suckers (Moxostoma duquesnei; M. erythrurum), and several species of catfish (Ictalurus natalus; I. nebulosus; I. punctatus; Pyiodictis olivaris) were collected for trace metal analysis at every flowing-water site by electrofishing. Smallmouth bass (Micropterus dolomieu) were collected at every site except downstream from Clearwater Dam, where spotted bass (M.

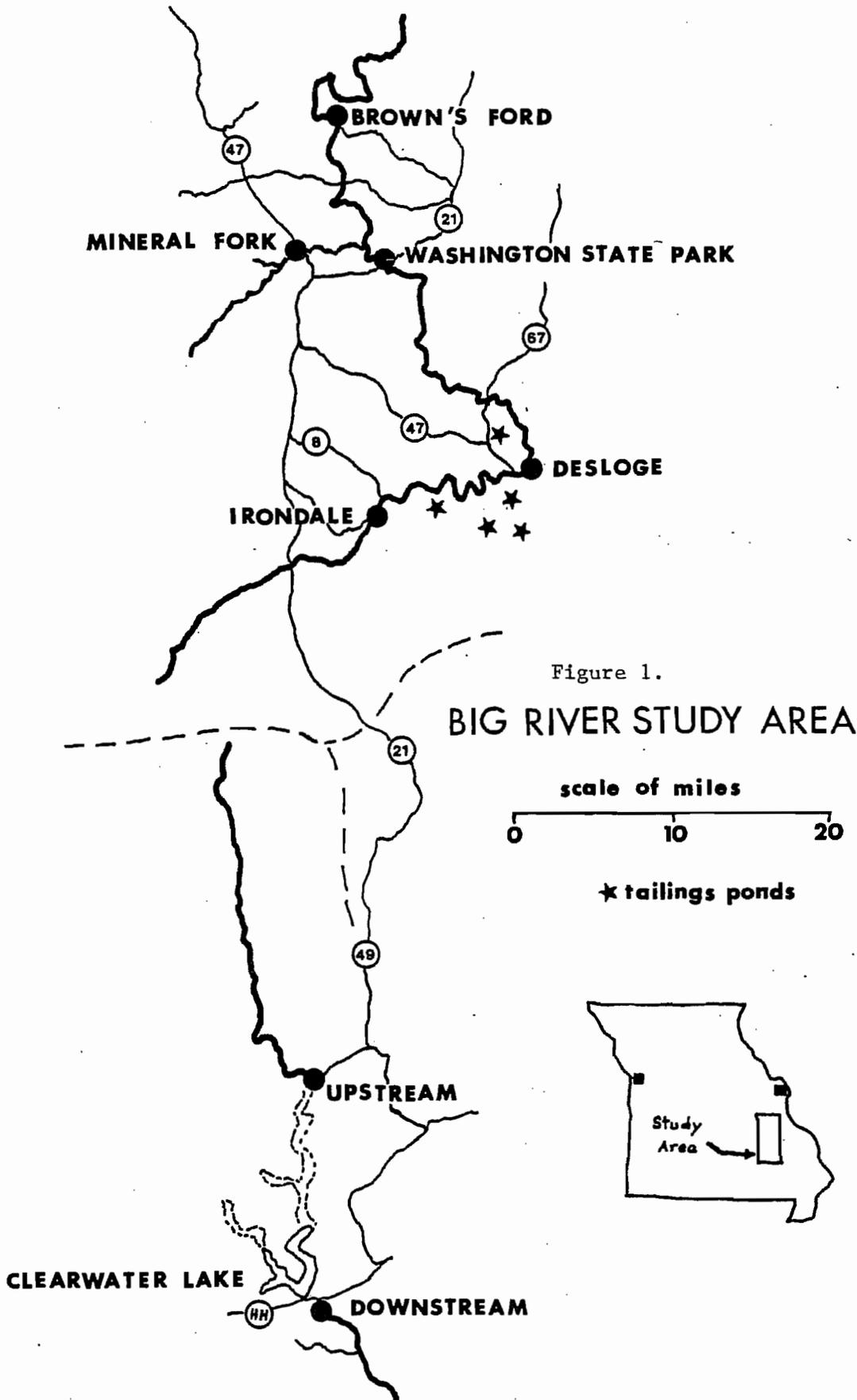


Table 1. Collection sites, Big and Black Rivers

River Basin Site	CNFR L Site#	USACE Site#	County	Narrative Description
Big River				
Irondale	3	12A	Washington	All samples collected at Highway U Bridge, upstream (West) of Irondale.
Desloge	2	10	St. Francois	Water and biota samples collected near the south U.S. 67 bridge, 0.5 mi (.8 km) upstream of the confluence of Flat River Creek. Sediment samples collected about 0.5 mi downstream of the confluence, on the property owned by W.C. Counts.
Washington State Park				
	9	5	Washington	Water and biota samples collected at the Highway 21 bridge. Sediment samples collected within the park.
Mineral Fork				
	0	6	Washington	All samples collected at Highway 47 bridge.
Brown's Ford				
	1	4	Jefferson	All samples collected at the Brown's Ford bridge.
Black River				
Upstream				
	4	3	Iron	Water, plant, some fish, and crayfish samples collected near the Highway K bridge ("K Park") - sediment samples and some sunfish collected at Champion Springs, near the USGS streamflow gage.
Clearwater Lake				
	6	2	Reynolds	All samples collected in the former Black River channel near the confluence of the Black River and Logan Creek arms of the Lake.
Downstream				
	5	1	Reynolds	All samples collected within the grounds of the Clearwater Dam Park.

punctulatus) were substituted. Blood samples were taken from longear sunfish to determine levels of the enzyme δ -amino levulinic acid dehydratase (ALA-D), an indicator of chronic exposure to lead (Hodson 1976). Blood was collected in the field immediately upon capture. The fish were anesthetized in MS-222. Blood was then drawn from the caudal artery with sterile, heparinized syringes and frozen immediately in capped heparinized vials. Pocketbook mussels (Lampsilis ventricosa), crayfish (Orconectes luteus, O. punctimanus), water willow (Justicia americana), and attached algae (Oscillatoria sp.) were also collected for the survey. All samples were refrigerated after collection and frozen upon return to the laboratory. Freshwater mussels were depurated in the laboratory a minimum of two days before freezing.

In addition to the fish collected for the survey, redhorse suckers and northern hogsuckers (Hypentelium nigricans) were collected at Desloge, Washington State Park, Leadwood, and Irondale in March 1981. Blood was collected from these fish and frozen in capped heparinized vials to be analyzed later for ALA-D and blood-Pb concentrations. Tissue samples from these fish were also analyzed for Pb.

Water samples were collected at low flow (July 1980), medium flow (April 1981), and high flow (May 1981). Multi-vertical, depth-integrated samples for water quality and trace metal analyses were collected at equally spaced intervals across the river channel and transferred into a Nalgene USGS churn-type splitter (USGS 1977). Particles were kept in suspension in this container by constant churning of the collected water. From this larger volume, subsamples were dispensed into polyethylene cubitainers. Unfiltered water samples were

acidified immediately to pH 2 with HNO_3 . Filtered samples were acidified after passing through a 0.45μ nitrocellulose membrane filter. At low flow three filtered and three unfiltered water samples were collected at every river site, and single samples were taken at the surface and at depths of 5 m and 10 m in Clearwater Lake. Trace metal results from these low flow samples indicated no significant differences ($p < 0.01$) among replicates of filtered or unfiltered water samples. Replication at medium and high flow was therefore reduced to collection of two filtered and two unfiltered samples. Additional samples were collected for analyses of other water quality parameters.

Transport of material along the channel bottom was also measured at low, medium, and high flow. Movement was measured at low and medium flow with a GBC hand-held bedload sampler (GBC, Inc., Denver, Col.) and at high flow with a cable suspended bedload sampler (Helley and Smith 1971; GBC, Inc.). Samples were taken in right, left, and center channel locations.

Another phase of the study was designed to evaluate the bioavailability of heavy metals in the aquatic environment as indicated by the uptake of metals by organisms. The pocketbook mussel was selected for this study because (a) it occurs naturally throughout the study area; (b) its characteristic filter feeding makes it directly susceptible to suspended metals; and (c) other studies (e.g., Schulz-Baldes 1978) have shown it to be a good accumulator of metals that is relatively unaffected by handling and confinement for extended periods. About 300 pocketbook mussels were collected from the Bourbeuse River south of Owensville, Mo. and submerged in weighted, epoxy-coated,

hardware cloth cages at Brown's Ford, Desloge, Irondale, Black River upstream of Clearwater Lake (Champion Springs), in a deep area of Clearwater Lake, and at a site downstream of Clearwater Dam. From October through December, 1980, mussels were removed from the cages every two weeks for an 8-wk period, returned to the laboratory for a 3-day depuration period, and frozen for subsequent trace metal analyses. The 8-wk exposure study was repeated between July and September, 1981. In this second study, an additional site at Washington State Park was included. Clearwater Lake was deleted from the second study because of summer stratification in the lake and because of repeated vandalism.

Concurrent with the mussel accumulation studies, active streambed sediments were collected in December 1980 and in August 1981 and returned to the laboratory for analysis to determine the concentrations and chemical forms of heavy metals in the surficial sediments. "Riffle" (scouring) and "pool" habitats were identified at each stream site and three sediment samples of each type were collected at each location. Scuba divers collected bottom sediments from Clearwater Lake. Because of equipment problems that developed during the December trip, several modifications of sampling equipment and procedures resulted. The following technique was developed and utilized for the August sample collection: A 3-inch diaphragm pump (Homelite) drew bottom sediments through a 2-mm mesh sieve and 3-inch diameter polyethylene hose into a conical, acid washed, 200-L settling container. The container was then sealed and purged with nitrogen to prevent further oxidation of the sediments. Sediments were allowed to settle for 90 min and were then drawn from the bottom of the container into acid washed, linear

polyethylene bottles. To avoid oxidation, each sample was purged with nitrogen and sealed immediately after collection. Samples were packaged in ice and transported to the laboratory within 24 h after termination of collection.

Laboratory Analyses

All samples were analyzed for residues of Pb, Cd, Cu, Zn, Fe, Mn, and Ba. Initially, samples were also analyzed for Ag, but because of extremely low or non-detectable levels, this metal was deleted. Analyses were by flame atomic absorption (flame AA; Perkin-Elmer Model 603 atomic absorption spectrophotometer with a deuterium background corrector and a Model 56 recorder) and by furnace atomic absorption (furnace AA; Perkin-Elmer HGA 2200 heated graphite atomizer with a Model AS-1 auto sampling system). Detection limits are listed in Table 2. Samples that were relatively high in trace metal concentration (greater than three times the detection limit) were analyzed by flame AA. Generally, Cu, Zn, Fe, and Mn were analyzed by flame AA, and Pb and Cd were analyzed by furnace. A scan of all metals was done on a Jarrel-Ash Model 975 Inductively Coupled Argon Plasma (ICAP) spectrophotometer. This method yielded the best estimates of Ba concentrations.

The quality control matrices used for this study were NBS bovine liver, tuna, and oyster tissue. Results were deemed acceptable if values generated by laboratory analysis were within 20% or 2 standard deviations of certified values for the samples. Within every set of samples analyzed, 10% were blanks to monitor any sample preparation contamination, and an additional 20% were blind replicates and spiked samples.

Table 2. Detection limits¹ for biota, sediment, and water samples

Matrix							
Limit	Pb	Cd	Cu	Zn	Fe	Mn	Ba
Biota ($\mu\text{g/g}$)	0.01	0.01	0.01	0.01	0.01	0.01	N/A ²
Sediment ($\mu\text{g/g}$)	4.00	0.40	0.40	0.40	N/A	N/A	0.04
Water (mg/L)	0.005	0.001	0.005	0.01	0.001	0.001	0.001

¹Detection limit is the lowest detectable level

²N/A: Not analyzed

Laboratory preparation varied with the type of sample being processed, as follows:

Crayfish were lyophilized and homogenized with mortar and pestle before analysis. Each crayfish sample was a single species composite of 10 to 15 specimens. No effort was made to remove the digestive tract.

Both water willow and algae were rinsed repeatedly with distilled water to remove sediment contamination. Water willow samples were separated into roots, stems, and leaves for analysis. Each sample was lyophilized and homogenized before analysis.

Freshwater mussel soft tissue was separated from the shell and homogenized in a blender with stainless steel blades prior to lyophilization and analysis. The shell was scrubbed with distilled water to remove any attached algae or sediment, air dried, and then pulverized in a Spex Mixer Mill.

Both whole fish and muscle tissue fillets were prepared for analysis. Whole body samples, composites of 3 to 5 fish of each species, were ground repeatedly in a Hobart meat grinder. Samples were then lyophilized and rehomogenized. Scaled, boneless fillets from the right side of individual fish were prepared in a certified clean room. A portion of the fillet was rinsed with distilled water and frozen for subsequent analysis. This sample was handled as a fisherman might prepare fish for consumption and will be referred to as an "edible portion." Preparation of the remaining portion was based on the technique described by Patterson and Settle (1976). The tissue, with skin removed, was placed on acid-cleaned polyethylene sheeting.

Acid-cleaned stainless steel razor blades were then used to remove any potentially-contaminated surface tissue; a cube of clean, boneless, muscle tissue remained. This material, handled throughout the procedure with acid-cleaned forceps, was then placed in a polyethylene bag and frozen for later analysis.

Digestion of crayfish, water willow, algae, mussels, and fish prior to analysis was by nitric-perchloric acid procedure. A known weight of sample was digested in an acid-washed Kjeldahl flask with 15-20 mL concentrated HNO_3 and 2-4 mL HClO_4 and heated until the volume was reduced to approximately 5 mL. Samples were then diluted with distilled water to a volume of 25 or 50 mL and analyzed. Clean processed cubes of fish tissue were digested in the clean room.

The technique for analysis of ALA-D activity in fish blood was adapted from Hodson (1976) and required approximately 100 μL of blood. Briefly, the assay involved the combination of 200 μL Triton X-100, 200 μL amino levulinic acid, and 100 μL blood. This mixture was incubated for 2 h at 15° C, then combined with 700 μL of protein precipitant and centrifuged for 5 min. Then, 700 μL of the supernatant was mixed with 600 μL of Ehrlich's reagent. This mixture's absorbance was measured at 553 nm against a blank. ALA-D activity was measured in terms of μM porphobilinogen (PBG) produced after 2-h incubation, per mg DNA, and per mg hemoglobin. DNA was determined with a procedure described by Schneider (1957), and hemoglobin was measured using the procedure described by Natelson (1971).

Filtered and unfiltered water samples were digested in 100-mL beakers that had been cleaned by a 30-min, sub-boiled concentrated

HNO₃ reflux cycle. Approximately 40 mL of the sample was poured into the beaker and combined with 5 mL concentrated HNO₃. This sample was heated until the volume was reduced and diluted with distilled water for AA analysis. All water quality analysis was done by the Water Quality Section of the St. Louis District Army Corps of Engineers (Table 3). Filtered samples were analyzed for nitrate, nitrite, ammonia, and ortho phosphate and total dissolved solids. Unfiltered samples were analyzed for total phosphates, chloride, sulfate, specific conductance, turbidity, total alkalinity, total hardness, total suspended solids, and volatile suspended solids. Temperature, pH and dissolved oxygen were measured at the time of collection (Table 3).

Sediment samples were placed in a nitrogen glove box immediately upon return to the laboratory. One subsample was retained in the glove box for immediate sequential extraction analysis and two subsamples were set aside for particle size analysis and total trace metal determinations.

The subsample for total trace metal analysis (= 1 g dry weight) was digested in a 100-mL teflon beaker with 5 mL distilled water, 2 mL 70% HClO₄ and 12 mL 40% HF and heated to near dryness. An additional 8 mL of HF was added and the sample was heated to dryness. Several mL of water and 2 mL HClO₄ were then added and the sample was once again heated to dryness. The residue was dissolved in 8 mL of 1:1 HCl and 20 mL of water, diluted to 100 mL with distilled water, and analyzed by atomic absorption.

An aliquot (= 5 g wet weight) of the subsample retained for particle size analysis was analyzed for total organic carbon. The

Table 3. Water quality parameters other than metals measured in Big and Black River watershed water samples, and methods of determination.

Parameter	Method of Determination
Temperature ^a	Yellow Springs Inst. Co. Meter (field)
Dissolved Oxygen ^a	" "
pH ^a	Corning pH meter (field)
Conductivity	Wheatstone bridge conductance cell
Hardness	Titrimetric, w/EDTA
Alkalinity	Titrimetric w/standard acid
Sulfate	Colorimetric, w/BaCl ₂
Chloride	Titrimetric, w/HgCl ₂
COD	Low-level dichromate
Nitrate	Technicon Autoanalyzer
Nitrite	" "
Ammonia N	" "
Total P	" "
Ortho-P	" "
Total Dissolved Solids	Gravimetric
Total Suspended Solids	"
Volatile Suspended Solids (LOI)	"
Turbidity	Nephelometric (Hach turbidimeter)

^aIn Clearwater Lake, a temperature-pH-dissolved oxygen profile was measured using a Martek water quality analyzer.

remainder of the subsample (≈ 100 g) was dried and sieved (20, 30, 50, 100, 200, and 270 mesh). The fraction that remained (particles less than 60μ) was resuspended in deionized water. Grain size distributions of particles in this fraction were determined with a HIAC Model PC-320 particle size analyzer.

The subsample for sequential sediment extraction was handled in the nitrogen glove box throughout the analysis. From this subsample an aliquot (≈ 5 g) was removed for gravimetric determinations of percent moisture. Wet weight aliquots of sediment equivalent to 1 g dry material were weighed into 50-mL polysulfone (PSF) Oak Ridge-type centrifuge tubes with Viton O-ring sealing cap assemblies. The sequential chemical extraction was modified from the procedure of Tessier et al. (1979). Initial testing of the sequential extraction procedure with polypropylene tubes indicated a problem with heat distortion; distorted tubes could not be properly seated into the JA-17 centrifuge rotor. Search for a more heat resistant, higher tensile strength material led to the testing of the PSF centrifuge tubes. This material was clearly superior in performance to polypropylene and was used for all subsequent extractions. In addition, care was exercised in the bound-to-organic steps to assure that all caps were loose enough to allow the escape of gaseous by-products. Primary modifications to the procedure outlined by Tessier et al. (1979) were: (1) samples were purged with nitrogen through the first three steps of the extraction to avoid oxidation; (2) use of PSF tubes instead of polypropylene; (3) centrifugation at 15,000 rpm for 15 min with a Beckman JT-21 centrifuge and JA-17 rotor; (4) a deionized water wash was added to the reagent

supernatant; and (5) a shaking water bath was employed in the bound-to-oxides and bound-to-organics extraction steps.

The basic sequential extraction scheme was:

(a) Exchangeable Metals (Fraction 1). The sediment was extracted at room temperature for 1 h with 10 mL 1-M MgCl_2 (pH 7) with continuous agitation (Burrell wrist-action shakers). After leaching with MgCl_2 , separation was achieved by centrifugation at 15,000 rpm for 15 min. Under nitrogen atmosphere, the supernatant was removed by pipet and placed in an acid-cleaned borosilicate glass tube. The sediment residue was washed with 10 mL deionized H_2O and centrifuged for 15 min, with this supernatant being added to the first.

(b) Bound to Carbonates (Fraction 2). Residue from (a) was extracted at room temperature with 10 mL of 1-M NaOAc adjusted to pH 5 with HOAc . Because of the fine texture of the sediment samples, extraction time was limited to 5 h. The extraction was followed by the centrifugation-washing step described in (a).

(c) Bound to Iron and Manganese Oxides (Fraction 3). The residue from (b) was extracted with 20 mL of 0.04-M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% HOAc at $96 \pm 3^\circ \text{C}$ for 6 h, followed by centrifugation and a 5 mL distilled H_2O wash.

(d) Bound to Organic Matter (Fraction 4). To the residue in (c) was added 3 mL of 0.02-M HNO_3 and 5 mL 30% H_2O_2 adjusted to pH 2 with HNO_3 . The mixture was heated to $85 \pm 2^\circ \text{C}$ for 2 h with agitation. A second 3-mL aliquot of 30% H_2O_2 was then added and the sample heated again for an additional 3 h with agitation. After cooling, 5 mL of 3.2-M NH_4OAc

in 20% HNO_3 was added and the sample was agitated for 30 min.

Centrifugation and a 5 mL H_2O wash followed.

(e) Residual Metals (Fraction 5). The solid from (d) was digested with a 5:1 mixture of HF and HClO_4 . The sample was first digested in a teflon beaker with 2 mL concentrated HClO_4 and 10 mL HF to near dryness. Another 1 mL of HClO_4 was added and the sample was evaporated until white fumes appeared. The residue was dissolved in HCl and diluted for analysis. After processing, the extracts and wash from steps (a) through (d) were diluted to a final volume of 25 mL, acidified to pH 2 with HNO_3 , and stored in a cool, dark place until analysis.

Metal concentrations were determined with a Perkin-Elmer Model 5000 atomic absorption spectrophotometer equipped with an AS-50 autosampler. The readout of the Model 5000 was calibrated directly in units of concentration using reagent-matched standards. Low levels of background absorption were observed in the carbonate and Fe-Mn oxides fractions. Background correction for these extracts was accomplished with a deuterium arc lamp continuum. For Ba, background emission correction was performed by averaging intensities at 553.4 and 533.8 nm and subtracting from the intensity at the Ba 553.6 line. To check for matrix interferences, a single standard addition was performed for each element on selected individual samples with spiking concentrations approximately equivalent to the concentrations in the samples. Tessier et al. (1979) report as much as 15% suppression of the analyte signal from matrix effects. In the present study, recoveries of spiked elements (Pb, Cd, Cu, and Zn) from the first four extraction steps indicated less than 10% signal suppression or enhancement from the

sample matrix. This degree of matrix interference was considered negligible, making method-of-additions determinations unnecessary.

For elements determined by atomic absorption, the detection limits were estimated to be twice the standard deviation of displayed concentration units following repetitive aspiration of ultra-pure H₂O. For Ba, background emission limited gain setting, thereby increasing the detection limit considerably above that obtainable under ideal conditions. The instrumental detection limit, dilution volume of 25 mL, and 1 g dry weight led to the final detection limits (Table 2).

Data Handling and Statistical Analyses

Statistical Analysis System (SAS) programs (SAS Institute, 1979), available through the University of Missouri-Columbia's Computer Network, were used for all data handling and numerical analyses. Procedures for performing analysis of variance, analysis of covariance, linear and multiple linear regression, and correlation analyses were used repeatedly throughout this investigation. Standard references for these procedures include Snedecor and Cochran (1967), Sokal and Rohlf (1969), Draper and Smith (1972), and Neter and Wasserman (1974).

RESULTS AND DISCUSSION

Metals in Water

General trends in metals levels. Due to the great quantity of water data to be summarized, Table 4 contains only the results for metals analyses completed for low, medium, and high-flow conditions during 1980-81. The results for other water quality parameters measured during this period, as well as the peak flood data for water quality and metals collected by the St. Louis District at Brown's Ford during March and April, 1978 are tabulated in Appendix A. Relationships among these parameters are presented in Table 5 as a matrix of product-moment correlation coefficients.

Pb, Cd, and Cu concentrations were highest at the three Big River sites affected by mine tailings--Desloge, Washington State Park, and Brown's Ford, with total concentrations far exceeding dissolved levels in all samples. Concentrations of these three metals--in both filtered and unfiltered samples--tended to increase with flow at all three sites. Highest measured total Pb (0.68 mg/L) occurred at Washington State Park; highest dissolved Pb (.026 mg/L) occurred at Brown's Ford. However, the flood peak in the high-flow collection was not sampled at Desloge. Cu concentrations (total and dissolved) were also higher at Washington State Park and Brown's Ford. Cd concentrations were at or near detection limits (.002 mg/L) in all samples.

Zn behaved differently than either Pb, Cd, or Cu. At Desloge, highest total Zn concentrations occurred at low flow, and dissolved Zn was always significant. Concentrations at the downstream

Table 4. Dissolved (D) and total (T) metals concentrations (mg/L) in water samples collected in the Big and Black Rivers (A) and in Clearwater Lake (B), 1980-1981.

A. Big and Black Rivers

Location Stage	Flow (cfs)	Pb		Cd		Cu		Zn		Ag		Fe		Mn		Ba	
		D	T	D	T	D	T	D	T	D	T	D	T	D	T		
MINERAL FORK																	
Low	29.6	.005	.009	.001	.001	.005	.005	<.01	<.01	.001	.001	.01	.11	.01	.02	.59	.62
Med.	160.0	.006	.005	.001	.001	.005	.005	<.01	<.01	.001	.001	.03	.05	.01	.01	.35	.36
High	505.0	.005	.009	.001	.001	.005	.005	<.01	<.01	.001	.001	.03	.34	.01	.05	.24	.28
BROWN'S FORD																	
Low	95.6	.005	.043	.001	.001	.005	.005	.02	.03	.001	.001	.01	.27	.03	.07	.47	.49
Med.	650.0	.007	.084	.001	.001	.006	.011	.01	.03	.001	.001	.05	.61	.01	.13	.32	.38
High	11900.0	.026	.440	.001	.001	.037	.024	.05	.17	.001	.001	.14	.50	.05	.34	.10	.22
WASHINGTON STATE PARK																	
Low	70.2	.009	.091	<.001	<.001	<.005	<.005	.01	.04	<.001	<.001	.02	.38	.04	.14	.42	.45
Med.	490.0	<.005	.140	<.001	<.001	.007	.005	.01	.07	<.001	<.001	.05	.78	.02	.17	.16	.22
High	11395.0	.021	.680	<.001	<.004	<.005	.017	-	.22	<.001	<.001	.08	3.00	.04	.51	.10	.19
DESLOGE																	
Low	45.3	.020	.041	.002	.004	.005	.005	.31	.36	.001	.001	.02	.09	.07	.08	.15	.14
Med.	298.0	.010	.085	.001	.001	.005	.005	.06	.11	.001	.001	.04	.42	.03	.08	.09	.09
High	932.0	.012	.110	.002	.004	.005	.006	.10	.16	.001	.001	.05	.63	.05	.12	.07	.07
IRONDALE																	
Low	7.1	.005	.005	.001	.001	.005	.005	<.01	<.01	.001	.001	.02	.32	.02	.12	.15	.15
Med.	160.0	.005	.005	.001	.001	.005	.005	<.01	<.01	.001	.001	.02	.26	.03	.07	.08	.08
High	300.0	.005	.005	.001	.001	.005	.005	<.01	<.01	.001	.001	.03	.23	.02	.07	.06	.07
UPSTREAM CLEARWATER LAKE																	
Low	-	.005	.005	.001	.001	.005	.005	<.01	<.01	.001	.001	.02	.03	.01	.01	.05	.04
Med.	-	.005	.005	.001	.001	.005	.005	<.01	<.01	.001	.001	.01	.04	.01	.01	.04	.03
High	-	.005	.005	.001	.001	.005	.005	<.01	<.01	.001	.001	.02	.12	.03	.02	.03	.03
DOWNSTREAM CLEARWATER LAKE																	
Low	200.0	.005	.005	.001	.001	.005	.005	<.01	<.01	.001	.001	.02	.11	.21	.27	.07	.07
Med.	1040.0	.005	.005	.001	.001	.005	.005	<.01	<.01	.001	.001	.01	.03	.01	.03	.04	.04
High	160.0	.005	.005	.001	.001	.005	.005	<.01	<.01	.001	.001	.09	.12	.01	.03	.03	.03

Table 4. (cont'd)

B. Clearwater Lake																			
Month Depth	Pb		Cd		Cu		Zn		Ag		Fe		Mn		Ba		pH	O.O.	Temp.
	D	T	D	T	D	T	D	T	D	T	D	T	D	T	D	T			
July 1980																			
Surface	<0.005	<0.005	<0.001	<0.001	<0.005	<0.005	<0.1	<0.1	<0.001	<0.001	0.02	0.02	0.01	0.01	0.05	0.05	8.5	8.0	27.4
5 m	<0.005	<0.005	<0.001	<0.001	<0.005	<0.005	<0.1	<0.1	<0.001	<0.001	0.02	0.04	0.01	0.01	0.05	0.05	8.2	6.7	25.4
Bottom	<0.005	<0.005	<0.001	<0.001	<0.005	<0.005	<0.1	<0.1	<0.001	<0.001	0.13	0.45	1.68	1.73	0.07	0.07	7.4	0.2	18.1
April 1981																			
Surface	<0.005	<0.005	<0.001	<0.001	<0.005	<0.005	<0.1	<0.10	<0.001	<0.001	0.02	0.18	0.01	0.03	0.04	0.04	8.0	8.3	18.5
Bottom	<0.005	<0.005	<0.001	<0.001	<0.005	<0.005	<0.1	<0.10	<0.001	<0.001	0.02	0.18	0.01	0.03	0.04	0.04	7.7	8.4	16.7
May 1981																			
Surface	<0.005	<0.005	<0.001	<0.001	<0.005	<0.005	<0.1	<0.1	<0.001	<0.001	0.01	0.11	<0.01	<0.01	0.03	0.03	7.8	8.7	20.8
5 m	<0.005	<0.005	<0.001	<0.001	<0.005	<0.005	<0.1	<0.1	<0.001	<0.001	0.02	0.10	<0.01	0.02	0.03	0.03	7.5	7.8	15.9
10 m	<0.005	<0.005	<0.001	<0.001	<0.005	<0.005	<0.1	<0.1	<0.001	<0.001	0.07	0.32	0.01	0.05	0.02	0.03	7.2	7.4	14.3
Bottom	<0.005	<0.005	<0.001	<0.001	<0.005	<0.005	<0.1	<0.1	<0.001	<0.001	0.07	0.27	0.01	0.04	0.02	0.03	7.1	7.8	13.9

Table 5. Product-moment correlation coefficients (A) among total metal concentrations, solid phase water quality parameters, and flow; and (B) among dissolved metals concentrations, liquid-phase parameters, and flow. Big River watershed above, Black River watershed below.

A. Solid-phase Correlations		BIG RIVER														
		CORRELATION COEFFICIENTS / NUMBER OF OBSERVATIONS														
		TPB	ICD	TZN	TCU	TBA	TFE	TMN	TURB	COB	TSSOLID	VOLSSOL	FLOW	PCTSAND	PCTSILT	PCTCLAY
TPB	0.17284 56	0.92543 56	0.90509 56	-0.13482 15	0.93164 56	0.96684 56	0.96735 23	0.96216 30	0.97276 23	0.97327 23	0.75269 56	0.27034 56	-0.45835 56	0.32724 56		
ICD	0.00000 15	0.36115 56	0.21241 56	-0.36635 15	0.16555 56	0.16427 56	0.82198 23	0.33040 30	0.84515 23	0.82463 23	0.27620 56	0.00025 56	0.08271 56	-0.10806 56		
TZN	0.00000 15	0.89857 56	0.89857 56	-0.37371 15	0.93473 56	0.91384 56	0.87460 23	0.89563 30	0.88393 23	0.88444 23	0.77201 56	0.23977 56	-0.39099 56	0.26975 56		
TCU	0.00000 15	0.00000 15	0.00000 15	-0.06196 15	0.89672 56	0.88055 56	0.97354 23	0.95213 30	0.97614 23	0.98073 23	0.72852 56	0.31201 56	-0.50962 56	0.35513 56		
TBA	0.00000 15	0.00000 15	0.00000 15	0.00000 15	-0.16432 15	-0.18668 56	-0.14600 15	-0.24870 15	-0.12308 15	-0.16223 15	-0.13512 15	-0.24017 15	0.33060 15	-0.25634 15		
TFE	0.00000 15	0.00000 15	0.00000 15	0.20979 15	0.95778 56	0.94511 23	0.93678 30	0.93678 30	0.96012 23	0.94826 23	0.77265 56	0.18337 56	-0.09719 56	0.33357 56		
TMN	0.00000 15	0.00000 15	0.00000 15	0.70502 15	0.71333 15	0.98078 23	0.96822 30	0.96822 30	0.99523 23	0.98865 23	0.76438 56	0.25328 56	-0.42205 56	0.29743 56		
TURB	0.00000 15	0.00000 15	0.00000 15	-0.41810 15	0.35970 15	0.09661 15	0.97969 23	0.97969 23	0.98484 23	0.99326 23	0.75555 23	0.63173 23	-0.61305 23	0.16928 23		
COB	0.00000 15	0.00000 15	0.00000 15	-0.71492 15	0.34201 15	-0.25180 15	0.81044 15	0.81044 15	0.96876 23	0.98305 23	0.73609 30	0.45662 30	-0.50046 30	0.22886 30		
TSSOLID	0.00000 15	0.00000 15	0.00000 15	0.56843 15	0.72597 15	0.93618 15	0.16937 15	-0.04681 15	0.73166 15	0.98953 23	0.68396 23	0.61671 23	-0.57897 23	0.13346 23		
VOLSSOL	0.00000 15	0.00000 15	0.00000 15	0.62914 15	0.39311 15	0.77385 15	-0.34817 15	-0.40843 15	0.73166 15	0.98953 23	0.76742 23	0.66077 23	-0.62019 23	0.14276 23		
FLOW	0.00000 3	0.00000 3	0.00000 3	-0.25819 3	-0.99284 3	-0.46474 3	-0.93097 3	0.46474 3	-0.72897 3	0.53445 3	-0.06771 56	-0.06771 56	-0.29566 56	0.45369 56		
PCTSAND	0.00000 9	0.00000 9	0.00000 9	0.00000 9	0.00000 9	0.00000 9	0.00000 9	0.00000 9	0.00000 9	0.00000 9	0.00000 3	0.00000 3	-0.66264 60	-0.12974 60		
PCTSILT	0.00000 9	0.00000 9	0.00000 9	0.00357 9	0.22003 9	0.34650 9	0.38760 9	0.27440 9	0.67074 9	0.00650 9	-0.99861 3	0.00000 9	-0.65644 60			
PCTCLAY	0.00000 9	0.00000 9	0.00000 9	-0.00357 9	-0.22003 9	-0.34650 9	-0.38760 9	-0.27440 9	-0.67074 9	-0.00650 9	0.99861 3	0.00000 9	-0.65644 60			

Table 5 (cont'd)

B. Liquid-phase correlations

BIG RIVER

CORRELATION COEFFICIENTS / NUMBER OF OBSERVATIONS

	OPB	DCD	DZN	DCU	DBA	DFE	DMN	DO	PH	TALK	CHL	SULF	SPCOND	COD	NITRATE	NITRITE	AMMON	TPHOS	OPHOS	THARD	TDSOLIO	FLOW	
DPB		0.280 55	0.481 54	0.531 55	-0.395 15	0.488 55	0.351 55	-0.026 22	-0.155 21	-0.484 22	0.424 22	0.210 22	-0.266 22	0.145 29	0.474 29	0.002 29	0.565 22	0.122 29	0.179 29	-0.312 22	-0.118 22	0.011 55	
DCD	0.000 15		0.646 54	-0.051 55	-0.280 15	-0.165 55	0.250 55	0.045 22	-0.020 21	-0.031 22	0.220 22	0.465 22	0.188 22	-0.102 29	0.480 29	0.025 29	0.293 22	-0.074 29	0.090 29	0.165 22	0.273 22	-0.268 55	
DZN	0.000 15	0.000 15		0.112 54	-0.286 14	0.033 54	0.427 54	0.024 21	0.357 20	0.066 21	0.508 21	0.796 21	0.409 21	-0.132 28	0.515 28	0.135 28	0.519 21	-0.075 28	0.165 28	0.362 21	0.550 21	-0.061 54	
DCU	0.000 15	0.000 15	0.000 15		-0.202 15	0.211 55	0.063 55	-0.064 22	-0.061 21	-0.228 22	0.459 22	-0.071 22	-0.203 22	0.021 29	0.034 29	-0.118 29	0.337 22	-0.025 29	0.094 29	-0.225 22	-0.169 22	0.108 55	
DBA	0.000 15	0.000 15	0.000 15	0.000 15		-0.426 15	-0.336 15	-0.101 15	0.132 15	0.812 15	0.046 15	-0.016 15	0.498 15	-0.432 15	-0.694 15	-0.161 15	-0.082 15	-0.429 15	-0.232 15	0.587 15	0.421 15	-0.322 15	
DFE	0.000 15	0.000 15	0.000 15	0.000 15		0.209 15	0.461 55	0.145 22	-0.561 21	-0.624 22	-0.011 22	-0.226 22	-0.580 22	0.710 29	0.060 29	0.382 29	0.177 22	0.704 29	0.272 29	-0.578 22	-0.443 22	0.460 55	
DMN	0.000 15	0.000 15	0.000 15	0.000 15	0.592 15	0.743 15		-0.122 22	-0.213 21	-0.419 22	0.425 22	0.409 22	-0.139 22	0.586 29	0.162 29	0.286 29	0.346 22	0.613 23	0.550 29	-0.168 22	0.046 22	0.549 55	
DO	0.000 15	0.000 15	0.000 15	0.000 15		-0.599 15	-0.738 15	-0.947 15		-0.048 22	-0.439 23	-0.444 23	-0.292 23	-0.463 23	0.240 23	0.157 23	0.058 23	0.090 23	0.158 22	-0.008 23	-0.455 23	-0.429 23	0.159 23
PH	0.000 15	0.000 15	0.000 15	0.000 15		0.097 15	-0.166 15	-0.253 15	0.254 15		0.525 22	0.180 22	0.436 22	0.599 22	-0.745 22	-0.032 22	-0.372 22	0.212 22	-0.699 23	-0.121 22	0.561 22	0.529 22	-0.465 22
TALK	0.000 15	0.000 15	0.000 15	0.000 15		0.686 15	-0.158 15	0.212 15	-0.206 15	0.287 15		0.272 23	0.426 23	0.902 23	-0.724 23	-0.448 23	-0.128 23	-0.059 23	-0.614 23	-0.311 23	0.935 23	0.820 23	-0.751 23
CHL	0.000 15	0.000 15	0.000 15	0.000 15		0.171 15	-0.365 15	-0.052 15	0.056 15	0.076 15	0.709 15		0.763 23	0.537 23	-0.047 23	0.102 23	0.277 23	0.272 23	0.034 23	0.523 23	0.499 23	0.642 23	0.072 23
SULF	0.000 15	0.000 15	0.000 15	0.000 15		-0.369 15	-0.394 15	-0.293 15	0.349 15	-0.039 15	0.252 15	0.773 15		0.764 23	-0.312 23	0.330 23	0.290 23	0.273 23	-0.185 23	0.309 23	0.714 23	0.859 23	-0.285 23
SPCOND	0.000 15	0.000 15	0.000 15	0.000 15		0.435 15	-0.271 15	0.094 15	-0.021 15	0.278 15	0.910 15	0.835 15	0.542 15		-0.690 23	-0.137 23	0.044 23	0.055 23	-0.561 23	-0.088 23	0.992 23	0.973 23	-0.697 23
COD	0.000 15	0.000 15	0.000 15	0.000 15		-0.791 15	-0.013 15	-0.253 15	0.247 15	-0.372 15	-0.851 15	-0.353 15	0.098 15	-0.704 15		-0.148 30	0.584 30	0.067 23	0.982 30	0.618 30	-0.667 23	-0.554 23	0.736 30
NITRATE	0.000 15	0.000 15	0.000 15	0.000 15		-0.723 15	-0.018 15	-0.346 15	0.452 15	-0.240 15	-0.414 15	0.135 15	0.628 15	-0.093 15	0.520 15		0.158 30	0.398 23	-0.162 30	0.000 30	-0.203 23	-0.060 23	-0.332 30

Table 5 (cont'd)

	OPB	DCD	DZN	DCU	DBA	DFE	DMN	DO	PH	TALK	CHL	SULF	SPCOND	COD	NITRATE	NITRITE	AMMON	TPHOS	OPHOS	THARO	TOSOLID	FLOW
NITRITE	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15		0.188 23	0.606 30	0.400 30	0.034 23	0.142 23	0.461 30
AMMON	0.000 15	0.000 15	0.000 15	0.000 15	0.558 15	0.777 15	0.791 15	-0.683 15	-0.202 15	0.099 15	-0.295 15	-0.508 15	-0.021 15	-0.332 15	-0.189 15	0.000 15		0.094 23	0.253 23	0.041 23	0.137 23	0.262 23
TPHOS	0.000 15	0.000 15	0.000 15	0.000 15	-0.505 15	-0.098 15	-0.126 15	0.148 15	-0.508 15	-0.637 15	-0.386 15	0.032 15	-0.530 15	0.693 15	0.279 15	0.000 15	-0.257 15		0.640 30	-0.533 23	-0.411 23	0.734 30
OPHOS	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15	0.000 15		-0.106 23	0.033 23	0.537 30
THARD	0.000 15	0.000 15	0.000 15	0.000 15	0.473 15	-0.126 15	0.204 15	-0.153 15	0.211 15	0.914 15	0.807 15	0.508 15	0.902 15	-0.636 15	-0.145 15	0.000 15	0.137 15	-0.534 15	0.000 15		0.964 23	-0.701 23
TDSOLID	0.000 15	0.000 15	0.000 15	0.000 15	0.543 15	-0.273 15	0.122 15	-0.057 15	0.197 15	0.934 15	0.734 15	0.340 15	0.903 15	-0.737 15	-0.251 15	0.000 15	0.069 15	-0.551 15	0.000 15	0.906 15		-0.577 23
FLOW	0.000 3	0.000 3	0.000 3	0.000 3	-0.259 3	-0.576 3	-0.460 3	0.238 3	-0.040 3	0.415 3	0.957 3	0.980 3	0.829 3	0.464 3	0.399 3	0.000 3	-0.988 3	0.000 3	0.000 3	0.786 3	0.684 3	

sites--Washington State Park and Brown's Ford--were also high relative to "control sites"--Irondale and Mineral Fork--but were lower than concentrations at Desloge.

Concentrations of Pb, Cd, Zn, and Cu were always less than detection thresholds at the three sites investigated in the Black River/Clearwater Lake watershed. Likewise, Ag was virtually undetectable in all Big and Black River samples collected in this investigation. Arsenic, which was not measured in this study but was quantitated by the St. Louis District in their 1978 flood study, ranged from 0.006 to 0.058 mg/L (total), with dissolved arsenic concentrations at the detection threshold (0.005 mg/L) in all samples. Like Pb and Cu, total As concentrations tended to increase with discharge at Brown's Ford.

As expected, Ba concentrations were highest in samples from those sites on the Big River representing areas of the watershed currently being mined for barite (Washington State Park, Mineral Fork and Brown's Ford). Total Ba concentrations in unaffected areas of the Big River watershed and in the Black River/Clearwater Lake watershed ranged from 0.02 to about 0.15 mg/L. At affected Big River stations, total Ba concentrations ranged from a low of 0.10 mg/L (Washington State Park and Brown's Ford at high flow) to a high of 0.62 mg/L (Mineral Fork at low flow). At all sites there was little difference between filtered and unfiltered samples; highest concentrations occurred at low flow; and lowest concentrations occurred at high flow.

Given that the Big River contains generally hard, alkaline water, Fe and Mn concentrations were generally high; dissolved Fe ranged from 0.01 mg/L (Mineral Fork and Brown's Ford at low flow) to 0.14 mg/L

(Brown's Ford at high flow), and total Fe reached 3.00 mg/L at Washington State Park during high flow. Similarly, dissolved Mn ranged from 0.01 mg/L (Mineral Fork, all samples) to 0.07 mg/L (Desloge, low flow), and total Mn reached 0.51 mg/L at Washington State Park during high flow. With the exception of dissolved Mn at Desloge, Fe and Mn concentrations tended to increase with flow. The high concentrations in the lower Big River and Mineral Fork suggest that the open-pit sand/gravel and barite mining activities in this part of the watershed are likely sources of Fe and Mn, as well as Ba.

Fe and Mn concentrations in the Black River above Clearwater Lake were generally lower than concentrations in the Big River--up to 0.12 mg/L total Fe, with dissolved Fe and Mn at or near detection limits (0.01-0.03 mg/L) in all samples. Samples from downstream of Clearwater Lake and from within the lake showed evidence of predominant reducing conditions during summer stratification. Near the bottom of the lake, Mn concentrations reached 1.73 mg/L (total; 1.68 mg/L dissolved) in July, 1980. Total Fe at this time was 0.45 mg/L; dissolved Fe reached 0.13 mg/L. Downstream of the lake, concentrations of Fe and Mn tended to reflect conditions in the lake--Mn reached 0.27 mg/L (total; 0.21 mg/L dissolved), and total Fe reached 0.11 mg/L in July 1980. However, Fe concentrations (total and dissolved) were higher in May, 1981, during a period of comparatively low water releases (160 cfs) from the lake.

To examine further the relationships among solid-phase constituents, dry-weight suspended concentrations of the metals were computed based on measured concentrations of total suspended solids (Table 6). Although these values are based on different numbers of samples and non-uniform flow conditions among the locations, several

Table 6. Geometric mean suspended metals concentrations, $\mu\text{g/g}$ dry weight.¹

River Site	Pb	Cd	Zn	Cu	Ba	Fe	Mn
Big R.							
Irondale	²	-	-	-	337	29710	6966
Desloge	5397	180	5182	32	311	25399	3005
Washington St. Park	3779	17	1457	70	1042	17697	3681
Mineral Fork	316	-	-	-	3271	12745	1756
Brown's Ford	3125	-	1004	167	1593	11054	3258
Black R.							
Above Clearwater L.	-	-	-	-	111	8206	750
Clearwater L.	-	-	-	-	623	34080	5587
Below Clearwater L.	-	-	-	-	408	9396	8234

¹ $\left[\frac{\text{Total metal (mg/L)} - \text{dissolved metal (mg/L)}}{\text{Total suspended solids (mg/L)}} \right] \cdot [10^3 \mu\text{g/mg}] \cdot [10^3 \text{mg/g}]$

²Dash indicates concentrations too close to detection threshold for meaningful comparison.

important features emerge. First, it appears that in the Big River there was a dilution of the suspended metals concentrations (other than Ba) with distance downstream from Desloge. Similarly, Fe and Mn levels, which were highest at Irondale, also declined with distance downstream in the Big River. Pb, Cd, and Zn concentrations were highest at Desloge, and decreased downstream (Table 6). Dry weight suspended Fe and Mn levels in Mineral Fork were lower than those in the Big River; consequently, Fe and Mn concentrations were lower at Brown's Ford than at Washington State Park. Pb concentrations, on a dry weight basis, were higher than anticipated in Mineral Fork (Table 6), probably reflecting the influences of (a) an area of lead mineralization and old mine workings in the upstream portion of the Mineral Fork watershed, and (b) small amounts of galena that frequently occur with barite in the Washington County deposits (USGS 1967).

As discussed previously, Ba occurred primarily in the liquid phase. However, measurable suspended Ba was present at all sites. As expected, dry weight suspended Ba concentrations were highest in the Mineral Fork and at the downstream-most stations on the Big River (Washington State Park and Brown's Ford).

In the Black River and Clearwater Lake, only Ba, Fe, and Mn suspended concentrations were sufficiently high for computation of dry weight concentrations (Table 6). Concentrations of these metals in the Black River upstream of Clearwater Lake were substantially lower than corresponding levels in the Big River. However, average concentrations were higher within the lake than upstream of the lake by factors of 5.6 for Ba, 4.2 for Fe, and 7.4 for Mn. Release waters were also higher in the dry weight concentrations of all these metals than were influent

waters, but, except for Mn, were lower than lake waters. Dry weight suspended Mn concentrations were 11 times higher in release waters than in influent waters; Fe concentrations were only slightly higher.

Collectively, these data and the metals in water data (Table 4) suggest that the seasonal cycle of Fe and Mn in Clearwater Lake is such that proportionately more Fe than Mn is re-precipitated and retained within the lake. During stratification and reduction, Mn is reduced and solubilized slightly before Fe; upon oxidation, the converse holds--Fe is precipitated before Mn. In addition, the oxidation of Fe^{+2} proceeds more rapidly than the oxidation of Mn^{+2} (Tessier et al. 1979). As a result, dissolved Mn concentrations in the summer hypolimnion of Clearwater Lake are far higher than dissolved Fe concentrations, but particulate Fe levels (total-dissolved) exceed particulate Mn concentrations. Mn appears to be exported in dissolved form to the river downstream, where it is subsequently oxidized and precipitated.

Relationships among metals and other water constituents. The correlation matrices (Table 5) illustrate close relationships among many solid-phase and liquid-phase constituents in the Big and Black River watersheds (in these tables, correlation coefficients for Big River samples are above the principal diagonal; those for the Black River and Clearwater Lake are below the principal diagonal). In the Big River, concentrations of total Pb, Zn, Cu, Fe, and Mn were highly intercorrelated ($r > 0.88$, Table 5). Total Pb was most closely correlated with total Mn ($r > 0.97$). Among the other parameters measured, total concentrations of Pb, Zn, Cu, Fe and Mn were most closely correlated with turbidity, total suspended solids, and volatile suspended solids

($r > 0.95$, Table 5). Pb, Zn, Cu, Fe, and Mn concentrations were all positively correlated with flow ($r > 0.75$). However, this correlation must be interpreted with caution because "flow" differences are also related to sampling site. Correlation coefficients for total Cd were generally lower, probably as a result of the lower concentrations; like the other five metals, total Cd was also most closely correlated with turbidity, total suspended solids, and volatile suspended solids ($0.82 < r < 0.85$), but was not highly correlated with any other metals ($r < 0.36$).

Total Ba generally behaved differently from the other metals in the Big River watershed. Because Ba is much more soluble under conditions typical of the Big River, liquid-phase transport is more important for Ba than for Pb, Cd, Zn, Cu, Fe, or Mn. As a result, total Ba concentrations are negatively correlated with most solid-phase constituents.

Given the foregoing discussion of total Ba it is therefore not surprising that dissolved Ba concentrations in the Big River watershed were more closely correlated with some liquid-phase parameters than with the solid-phase constituents. Dissolved Ba concentrations were positively correlated with alkalinity ($r > 0.81$) and, to a lesser extent, with hardness, specific conductivity, and total dissolved solids (Table 5). Correlations among the dissolved metals were weaker than those among total metals, with the lowest occurring for Cd (probably because the levels were generally below detection limits) and the highest ($r > 0.53$) between Cu and Pb (Table 5). Other correlations among the metals that tend to be transported primarily in the solid phase--Pb, Zn, Fe, Mn, and Cu--were less distinct ($0.35 < r < 0.46$). The relatively high

correlation between dissolved Zn and dissolved Cd ($r > 0.64$) may be either an artifact of low Cd concentrations or an indication that both metals are solubilized to some extent.

Among the liquid-phase parameters other than metals, most positive correlations indicate either closely related constituents that tend to rise and fall together, or water-quality parameters that overlap in the constituents they measure. Among those that overlap, hardness, alkalinity, total dissolved solids, and specific conductivity are all highly responsive to changes in levels of dissolved Ca and Mg and therefore exhibit a high degree of positive intercorrelation ($r > 0.97$). Among the closely-related constituents, for example, a high correlation ($r > 0.81$) between dissolved Zn and sulfate (SO_4) concentrations suggests that the mechanism of ZnS reduction postulated by Kramer (1976) as an explanation for high dissolved Zn levels in Flat River Creek may also hold for other areas of the Big River watershed. Pb and Cd were also correlated with SO_4^{-2} , but not as strongly; for Cd, $r = 0.47$; for Pb, $r = 0.22$ (Table 5).

Positive correlations with flow are generally indicative of dissolved parameters associated with surface runoff; conversely, negative relationships suggest parameters most closely associated with groundwater, with the negative correlation occurring when increased rainfall and surface runoff dilute the groundwater. Positive correlations with flow in the Big River occurred for dissolved Fe and Mn, chemical oxygen demand, nitrite, and total- and ortho-phosphorus (Table 5). Negative correlations with flow were most apparent for alkalinity, hardness, specific conductivity, total dissolved solids, nitrate, pH, and to a lesser extent, dissolved Ba. As discussed

earlier, however, all correlations with flow must be interpreted cautiously because multiple locations and differing flow conditions were included in the analysis.

The most immediately apparent features of the Black River-Clearwater Lake correlation matrices are the preponderance of zero values for some of the metals. This was caused by most measurements being at or near detection limits (Table 5). Nevertheless, some of the measurable parameters were correlated.

Although the relationships among solid-phase parameters were less distinct for the Black River than for the Big River, most of the correlations noted for the Big River were also present for the Black River. Like the Big River, the relationship between total Mn and total suspended solids was especially distinct.

Among the dissolved constituents, the expected positive relationships between conductivity, total dissolved solids, alkalinity, and hardness were present, as was the positive correlation ($r > .74$) between dissolved Fe and dissolved Mn (Table 5). The correlations between water quality parameters and flow in the Black River are not related so much to discharge as they are to season--the parameters are dominated by redox processes rather than meteorological events because flows upstream and downstream of Clearwater Lake are regulated by dams. The negative association of dissolved Mn (and to a lesser extent, dissolved Fe) with dissolved oxygen was especially distinct (Table 5). This negative correlation illustrates again the solubilization of Fe and Mn by reductive processes within the hypolimnion of Clearwater Lake during periods of stratification.

Transport of metals in the lower reaches of the Big River. The water quality data in Table 4 and the correlation coefficients in Table 5 provide a general indication that concentrations of most solid-phase constituents, including the toxic metals of interest, vary directly with discharge in the Big River. Since these relationships are important in evaluating the overall transport of metals in the watershed, they were investigated further using water quality data generated by this investigation, by the St. Louis District during their 1978 survey of spring floods at Brown's Ford, and continuous flow records from the U. S. Geological Survey's gauge on the Big River at Mammoth Bridge (near DeSoto).

As illustrated by Table 5 and discussed earlier, total suspended solids concentrations were closely correlated with suspended Fe, suspended Mn and, to a lesser extent, other suspended metals. Multiple linear regression and the available data for Brown's Ford (10 observations) revealed that the relationship

$$Y = 6.509 x_1 + 482.815 x_2 - 1871.163 x_3 - 20.534$$

where Y = total suspended solids, x_1 = suspended Fe, x_2 = suspended Mn, and x_3 = suspended Cu, accounted for 99.8% of the observed variability in suspended solids concentrations. The intercept and the regression coefficient for Mn were highly significant ($p < 0.01$); the parameters for Fe and Cu were also significant ($0.01 < p < 0.05$). Values for total suspended solids estimated by this relationship, along with corresponding observed values, are plotted against measured concentrations of suspended Mn, Fe, and Cu in Fig. 2. As these figures and the correlation coefficients in Table 5 illustrate, the fit for Mn was best, followed by Fe and Cu. Nevertheless, the fact that the

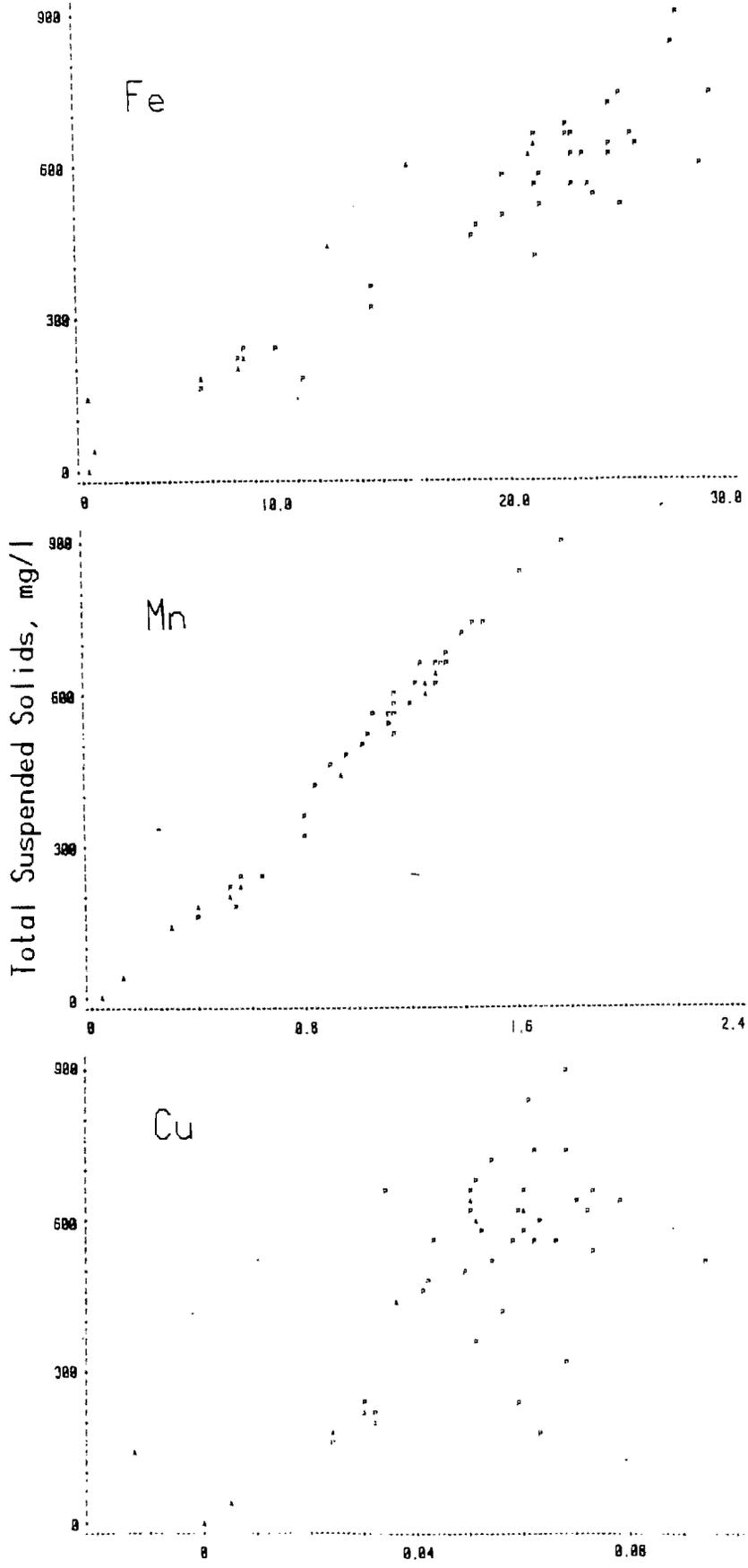


Figure 2. Total suspended solids concentrations at Brown's Ford plotted against corresponding suspended Fe, Mn, and Cu concentrations (all in mg/l).

coefficients for Fe and Cu were statistically significant indicates that a better estimate of total suspended solids is achieved if all three variables are used.

The data used in the foregoing analysis represented collections made in 1980-81 at discharge levels of 95.6, 650, and 11,900 ft³/sec, and in March, 1978 at flows of 6,600 to 7,400 ft³/sec. During the peak flood collection period of April, 1978, when discharge levels ranged from 8,500 to 34,800 ft³/sec (Appendix A), the St. Louis District was unable to measure total suspended solids concentrations. However, suspended metals concentrations and particle size distributions were determined. The regression equation computed on the basis of the 1980-81 and March, 1978 data were used to estimate total suspended solids concentrations during the April, 1978 flood. These 43 observations were then used to investigate further the relationship between suspended sediments and discharge.

Multiple linear regression was again used, this time to quantify the relationship between suspended solids and flow. Since any future considerations of mass transport will require the use of concentration data expressed in metric units (mg/L), values for flow in cfs (ft³/sec) were converted to metric units (m³/sec) using the conversion factor 0.02832 m³/ft³. After trying a variety of equation forms, the following log-log, quadratic expression was found to best explain the relationship between total suspended solids (Y, mg/L) and flow (x, m³/sec):

$$\log_{10} Y = 0.267 + 1.445(\log_{10} x) - 0.203(\log_{10} x)^2$$

This expression explained 75.7% of the variability in total suspended solids and was highly significant ($p < 0.01$); however, the intercept value was not significantly different from 0 ($p < 0.05$). Predicted and

observed values for this relationship are displayed in Fig. 3, where the letter "A" represents measured total suspended solids concentrations; "C" represents concentrations computed using measurements of the suspended Mn, Fe, and Cu concentrations; and "P" represents values predicted by the log-log quadratic relationship with flow. Given the 3-yr time span of the data base and the inherent difficulty of accurately measuring suspended solids at high flow, the fit depicted in Fig. 3 is acceptable. However, it must be remembered that this relationship is based on computed, rather than measured, concentrations at high flow and that the relationship used to compute these concentrations was extended beyond the range for which measured values were available.

Although the empirical relationship plotted in Fig. 3 appears to represent a reasonable approximation of the total suspended solids response to changes in flow, it is insufficient for a more detailed investigation of trace metal transport in that it is not sensitive to changes in the grain-size distribution of the suspended load. This is important for two main reasons: First, trace metal concentrations may not be uniform among different particle size classes; and second, the most accurate estimates of total sediment load (suspended load + bed load) can be achieved when the particle size distribution of the suspended load and of the bed sediments are known. Therefore, concentrations of suspended sand, silt, and clay-size particles were computed using the measured grain-size distributions of the suspended load samples and the measured and computed total suspended solids concentrations. Multiple linear regression was used to characterize the relationships between sand, silt, and clay-size suspended particle

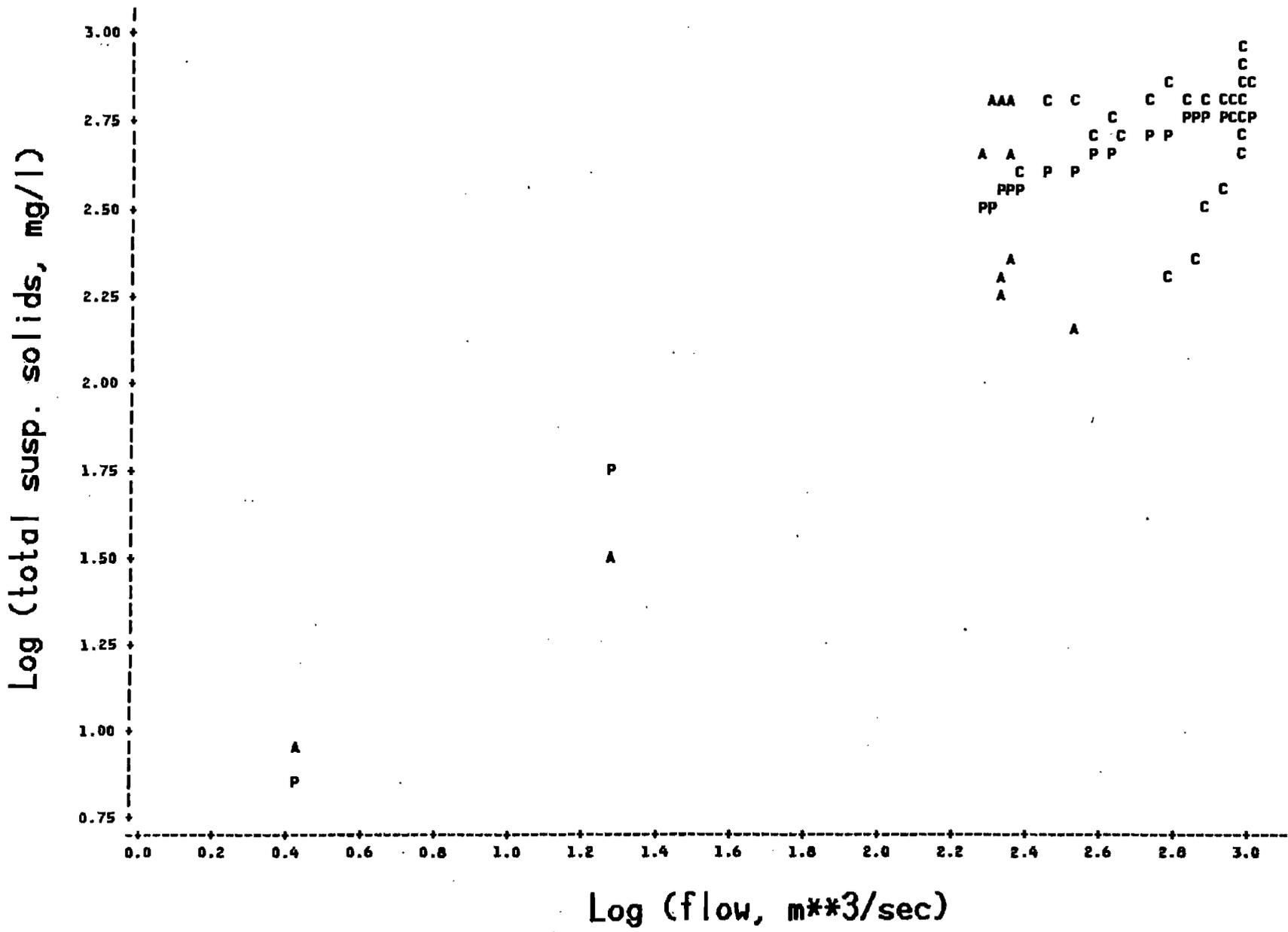


Figure 3. Measured (A), computed (C), and predicted (P) concentrations of total suspended solids (mg/l) vs. flow at Brown's Ford, 1978-1981.

concentrations and flow, with the following log-log quadratic relationships yielding the best fits:

$$\log_{10} Y_1 = -1.413 + 2.789(\log_{10} x) - 0.587(\log_{10} x)^2$$

$$\log_{10} Y_2 = 0.542 + 0.916(\log_{10} x) - 0.086(\log_{10} x)^2$$

$$\log_{10} Y_3 = -0.364 + 1.138(\log_{10} x) - 0.080(\log_{10} x)^2$$

where Y_1 , Y_2 , and Y_3 represent concentrations of suspended sand, silt, and clay-size particles (mg/L), respectively, and x = flow (m^3/sec). R^2 values were sand, 0.57; silt, 0.63; and clay, 0.71, and all three models were highly significant ($p < 0.01$). The intercept and both regression coefficients were highly significant ($p < 0.01$) for sand; for silt and clay, the coefficients for the linear responses were the only significant terms in the models--neither the intercepts nor the quadratic terms differed significantly from zero ($p > 0.05$). Predicted and observed values for these relationships are illustrated in Fig. 4.

In general, the fit of these models can best be described as "fair". For all three size fractions, there is more variability at high flow than at low even after log transformation. The basic form of the model selected appears correct only for silt; for both sand and clay, a cubic term may be required if the concentration is to be represented only in terms of total flow, and a "threshold flow" for suspension and transport of sand-sized particles needs to be more accurately determined.

As an alternative to further empirical investigations based solely on flow, greater predictive capability for suspended sediment transport might result if flow were to be decomposed into its components. Discharge, in units of volume/time, can be separated into area and velocity components; and area can be further divided into its components

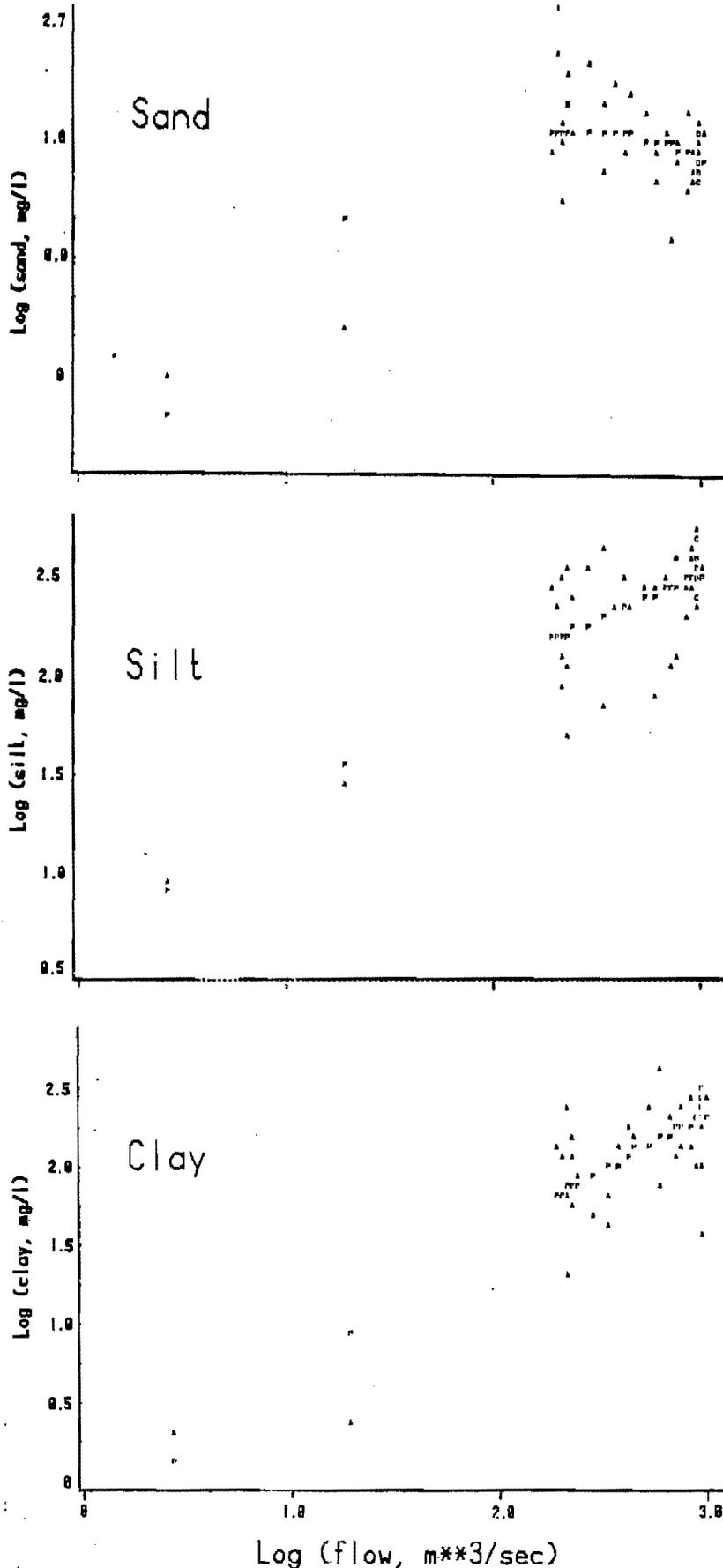


Figure 4. Measured (A=1 obs., B=2 obs., etc.) and predicted (P) concentrations of sand-, silt-, and clay-sized suspended particles vs. flow at Brown's Ford, 1978-1981.

of width and depth (discharge in m^3/sec) = (stream width in m) * (mean depth in m) * (mean velocity in m/sec). The relationships between the components of flow--cross-sectional area and velocity--as well as the components of area (stream width and depth), as functions of flow in the Big River, were investigated further.

Measurements of width, depth, area, and velocity made periodically by the USGS to calibrate the gauge at DeSoto from 1978 through 1981 were evaluated in this analysis. These data represent a 4-yr time-span, with most of the high-flow calibrations occurring in 1978 and 1979. During this period, considerable changes in channel morphometry could have occurred, which would tend to obscure trends related to flow alone. Calibration readings were therefore separated into "old" (1978-79) and "new" (1980-81) groups for comparison. As Fig. 5 illustrates, there were no readily apparent differences between the two sets of measurements in their relationships with discharge; the data were therefore treated together in subsequent analyses.

Statistical evaluation of the 58 sets of calibration measurements, again using multiple linear regression, revealed that cross-sectional area and its components--channel width and mean depth--varied in a fairly predictable manner with discharge. Results for velocity, however, were worse. Although a variety of transformations were employed, the following quadratic, semi-log relationships using untransformed measurements of width, depth, area, and velocity against \log_{10} transformed values for flow (here, in English units of ft, ft^2 , ft/sec, and ft^3/sec , respectively), yielded the best results:

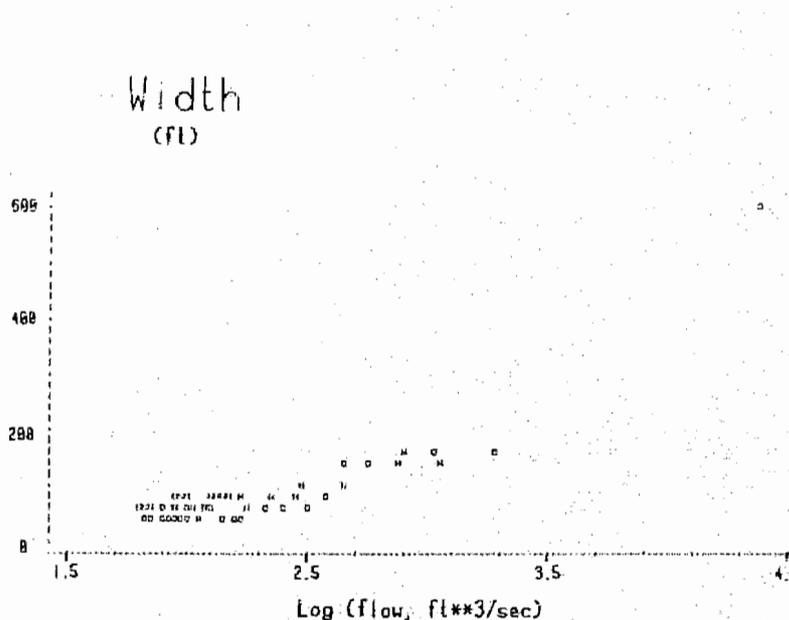
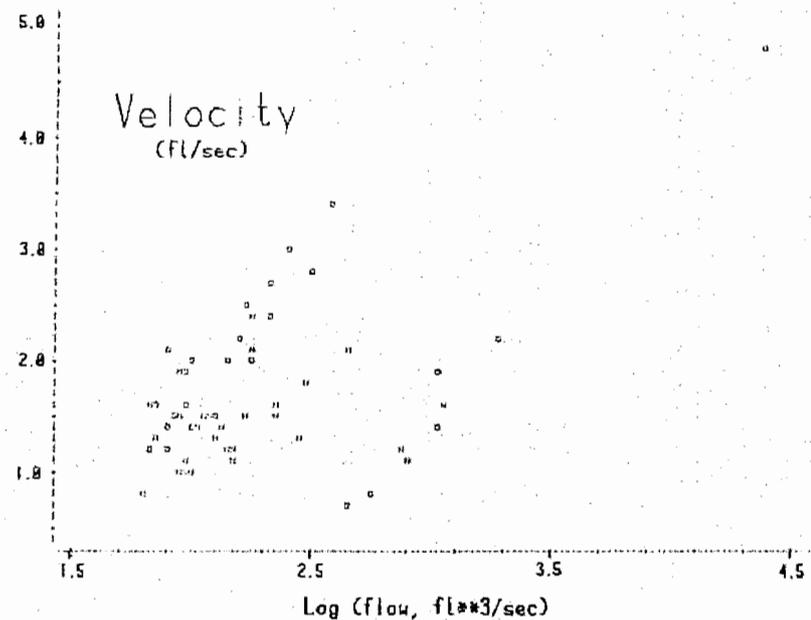
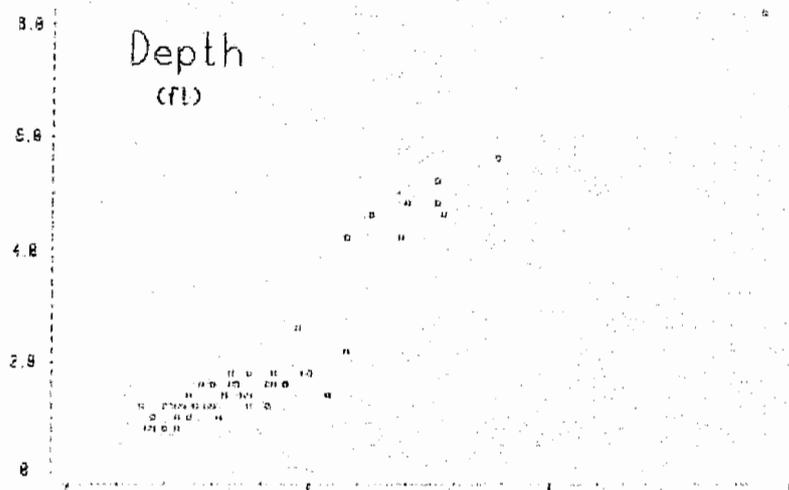
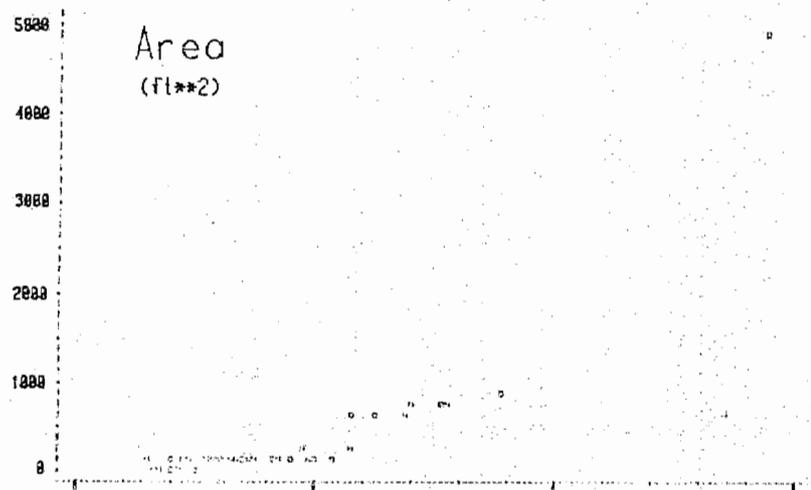


Figure 5. Width, depth, area and velocity of the Big River as measured by the USGS at Mammoth Bridge (near DeSoto) before (O) and after (N) January 1, 1978.

Parameter	Regression Coefficients			R ²	p
	Intercept	log ₁₀ Flow	(log ₁₀ Flow) ²		
Area	4024.16	-3780.64	898.41	.979	<0.01
Depth	-3.63	2.02	0.19	.886	<0.01
Width	403.29	-351.49	89.35	.951	<0.01
Velocity	3.05	-1.64	0.44	.351	<0.01

Although all the relationships are statistically significant ($p < 0.01$), the important one relative to sediment transport--between discharge and velocity--is noticeably worse than the others (Fig. 5), thus explaining to some extent the poor fit of the particle-size/flow relationships (Fig. 4).

Based on these results, it is not surprising that discharge alone does not describe sand, silt, or clay concentrations any better than the relationships depicted in Fig. 4. Suspended sediment transport is largely energy--and therefore, velocity--dependent, and knowledge of discharge alone will not enable accurate prediction of velocity (Fig. 5). It appears that in the lower reaches of the Big River, velocity at a given water level is somewhat more variable than the other determinants of discharge. Improvement over current abilities to predict suspended sediment discharge and, hence, total sediment yield and trace metal transport, will require that this variability be accounted for. The simplest approach would be to compute mean velocity for a given discharge level; width and depth respond very predictably, and a term related to this computed velocity (discharge/area) could be introduced into the equations describing the sediment concentrations. Another approach, which is considerably less empirical, would be to

examine some of the determinants of velocity--in particular, energy slope--in attempt to account for some of the observed variation in velocity. Impoundment of flood waters in the lower-gradient, downstream reaches of the Big and Meramec Rivers--which would lessen the energy slope--may explain the observed variability in velocity. This phenomenon could be quantified readily using stage records from the USGS gauge at Byrnesville for times corresponding to the collection of the 43 samples from Brown's Ford.

The foregoing discussion described the steps taken (or that need to be taken) to accurately estimate suspended sediment concentrations in the lower reaches of the Big River as part of an overall mass-balance approach to quantifying the dynamics of toxic trace metals. Better predictive capabilities for velocity--perhaps incorporating energy slope--will enable correspondingly better estimates of sand, silt, and clay-size particles in the suspended load and, ultimately, in the bed and total sediment loads.

Attempts at directly measuring bedload transport did not produce sufficient data for quantitation. In the three 1980-81 sampling periods, bedload collections with the Helley-Smith sampler showed measurable bed sediment movement at Brown's Ford only at high flow ($11,900 \text{ ft}^3/\text{sec}$), and no bedload samples were collected by the St. Louis District in 1978. Although the one bedload sample collected has not been quantitatively evaluated in terms of either particle-size distribution or metals content, visual examination revealed the presence of substantial amounts of gravel- to cobble-sized materials. Figure 6 is a frequency distribution of mean daily discharge recorded at the USGS gauge on the Big River at DeSoto from 1965 through 1980 (5,113 days).

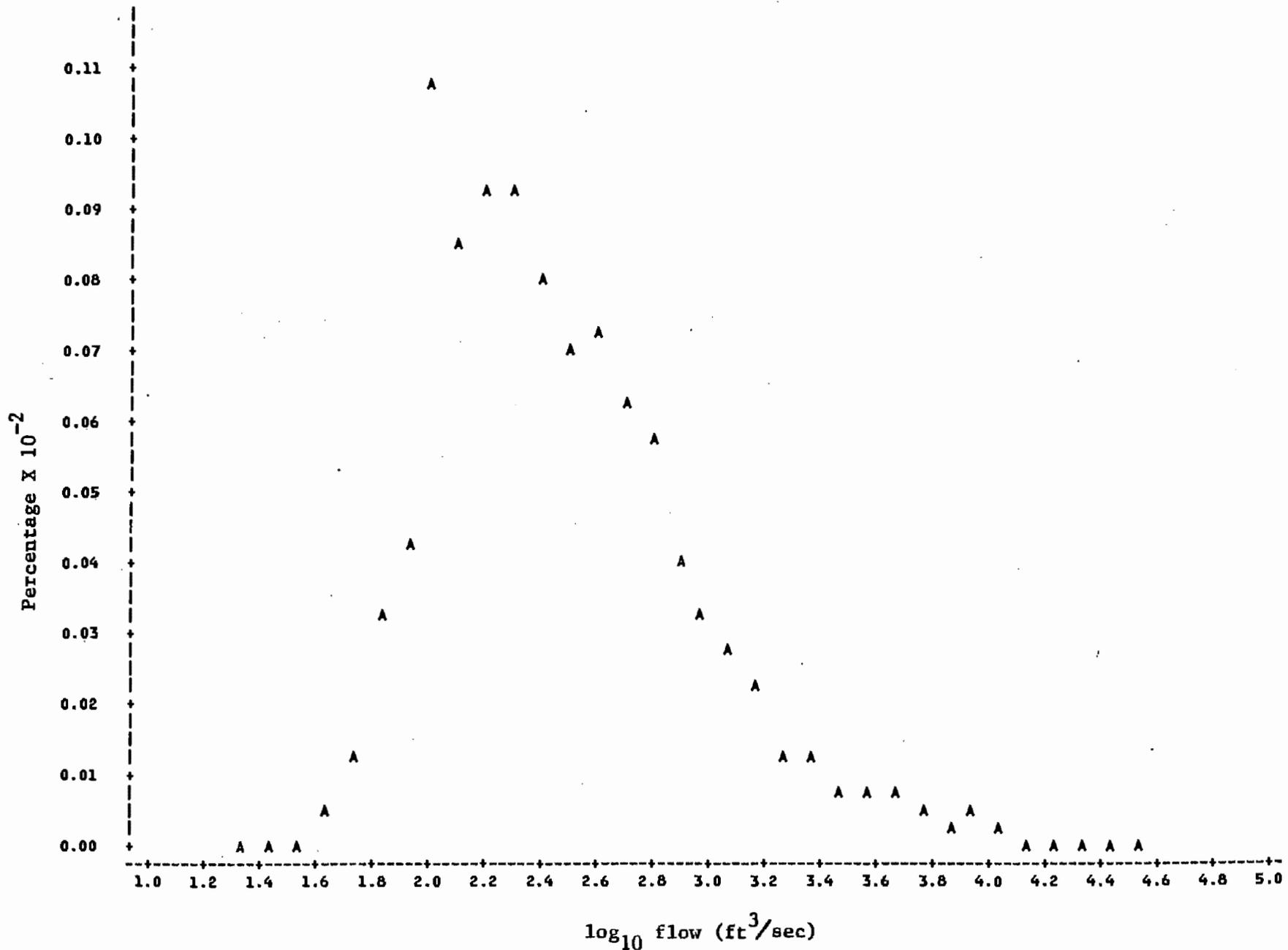


Figure 6. Frequency distribution of mean daily discharge of the Big River at DeSoto, 1965-1981.

As this figure illustrates, flow at DeSoto exceeds 10,000 ft³/sec infrequently. Further analysis of the data revealed that the daily means exceeded this level only about 0.5% of the time. However, 10,000 ft³/sec is nowhere near maximum flood conditions for the period of record. Mean daily discharge for the April 1978 flood exceeded 33,000 ft³/sec, and continuous records show that a peak flow of 34,200 ft³/sec was recorded during this flood (Appendix A). USGS (1981) reports that the flood of record at DeSoto was 55,800 ft³/sec (1580 m³/sec) and occurred on June 30, 1957; prior to the period of record, which began in October, 1948, the maximum flood (August, 1915) was estimated to have been 70,500 ft³/sec (2,000 m³/sec). From this information, it can be concluded that discharge levels capable of moving significant quantities of material in the lower reaches of the Big River as bedload occur infrequently, but that the quantity of material involved is probably significant. This material must be accounted for in evaluating total sediment transport.

The most accurate method for estimating total sediment transport (bedload + suspended load) in a river system is the "Modified Einstein Procedure" (Vanoni 1975). This procedure is accurate because it incorporates actual field measurements (suspended load and streambed textural composition, measured or computed velocities, etc.) and easily derived laboratory data (fall velocities and densities for several size classes of particles) to estimate transport in the unmeasured (bedload) portion of the stream channel. Other available techniques rely more on theory and less on actual data. Using this approach, it should be possible to estimate the total yield of sand, silt, and clay-sized particles based on refined estimates of suspended load concentrations

and velocity, as per earlier discussions. The already-defined relationships of particle concentrations with discharge and (eventually) mean velocity with discharge and energy slope can then be incorporated into the modified Einstein procedure, which will result in a relationship that estimates the total concentration in each size class as functions of discharge and energy slope. Mean annual total sediment yield for the lower portion of the Big River watershed can then be estimated by combining this total sediment concentration/flow relationship and the integrated form of the flow-frequency distribution (Fig. 6). If the flow-frequency distribution is not significantly different from normal, then the computational burden could be reduced greatly by using standardized areas of the normal distribution. However, analysis of the data represented in Fig. 6 by the Durbin-Watson test procedure (Sokal and Rohlf 1969) reveals that even after log-transformation the flow-frequency distribution for DeSoto is significantly different from normal ($D=0.35$; $p<0.01$). The simplest, most straight-forward approach, then, will be to integrate by dividing the curve up into segments and computing individual areas. This will be further simplified by the fact that the data used to generate Fig. 6 were originally reported by USGS in 22 classes (USGS 1981).

The final step in the mass-balance computations will be to relate annual yields of sediment to annual yields of metals--especially of Pb. As discussed earlier, this necessitates accounting for differing concentrations of the metals in the various particle-size fractions. However, a problem inherent in this type of investigation is that of accurately collecting sufficient quantities of suspended sediments to divide among several size fractions for trace metal analysis.

Alternatively, total metal concentrations and particle-size composition can be measured independently for each suspended sediment sample; the relationships between the grain-size distributions and metals concentrations can then be determined statistically. The more samples, the more particle size classes that trace metal concentrations can be estimated for. Ultimately, with many samples, this relationship could be smoothed into a continuous function of particle diameters. (In this study, the St. Louis District's 1978 data were quantified only in three size classes--sand, silt, and clay-sized particles.) Using the St. Louis District's data and the data from the 1980 and 1981 collections at Brown's Ford (43 observations) the following model was fit using multiple regression:

$$\log_{10} Y_i = b_1x_1 + b_2x_2 + b_3x_3 + \epsilon_i$$

where Y_i = total dry weight suspended metal concentration in $\mu\text{g/g}$ (suspended metal/measured or computed total suspended solids $\times 10^6$); x_1 , x_2 , and x_3 are the proportional representation (percentage/100) of sand, silt, and clay-sized particles, respectively; b_1 , b_2 , and b_3 are regression coefficients related to the metal concentrations in each fraction; and ϵ_i is random error. Results of these computations (Table 7) show that particle-size distribution accounts for >99% of the variability in the concentrations of suspended Pb, Zn, Fe, and Mn; >97% of the variability in suspended Cu; and >86% of the variability in suspended Cd. All models were highly significant ($p < 0.01$) as were all regression coefficients except that for Cd--sand, which was also significant but at a lower probability level ($p < 0.05$).

Several features of Table 7 are worth highlighting. First, suspended Pb concentrations in the three size fractions appear similar;

Table 7. Regression coefficients relating \log_{10} total dry-weight suspended metal concentrations ($\text{mg L}^{-1}/\text{total suspended solids} \times 10^6$) and proportional particle-size composition ($\%/100$) at Brown's Ford, 1978-1981 ($n=43$).^a

Metal	Coefficients			R^2	\bar{x}^b
	Sand	Silt	Clay		
Pb	3.346	3.348	3.258	.99	1,850.4
Cd	1.184	0.730	1.450	.86	9.5
Zn	2.982	3.017	2.970	.99	993.8
Fe	5.359	4.469	4.742	.99	34,434.0
Mn	3.326	3.429	3.164	.99	2,151.0
Cu	2.434	1.579	2.487	.97	95.8

^aAll models significant, $p < 0.01$; all coefficients significant ($0.01 < p \leq 0.05$ for Cd-sand, $p < 0.01$ for all others).

^bGeometric mean dry-weight concentration, $\mu\text{g/g}$.

and second, coefficients for Pb, Zn, and Mn appear highly correlated--although differences in the magnitude of the coefficients among size classes are small for all three of these metals, the small differences present are nearly identical for Pb, Zn, and Mn, and appear much more closely correlated than the coefficients for the other three metals. As the coefficients illustrate, concentrations of Pb, Zn, and Mn appear highest in the silt fraction; slightly lower in the sand fraction; and lowest in the clay fraction. Fe, Cu, and Cd concentrations were highest in the clay fractions; lowest Cu and Cd concentrations occurred in the silt fractions; and lowest Fe concentrations were in the sand fractions.

To briefly summarize the preceding discussion, the means are presently available to quantify the magnitude of sediment and sediment-borne metals transport in the Brown's Ford reach of the Big River. The conceptual framework and computational flow for this quantitation, although not yet completed, are outlined in Fig. 7. When completed, the analysis of sediment transport is certain to show the importance of major runoff events--flooding--in the transport of toxic metals in the solid phase.

The high concentrations of metals in the solid phase, as described, make it easy to overlook the relatively low concentrations present in the liquid phase. Yet, on a mass-balance basis liquid-phase transport may be as or more important than solid-phase transport simply because of the much greater volumes of water than of sediment passing through the river in any given time period. The approach to be taken in evaluating liquid-phase transport is essentially the same as that outlined for solid-phase transport, but is much simpler overall. The responses of

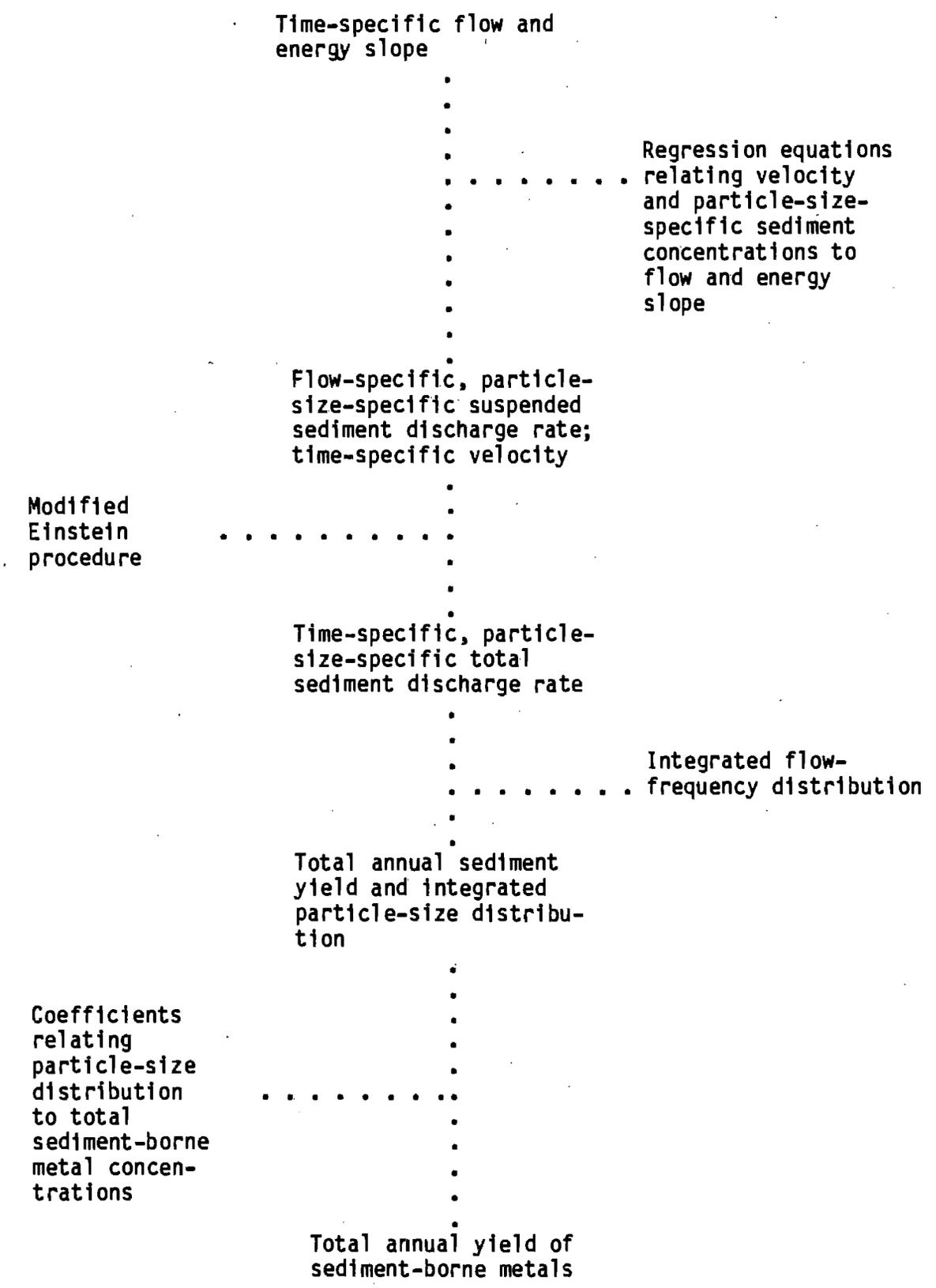


Figure 7. Narrative representation of computational procedures for estimating total annual yield of solid-phase metals.

the dissolved metals concentrations to changes in discharge need to be evaluated and quantified; then the flow-specific concentrations need only be weighed using the flow-frequency distribution (Fig. 6) to arrive at the flow-weighted annual mean yield of the metals in the liquid-phase. A much cruder approach is to use an unweighted average--say, 0.01 mg/L for Pb; 0.0005 mg/L for Cd; 0.025 mg/L for Zn; 0.075 mg/L for Fe; 0.03 mg/L for Mn; and 0.30 mg/L for Ba. The USGS reports the long-term average annual discharge for the Big River at DeSoto as 486,000 acre-ft/yr ($577 \text{ hm}^3/\text{yr}$). Multiplying the unweighted average concentrations by this figure and adjusting the units accordingly ($\text{MT} = \text{mg} \times 10^{-9}$; $\text{L} = \text{hm}^3 \times 10^{-8}$), a first approximation at annual liquid-phase export of metals from the Big River watershed is Pb, 0.57 MT; Cd, 0.03 MT; Zn, 1.44 MT; Mn, 1.73 MT; Fe, 4.33 MT; and Ba, 17.3 MT. Refined, flow-weighted estimates of these annual fluxes will have to be included along with the estimates of solid-phase transport in any consideration of water quality in the proposed Pine-Ford Lake. The fact that of the dissolved metals, only Ba concentrations exhibited any correlation with flow ($r=-0.32$, Table 5) may imply that an unweighted average, as used above, may be sufficiently accurate for all but Ba.

Metals in Sediments

The sequential sediment extraction procedure employed in this investigation was modified only slightly from the one developed and described by Tessier et al. (1979). As such, it is appropriate to begin this discussion with their original interpretations of the five fractions:

"Fraction 1. Exchangeable. Numerous studies ... on sediments or on their major constituents (clays, hydrated oxides of iron and manganese, humic acids) have demonstrated the adsorption of trace metals; changes in water ionic composition ... are likely to affect sorption - desorption processes."

"Fraction 2. Bound to Carbonates. ... significant trace metal concentrations can be associated with sediment carbonates; this fraction would be susceptible to changes of pH."

"Fraction 3. Bound to Iron and Manganese Oxides. It is well established ... that iron and manganese oxides exist as nodules, concretions, cement between particles, or simply as a coating on particles; these oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions (i.e., low Eh)."

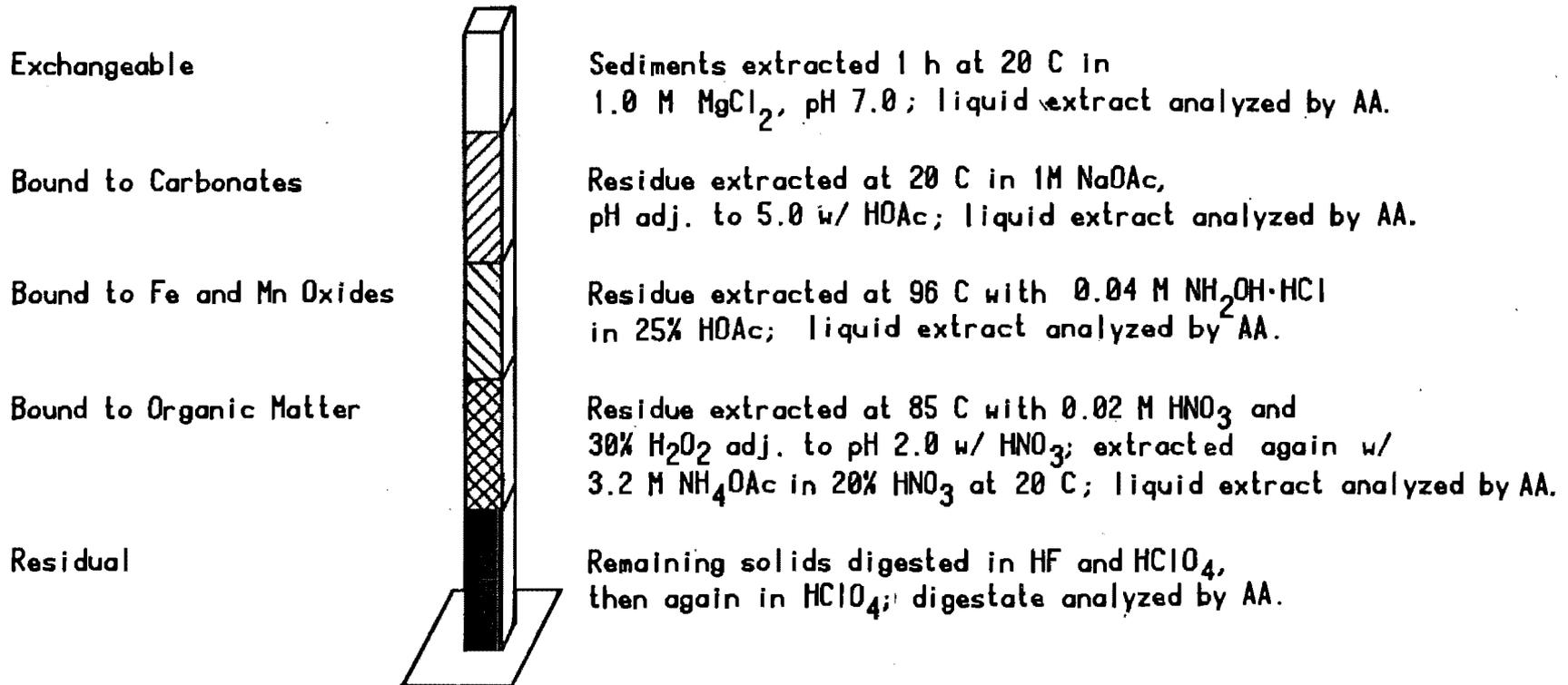
"Fraction 4. Bound to Organic Matter. Trace metals may be bound to various forms of organic matter: living organisms, detritus, coating on mineral particles, etc. The complexation and peptization properties of natural organic matter (notably humic and fulvic acids) are well recognized, as is the phenomenon of bioaccumulation in certain living organisms. Under oxidizing conditions in natural waters, organic matter can be degraded, leading to a release of soluble trace metals."

"Fraction 5. Residual. ... the residual solid should contain mainly primary and secondary minerals, which may hold trace metals within their crystal structure. These metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature."

The procedure is summarized in Figure 8.

Evaluation of the sequential extraction procedure. To assess the accuracy of the sequential extraction procedure, separate aliquots of each sediment sample was digested and analyzed for total metals using traditional acid digestion and atomic absorption procedures. These results are compared to corresponding sums of the sequentially-extracted fractions for Pb, Cd, Zn, Cu and Ba in Figure 9. As these plots illustrate, agreement between the two methods was excellent for Pb, good

Sequential Extraction of Sediments



After Tessier et al. (1979), Anal. Chem. 51:844-851

Figure 8. Summary of the sequential extraction procedure (modified from Tessier et al. 1979) and key to Figures 10-14.

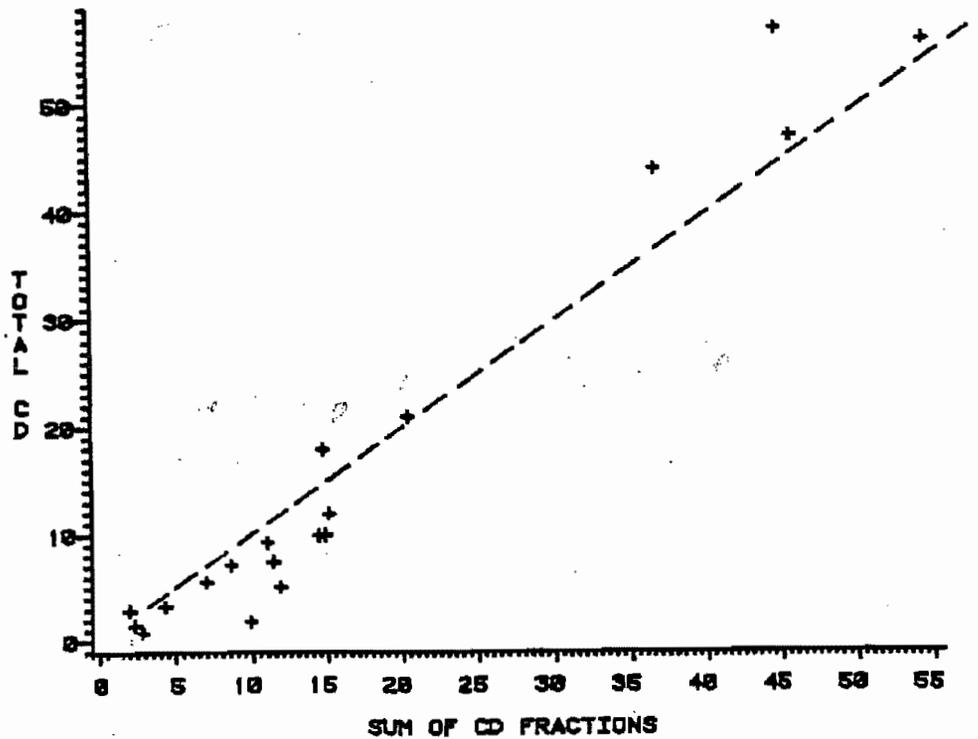
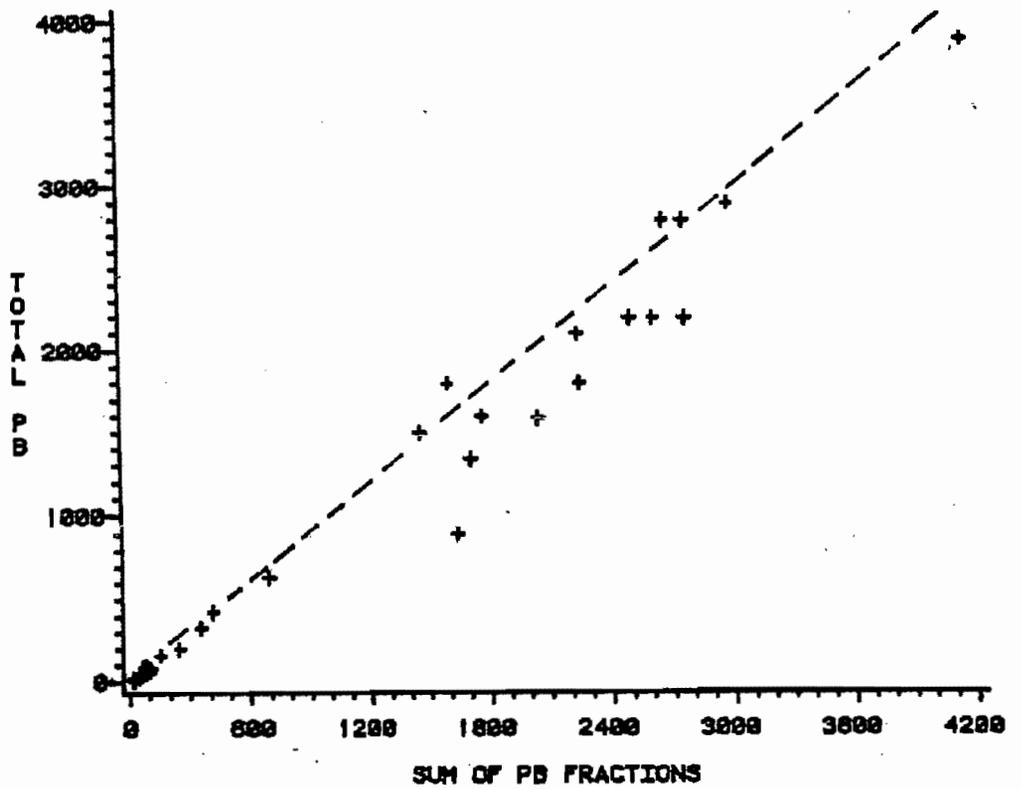


Figure 9. Total Pb, Cd, Zn, Cu, and Ba concentrations, $\mu\text{g/g}$ dry-weight. Y-axes as determined by conventional atomic adsorption spectrophotometry; X-axes, as the sum of sequentially-extracted fractions. Diagonal have slopes of 1.0.

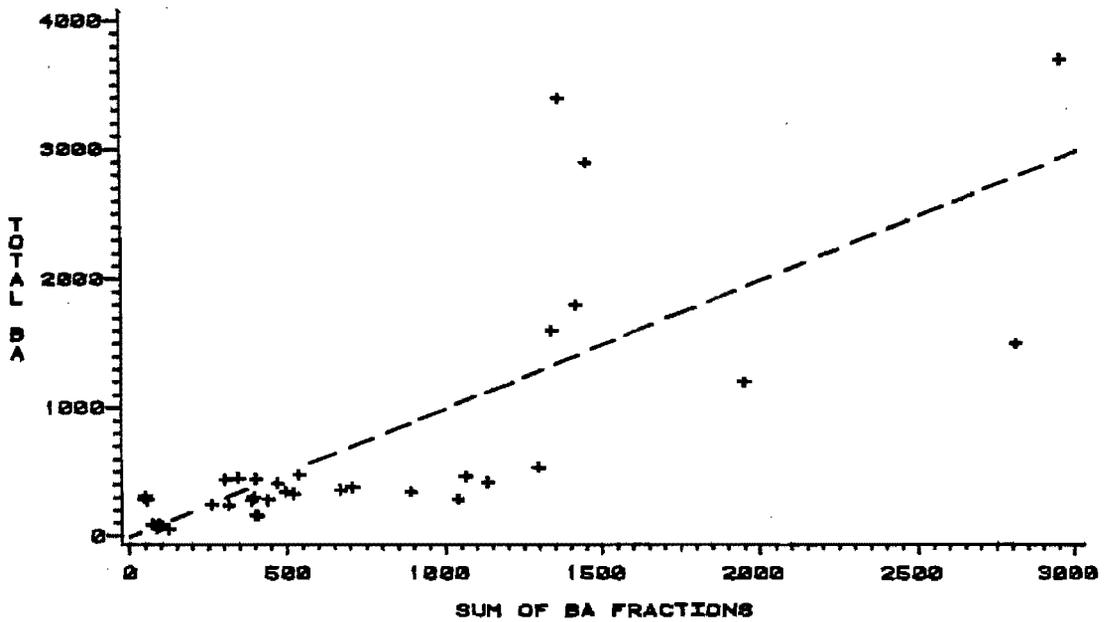
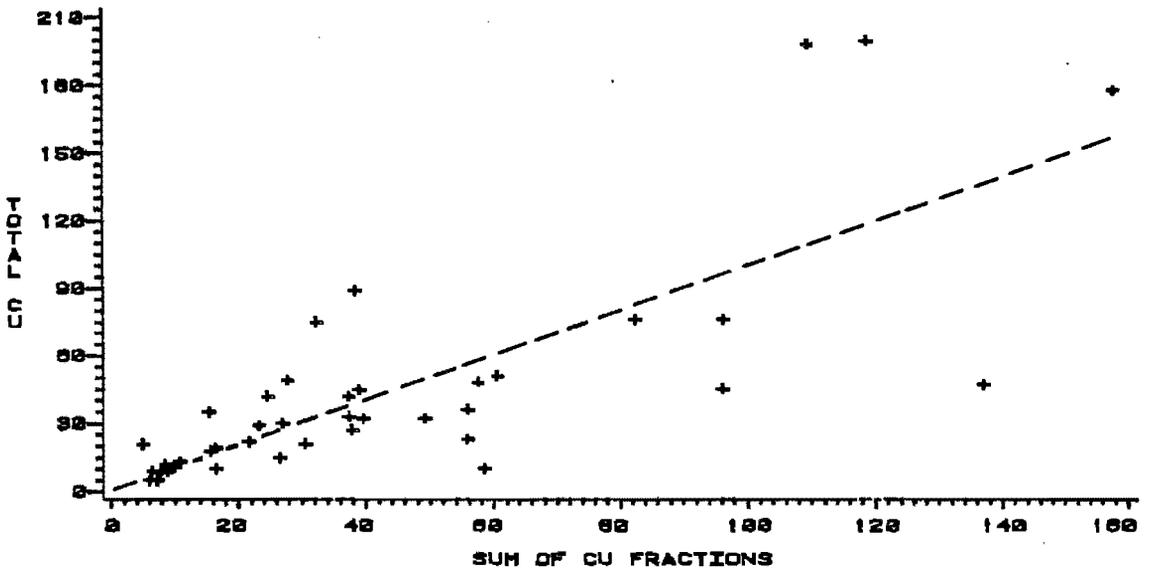
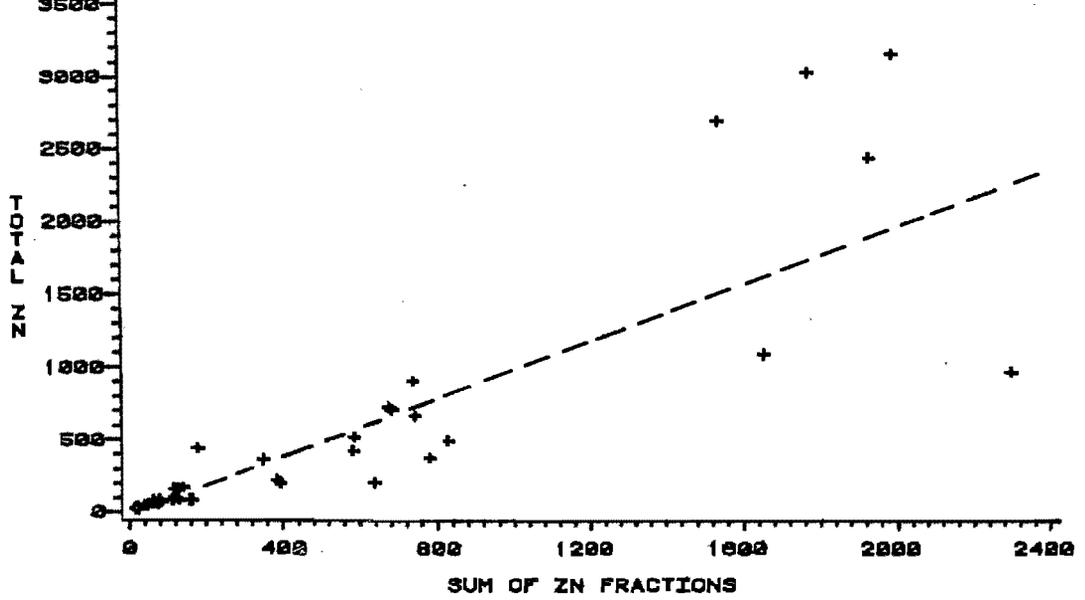


Figure 9 (cont'd)

for Cd, and "otherwise" for Cu, Zn and Ba. Statistically, these plots were evaluated using linear regression. The model

$$\log_{10} Y_i = a + b \log_{10} x + \epsilon_i$$

was fit, where Y_i = total metal concentration determined by conventional methods, a = intercept, b = regression coefficient (slope), x = the sum of the sequentially-extracted fractions, and ϵ_i = error. Perfect agreement between methods would yield linear relationships with $a = 0.0$, $b = 1.0$, and perfect correlation ($R^2 = 1.0$). As illustrated by Table 8, log transformation reduced the variability greatly for Pb, Cd and Zn, but not for Ba or Cu. For Zn, Ba and Cu, examination of the untransformed plots shows increasing variation with concentration, a trend which was probably not totally eliminated even after log transformation. From these results, it appears that the sequential extraction procedure is both accurate and precise for total Pb; is precise, but slightly underestimates total Cd; is fairly accurate for Zn but loses precision at higher concentrations; is marginally accurate and precise for Cu; and is of limited utility for assessing the availability of Ba. Based on these appraisals, the data for all metals studied are included in this report, but only results for Pb, Cd, and, to a limited extent, Zn are discussed in any details.

Adjusting for textural differences among sediment samples.

Although every effort was made to select "riffle" (scouring) and "pool" (depositional) areas at each site for sediment collections, cursory examination of the grain-size data (Appendix B) revealed that riffle-pool differences were not distinct at some sites, that the differences between riffles and pools were not consistent among the

Table 8. Intercept values (a), regression coefficients (b), and R^2 values determined for the relationship \log_{10} (total metal concentration) = a + b [\log_{10} (sum of sequential fractions)].

Metal	a	b	R^2
Pb	-0.22**	1.06**	.99
Cd	-0.42**	1.27**	.95
Zn	0.16	0.92**	.91
Cu	0.31*	0.79**	.65
Ba	0.57*	0.76**	.65

** $p < 0.01$

* $0.01 < p \leq 0.05$

sites, and that within sites there was some overlap--some "pool" samples had grain-size distributions more typical of "riffle" areas, and vice-versa. For example, at Brown's Ford, two of the three pool samples contained about 45% sand, 37% silt, and 18% clay; the third contained 72% sand, 23% silt, and 5% clay, and at Desloge, the pool samples were coarser in overall texture than were the riffle samples. Initial statistical analysis of the trace metal data for these samples suggested that observed differences between riffle and pool samples might be caused only by textural differences in the samples. The differences were substantial in some instances; at Brown's Ford, total Pb concentrations (on a dry weight basis) averaged 583 $\mu\text{g/g}$ for riffle samples and 2633 $\mu\text{g/g}$ for pool samples.

The easiest method of alleviating the grain-size problem is to use mean values for each site. However, averaging all samples from a site, although straightforward, would obfuscate any relationships related to particle size distribution, and hence, sediment transport, because all samples would be weighted equally. Instead, a more functional approach was taken. First, multiple regression was used to define the relationships between metals concentrations (total and for each sequential fraction) and particle size distribution for each site, as described previously for suspended metals. The model

$$\log_{10} Y_i = b_1x_1 + b_2x_2 + b_3x_3 + \epsilon_i$$

where Y_i = concentration of metal (total, or in a sequential fraction); x_1 , x_2 , and x_3 are the proportional representations of percent sand, percent silt, and percent clay, respectively; b_1 , b_2 , and b_3 are regression coefficients related to the relative metal concentrations in each size class; and ϵ_i is random error, was fitted to the data from

each site. The coefficients were then used to adjust the concentrations in each sample to the mean grain-size distribution for the site, using the formula generally applied to adjust treatment means in the analysis of covariance (Neter and Wasserman 1974);

$$Y_i^A = Y_i - b_1 (x_1 - \bar{x}_1) - b_2 (x_2 - \bar{x}_2) - b_3 (x_3 - \bar{x}_3)$$

where $Y_i^A = \log_{10}$ (adjusted concentration), $b_1 - b_3$ and $x_1 - x_3$ are as described above, and \bar{x}_1 , \bar{x}_2 , and \bar{x}_3 are the respective proportional representation of the mean sand, silt, and clay percentages for the site.

Results from the multiple regression portion of the above analyses are presented as tables of regression coefficients (Table 9a-f). All regressions were highly significant ($p < 0.01$), except where the concentration values for a fraction were all at detection levels. These fractions can be easily located in Tables 9a-f--they are the ones with identical coefficients for sand, silt, and clay fractions (see, for example, Table 9b: Cd at Irondale and in the Black River). R^2 values for most relationships exceed 0.95, indicating that grain-size composition alone accounted for most of the differences in metal concentrations among samples from a location.

The multiple-regression coefficients were used to adjust the concentrations of each fraction to the mean particle size content for the site from which the sample came (mean percentages for the sites are listed in Table 9f). The adjusted concentrations for each fraction were then averaged for each site and summed to arrive at the mean adjusted total metal concentration for each site. This new total was used as the basis for computing the average proportional contribution of the five sequential fractions. The adjusted totals and percentages thus computed

Table 9a. Multiple regression coefficients relating dry-weight concentrations of Pb (total and fractions) in the sediments to particle-size percentages. See text for explanation.

Big River

Phase	Brown's Ford			Desloge			Irondale		
	sand	silt	clay	sand	silt	clay	sand	silt	clay
Exchangeable	.60	2.74	.77	1.31	-8.80	10.86	.70	.70	.70
Carbonates	2.30	5.84	.26	2.76	10.31	4.66	.77	5.49	-19.83
Oxides	2.52	4.25	2.03	2.75	12.27	.77	1.22	-.79	23.38
Organics	1.66	3.28	.01	2.04	11.92	-9.33	.70	2.93	2.82
Residual	1.73	3.00	1.90	2.93	-1.25	-11.74	1.11	-3.67	22.89
Sum	2.80	5.28	1.63	3.33	7.99	1.52	1.62	.41	14.88
Total	2.69	5.02	2.22	3.28	7.94	3.25	1.47	1.24	13.02

Black River

Phase	Upstream Clearwater L.			Clearwater L.			Downstream Clearwater L.		
	sand	silt	clay	sand	silt	clay	sand	silt	clay
Exchangeable	.70	.70	.70	.70	.70	.70	.70	.70	.70
Carbonates	.70	.70	.70	1.28	1.68	.19	.70	.70	.70
Oxides	.76	-8.15	6.84	1.47	1.45	-5.90	1.63	1.61	3.50
Organics	.70	.70	.70	1.14	1.13	-3.87	1.39	32.79	-35.34
Residual	.71	3.04	-3.75	1.52	1.70	-32.44	1.66	30.79	-35.28
Sum	1.34	-.38	1.83	1.97	2.11	-9.16	2.07	12.27	-10.07
Total	.90	17.81	15.15	1.98	1.67	1.18	1.99	6.96	-5.32

Table 9b. Multiple regression coefficients relating dry-weight concentrations of Cd (total and fractions) in sediments to particle size percentages. See text for explanation.

Big River

Phase	Brown's Ford			Desloge			Irondale		
	sand	silt	clay	sand	silt	clay	sand	silt	clay
Exchangeable	.39	-.11	.43	.25	9.10	-1.47	.15	.15	.15
Carbonates	.42	2.09	-1.33	.87	3.28	-8.78	.15	.15	.15
Oxides	.20	1.17	.40	.48	5.21	5.19	.15	.15	.15
Organics	.19	-.19	1.58	.34	-.33	.19	.15	.15	.15
Residual	.07	-.20	1.99	1.61	7.16	-23.12	.01	.01	.01
Sum	.71	1.83	.16	1.70	6.22	-13.11	.42	.42	.42
Total	.66	1.29	1.15	1.73	10.74	-17.22	.04	.56	-1.07

Black River

Phase	Upstream Clearwater L.			Clearwater L.			Downstream Clear L.		
	sand	silt	clay	sand	silt	clay	sand	silt	clay
Exchangeable	.15	.15	.15	.15	.15	.15	.15	.15	.15
Carbonates	.15	.15	.15	.15	.15	.15	.15	.15	.15
Oxides	.15	.15	.15	.19	-.09	-1.16	.16	.67	.58
Organics	.15	.15	.15	.15	.15	.15	.15	.15	.15
Residual	.01	.01	.01	.02	.17	-1.64	.05	1.28	-1.96
Sum	.42	.42	.42	.44	.35	.84	.44	1.20	-.75
Total	.37	.37	.37	.22	1.86	-3.45	.13	.00	11.46

Table 9c. Multiple regression coefficients relating dry-weight concentrations of Zn (total and fractions) in sediments to particle-size percentages. See text for explanation.

Big River

Phase	Brown's Ford			Desloge			Irondale		
	sand	silt	clay	sand	silt	clay	sand	silt	clay
Exchangeable	.82	1.06	.64	1.24	7.23	-.53	.15	.15	.15
Carbonates	1.90	4.08	.79	2.30	17.47	-.21	.59	3.48	9.63
Oxides	2.09	3.30	1.30	2.29	11.93	1.53	.98	.81	16.98
Organics	1.31	1.69	2.20	1.60	7.76	-2.74	.37	1.81	1.79
Residual	2.08	3.17	.70	3.09	.02	.17	1.37	2.16	20.02
Sum	2.55	3.91	1.17	3.23	9.10	-1.39	1.57	2.37	18.83
Total	2.50	2.46	4.38	3.47	13.24	-17.24	1.71	4.70	-4.47

Black River

Phase	Upstream Clearwater L.			Clearwater L.			Downstream Clearwater L.		
	sand	silt	clay	sand	silt	clay	sand	silt	clay
Exchangeable	.15	.15	.15	.15	.15	.15	.15	.15	.15
Carbonates	.47	-7.03	11.59	.97	1.14	-.86	1.47	11.05	-14.35
Oxides	.68	-8.33	19.21	1.31	1.27	-4.72	1.60	2.39	-2.68
Organics	.24	-6.94	6.59	.86	1.03	3.19	.94	8.04	-8.60
Residual	1.14	-3.19	8.27	2.03	1.03	5.45	2.06	7.28	-9.43
Sum	1.31	-5.28	12.49	2.15	1.43	3.75	2.28	7.13	-8.03
Total	1.36	6.10	11.83	2.24	2.00	1.06	1.92	-4.69	8.32

Table 9d. Multiple regression coefficients relating dry-weight concentrations of Cu (total and fractions) in sediments to particle size percentages. See text for explanation.

Big River

Phase	Brown's Ford			Desloge			Irondale		
	sand	silt	clay	sand	silt	clay	sand	silt	clay
Exchangeable	.15	.15	.15	.15	6.91	-6.27	.15	.15	.15
Carbonates	.47	-.16	.02	.53	16.81	-17.56	.10	.54	4.92
Oxides	.50	-.32	1.23	.15	6.45	-5.52	.08	-1.60	16.79
Organics	.68	3.46	.65	1.10	7.82	4.17	.14	2.30	15.85
Residual	.71	6.01	-5.83	1.47	11.49	2.43	.89	3.69	5.09
Sum	1.13	4.57	-2.19	1.65	11.57	2.35	.96	3.49	8.71
Total	1.22	2.68	1.72	1.50	-2.96	13.96	1.24	7.56	-24.41

Black River

Phase	Upstream Clearwater L.			Clearwater L.			Downstream Clear Water L.		
	sand	silt	clay	sand	silt	clay	sand	silt	clay
Exchangeable	.15	.15	.15	.15	.15	.15	.15	.15	.15
Carbonates	.15	.15	.15	.15	.15	.15	.15	.15	.15
Oxides	.11	10.14	21.79	.38	-.02	-4.70	.28	-14.75	15.53
Organics	.26	-4.49	16.74	.88	.93	.31	.87	1.78	.56
Residual	.75	-7.21	8.15	1.51	1.58	-1.16	1.55	6.75	-9.40
Sum	.87	-2.40	15.41	1.61	1.65	-.86	1.63	4.50	-5.53
Total	.77	1.80	28.71	2.10	-.65	-15.28	1.67	-7.86	8.64

Table 9e. Multiple regression coefficients relating dry-weight concentrations of Ba (total and fractions) in the sediments to particle-size percentages. See test for explanation.

Big River

Phase	Brown's Ford			Desloge			Irondale		
	sand	silt	clay	sand	silt	clay	sand	silt	clay
Exchangeable	1.68	2.88	.79	.70	8.14	11.29	1.51	9.37	-24.29
Carbonates	1.64	2.45	1.19	.83	18.63	-1.49	1.47	7.93	-10.74
Oxides	1.80	2.74	.60	1.21	27.67	-15.56	1.62	-.28	22.10
Organics	1.48	1.30	1.63	.60	3.93	8.74	.72	9.76	-21.87
Residual	3.08	3.00	3.09	1.76	20.51	.31	2.35	2.93	3.76
Sum	3.15	3.18	3.11	1.93	20.61	-.10	2.52	4.39	1.77
Total	3.10	3.76	2.81	1.81	3.64	13.49	2.38	4.50	4.21

Black River

Phase	Upstream Clearwater L.			Clearwater L.			Downstream Clearwater L.		
	sand	silt	clay	sand	silt	clay	sand	silt	clay
Exchangeable	.72	-19.86	43.02	2.02	1.11	-7.62	1.90	3.76	-6.44
Carbonates	.53	-.84	22.38	1.62	1.61	3.00	2.30	4.54	-6.93
Oxides	.45	-20.79	19.56	.86	.62	-12.22	2.73	13.08	-15.81
Organics	.30	.30	.30	1.31	1.54	6.27	1.97	22.74	-24.68
Residual	1.97	2.50	-11.11	2.13	1.64	29.59	2.56	10.81	-11.25
Sum	2.02	.16	-4.77	2.46	1.98	17.54	3.11	11.77	-12.47
Total	1.78	6.92	15.56	2.65	2.56	3.61	2.61	5.56	-1.92

Table 9f. Multiple regression coefficients relating dry-weight concentrations of Mn and Fe (total and fractions) in the sediments to particle-size percentages, and values for mean percentages of sand, silt, and clay size particles at each site. See test for explanation.

Big River

Phase	Brown's Ford			Desloge			Irondale		
	sand	silt	clay	sand	silt	clay	sand	silt	clay
Exchangeable									
Carbonates	4.05	5.09	2.50	4.10	13.89	.96	4.09	5.91	3.97
Oxides	3.94	4.28	4.99	4.45	-3.02	10.91	4.04	7.87	-4.48
Organics									
Residual	1.78	3.12	.24	2.91	11.64	-3.50	1.87	4.76	-3.51
Sum	2.78	3.93	2.58	3.59	-4.35	11.42	2.93	5.42	7.55
Total	73.20	18.80	8.0	96.3	2.0	1.70	93.10	5.70	1.20

Black River

Phase	Upstream Clearwater L.			Clearwater L.			Downstream Clearwater L.		
	sand	silt	clay	sand	silt	clay	sand	silt	clay
Exchangeable									
Carbonates	3.64	-8.42	18.92	4.39	4.15	9.75	4.58	11.43	-10.22
Oxides	3.55	14.58	18.31	4.52	4.64	6.85	4.16	2.11	5.28
Organics									
Residual	1.42	-18.83	18.49	2.23	1.68	8.31	2.40	14.71	-16.36
Sum	1.94	15.60	36.10	3.30	3.69	-1.00	3.97	9.21	-4.89
Total	98.70	0.70	0.60	91.70	7.50	0.80	92.80	3.50	3.70

for each site are displayed graphically for Pb, Cd, Zn, Cu and Ba in Figs. 10-14, respectively. Concentrations and percentages for the tailings, Washington State Park, and Mineral Fork sites are simple arithmetic averages of the two samples collected from each site.

A summary of the computational procedure may make the sediment study seem less complex and easier to interpret. Figures 10-14 illustrate the total metal concentrations of the sediments from each location, adjusted to a common textural composition, and the relative concentrations of the five sequentially-extracted fractions in this adjusted total. The coefficients in Table 9a-f describe the distribution of the adjusted total and each sequentially extracted fraction to size classes within the sediment (for the 6 sites where there were sufficient data). When these coefficients are combined with the corresponding mean grain-size distributions (Table 9f) they describe the distribution of mass (rather than concentrations).

Lead, cadmium, and zinc in sediments. As expected, total sediment Pb concentrations were highest at Desloge (1776 $\mu\text{g/g}$) and in tailings material (1843 $\mu\text{g/g}$) and tended to decrease with distance downstream from the Desloge area (Fig. 10). The total Pb concentration at Irondale (49.6 $\mu\text{g/g}$) was the lowest found at the Big River sites. Concentrations in Mineral Fork, although lower by far than concentrations in the mainstem of the Big River anywhere below Desloge, were substantially higher than at Irondale (Fig. 10). This may be attributable to past Pb mining activities, to ongoing barite mining, or to both in the Mineral Fork watershed, as described previously in the discussion of suspended

Pb FORM DISTRIBUTION, BY LOCATION

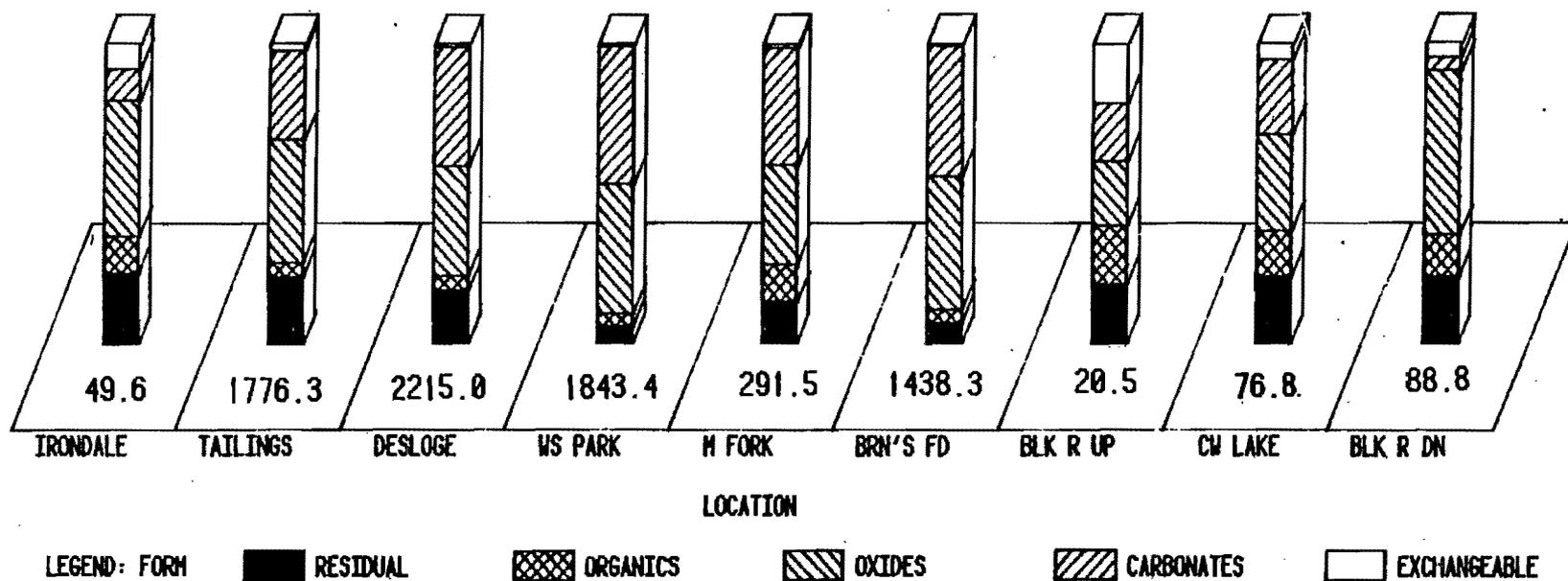


Figure 10. Adjusted total sediment Pb concentrations ($\mu\text{g/g}$, dry weight) and proportional representation of the five sequentially-extracted fractions. See Figure 8 and text for further explanation.

Cd FORM DISTRIBUTION, BY LOCATION

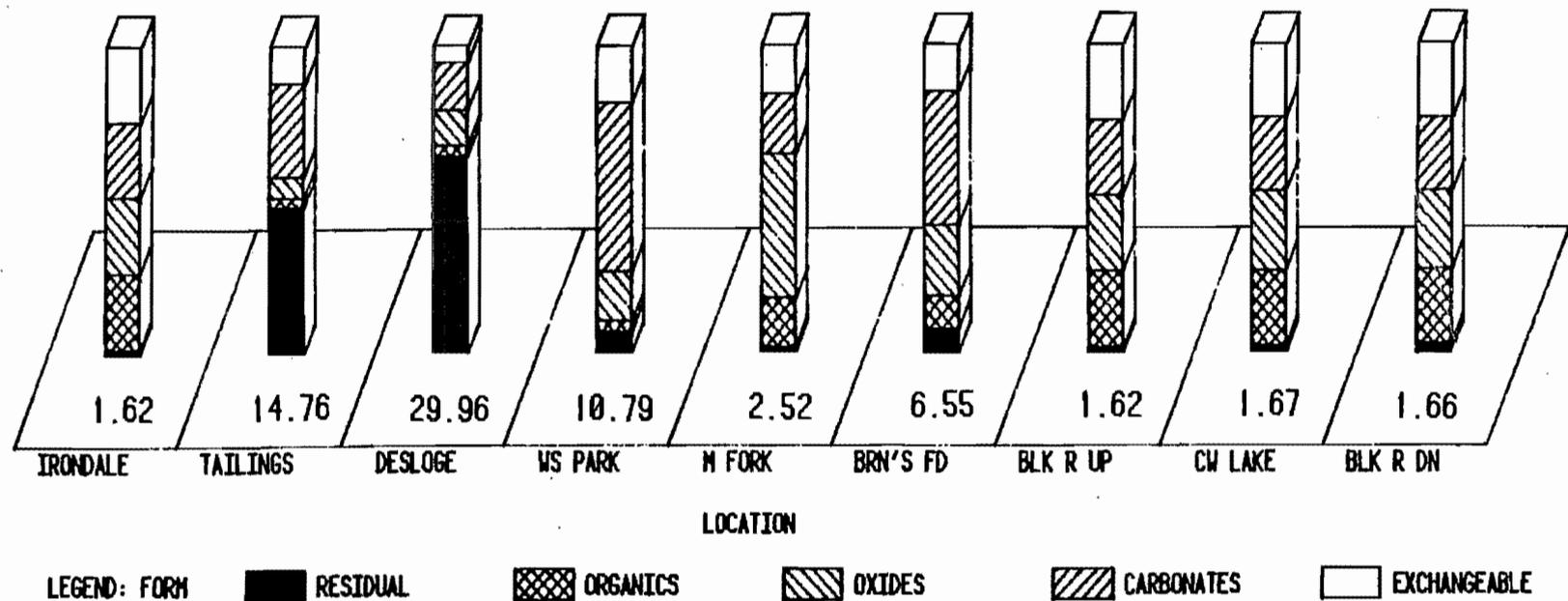


Figure 11. Adjusted total sediment Cd concentrations ($\mu\text{g/g}$, dry weight) and proportional representation of the five sequentially-extracted fractions. See Figure 8 and text for further explanation.

Zn FORM DISTRIBUTION, BY LOCATION

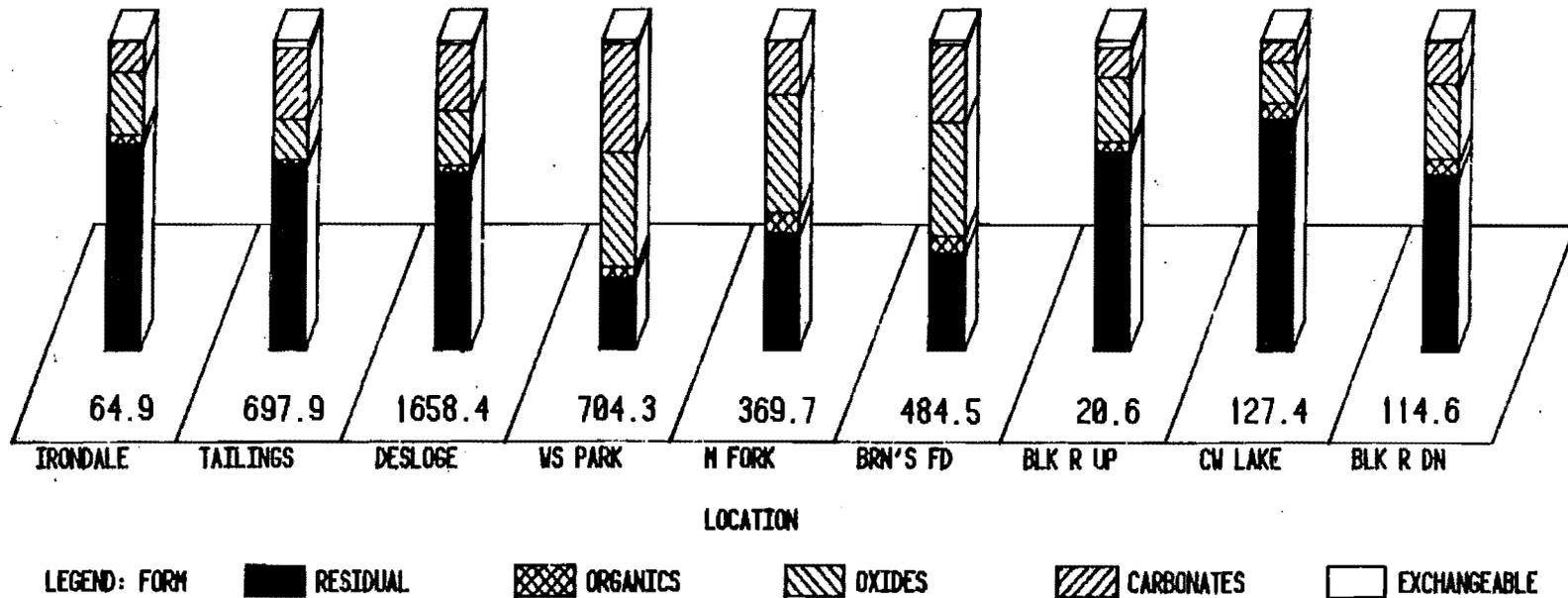


Figure 12. Adjusted total sediment Zn concentrations (µg/g, dry weight) and proportional representation of the five sequentially-extracted fractions. See Figure 8 and text for further explanation.

Ba FORM DISTRIBUTION, BY LOCATION

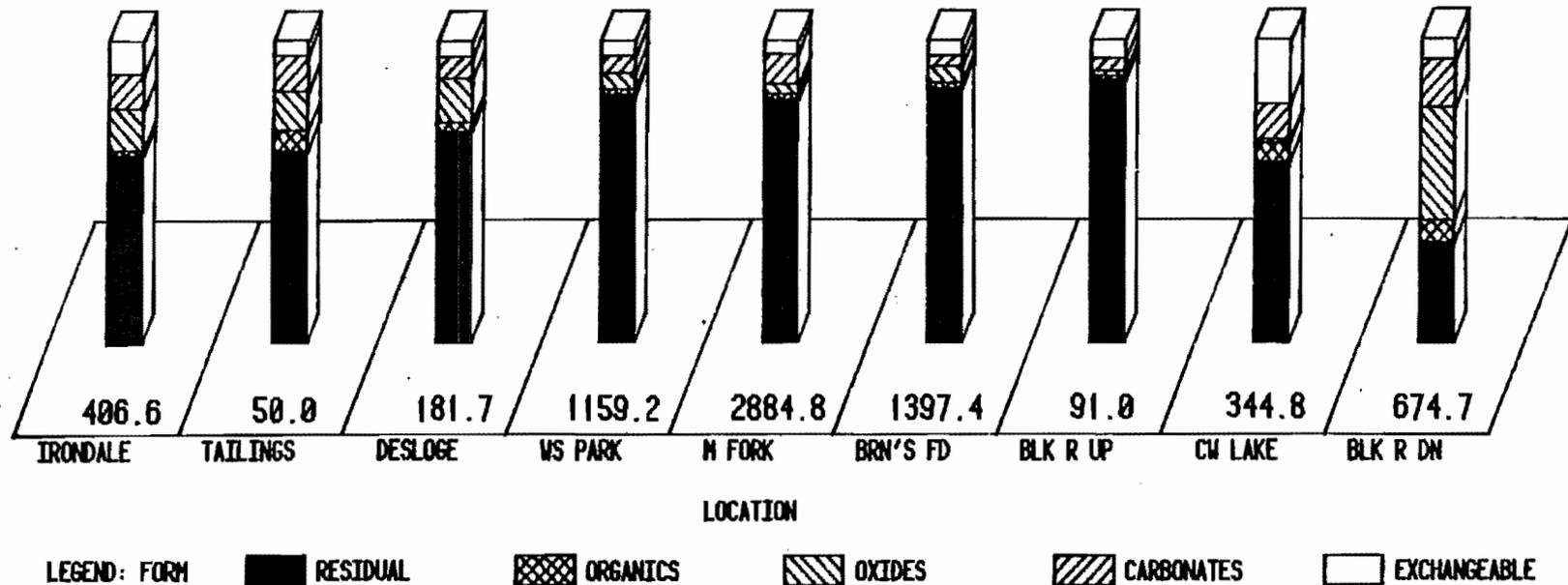


Figure 14. Adjusted total sediment Ba concentrations ($\mu\text{g/g}$, dry weight) and proportional representation of the five sequentially-extracted fractions. See Figure 8 and text for further explanation.

Cu FORM DISTRIBUTION, BY LOCATION

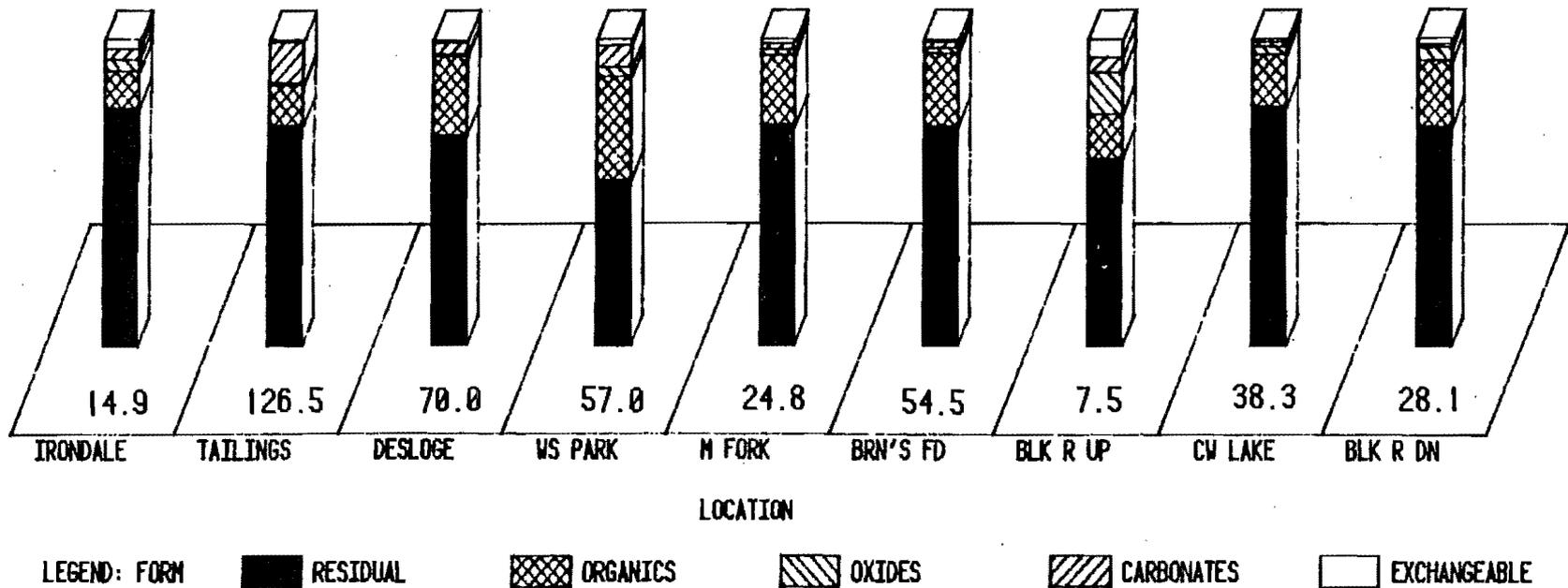


Figure 13. Adjusted total sediment Cu concentrations (µg/g, dry weight) and proportional representation of the five sequentially-extracted fractions. See Figure 8 and text for further explanation.

metals. Total Pb residues at the Black River/Clearwater Lake sites were far lower than in the Big River--21 $\mu\text{g/g}$ above Clearwater Lake, 77 $\mu\text{g/g}$ in the lake, and 89 $\mu\text{g/g}$ downstream.

The Big and Black Rivers are both hard, highly-buffered river systems; under such conditions, available sorption sites on sediment particles might be occupied by naturally-occurring Ca and Mg ions. Not surprisingly then, exchangeable Pb concentrations (as well as other exchangeable metals) were generally low. The exchangeable percentages appearing significant in Figs. 10-14 may therefore be artifacts of low total metal concentrations.

Carbonate-bound Pb was substantial at many sites, especially in the Big River. The proportional contribution of carbonate-bound Pb was greatest at the lower Big River stations (including Mineral Fork), slightly lower at Desloge and in tailings, and lower still in Clearwater Lake and in the Black River downstream of the lake (Fig. 10). At Desloge, Brown's Ford, and in Clearwater Lake, highest concentrations of carbonate-bound Pb were associated with particles in the silt-size fraction; at Irondale, with clay-sized particles; and at the two Black River sites, concentrations were too low for assignment to size fractions (Table 9a). Collectively, these results reflect the geochemistry of the region and the resulting importance of the carbonate-bicarbonate system in the Big River, where the watershed is mostly underlain by dolomitic limestone and the tailings themselves are actually ground dolomite. In the Black River watershed and in the headwaters of the Big River, other chemical systems may be more important in controlling Pb distribution.

The Fe and Mn oxide-bound fraction for sediment Pb was important at all sites. Proportionally, it was lowest in the Black River above

Clearwater Lake (22%) and highest downstream of the lake (55%) and at Irondale (45%) (Fig. 10). This fraction, together with the carbonate-bound fraction, accounted for about 88% of the total sediment Pb content at the two lower Big River sites (Washington State Park and Brown's Ford), 77% at Desloge, and 71% in the tailings. Concentrations of Fe and Mn oxide-bound Pb were highest in the silt fraction at Desloge and Brown's Ford and in the clay fraction at Irondale and both upstream and downstream of Clearwater Lake (Table 10). Within the lake, oxide-bound Pb was lowest for clay-sized particles and about equal for sand and silt-sized particles.

Compared to the carbonate and oxide-bound fractions, organically-bound Pb represented a relatively low percentage of the total sediment Pb concentration at all sites, ranging from a low of about 4.4-5.0% at Brown's Ford, Washington State Park, Desloge, and in tailings, to a high of 12-15% at the other sites. The highest percentages occurred within and above Clearwater Lake (Fig. 10). Generally, Pb associated with organic material represented <5% of the total in tailings and at sites that have experienced direct contamination by tailings, whereas at uncontaminated sites, it exceeded 12%. Organically-bound Pb concentrations were highest in silt-sized particles at all sites (Table 9a).

Residual Pb represented 22-24% of the total sediment Pb concentration at Irondale and at Mineral Fork in the Big River watershed, and at all three Black River/Clearwater Lake sites (Fig. 10). The percentage of total Pb comprised by the residual fraction was lower at the remaining Big River sites--18-20% in tailings at Desloge, and 5-7% at Washington State Park and Brown's Ford (Fig. 10). In addition

Table 10. Concentrations of the five sequentially-extracted fractions and total Pb in sediments from Brown's Ford and Washington State Park as proportions of the concentrations at Desloge.

Site	Fraction					Total
	Exchangeable	Carbonate	Oxides	Organics	Residual	
Desloge	1.00	1.00	1.00	1.00	1.00	1.00
Washington State Park	.43	.97	.98	.74	.25	.75
Brown's Ford	.53	.71	.79	.61	.24	.60

to the apparent decrease in the proportional contribution of residual Pb to the total, the residual concentrations also declined, from 391-397 $\mu\text{g/g}$ dry weight in tailings and at Desloge to 95-99 $\mu\text{g/g}$ at the two downstream sites. Residual Pb concentrations were highest in the silt fraction at Brown's Ford and within and downstream of Clearwater Lake; at Irondale, residual Pb concentrations were highest in the clay fraction; and at Desloge they were highest in the sand fraction, the fraction which also comprised 96% of the sediment (Table 9a).

If, as Tessier et al. (1979) contend, the residual fraction is truly refractory within time spans relevant to this study, then the changes in the residual Pb concentration between Desloge, Washington State Park, and Brown's Ford represent the effects of dilution by sediments with lower residual Pb content and the possible washout of smaller particles high in residual Pb. The ratios of residual Pb concentrations at Washington State Park and Brown's Ford to the concentration at Desloge were 0.25 and 0.24, respectively (Table 10). These values, which should be based only on transport-related phenomena, can be compared to ratios for the other fractions as an indication of the degree of interchange among the fractions that has taken place during transport. As the ratios for the other fractions and for total Pb illustrate, residual Pb changed far more than any other fraction or total Pb (Table 10). This anomaly can be illustrated further by the following: at Mineral Fork, for example, the residual Pb concentration was 40 $\mu\text{g/g}$; in tailings, it was 397 $\mu\text{g/g}$. If 40 $\mu\text{g/g}$ is representative of the "background" residual Pb content in downstream areas, then the ≈ 400 $\mu\text{g/g}$ concentration at Desloge would have to be diluted by about 7.5 times with material containing only 40 $\mu\text{g/g}$ to end up with ≈ 100 $\mu\text{g/g}$ at

Washington State Park and Brown's Ford. For carbonate- and oxide-bound Pb, which together represented about 200 $\mu\text{g/g}$ at Mineral Fork, the tailings ($\approx 1500 \mu\text{g/g}$) would only have to be diluted by a factor of about 1.5.

There are two immediately plausible explanations for the apparent contradiction represented by the fact that the residual Pb concentrations declined some 2 to 3 times more between Desloge and Brown's Ford than did the other fractions (Table 10). The first (and simplest) is that perhaps the residual fraction is not as refractory as envisioned by Tessier et al. (1979). However, this seems unlikely; compared to most naturally-occurring processes, even the sequential extraction steps that occur before final digestion of the residual fraction are severe. If anything, the residual fraction as measured by this procedure may be conservative; even Tessier et al. (1979) cautioned that the hydrogen peroxide oxidation at pH 2.0 may attack some sulfide minerals in the residual fraction. Yet, even if the organic and residual fractions are combined, the data in Table 10 show that the ratios for the carbonate- and oxide-bound concentrations would still differ from those of the more tightly-bound fractions, implying that a mechanism other than simple dilution is at work.

A more likely explanation is that substantial quantities of suspended and dissolved material derived from the Potosi and Eminence dolomites enter the river upstream of Washington State Park and from Mineral Fork, aided by the barite and gravel mining operations in those portions of the watershed. Relative to the Desloge tailings, the material derived from this region is low in residual Pb; it consists of dolomitic limestone with a fairly high percentage of Fe and Mn oxides.

These materials are known to be effective in scavenging trace metals from the liquid phase (e.g., Tessier et al. 1979; Jenne 1968). A plausible explanation of the differences between the fractions is that suspended material which is relatively low in Pb content enters the river downstream of Desloge, causing an initial dilution of the solid-phase Pb concentration. This material, together with tailings, become the "active" sediments--suspended, bedload, and bed sediments. Carbonates and hydrous oxides of Fe and Mn in these active sediments then sequester and concentrate Pb from the liquid phase, which tends to diminish the effect of the initial dilution of the tailings material. Some Pb from the liquid phase probably also precipitates as $PbCO_3$, which is insoluble and would be accounted for in the carbonate-bound fraction. Additional liquid-phase Pb is probably sequestered by organic material in the sediments, although the sequential extraction results suggest that the organic-bound fraction represents a much lower proportion of the sediment Pb reservoir than do the carbonate- and oxide-bound fractions. Even more important, however, is that the associations of metals with carbonates and with Fe and Mn hydrous oxides are by no means permanent; these fractions, as well as some of the organically-bound fraction, constitute "important sources of potentially available trace metals" (Tessier et al. 1979, citing Jenne and Luoma 1977).

The most prominent feature of the results for sediment Cd was the low concentrations. Total Cd levels were less than $1.0 \mu\text{g/g}$ dry weight at Irondale and at all three sites in the Black River. Adjusted total Cd levels were highest at Desloge ($30 \mu\text{g/g}$) and in tailings ($15 \mu\text{g/g}$), and decreased with distance downstream to $11 \mu\text{g/g}$ at Washington State Park and $6.5 \mu\text{g/g}$ at Brown's Ford. As reported for Pb, Cd

concentrations in Mineral Fork sediments ($2.5 \mu\text{g/g}$) were higher than concentrations at Irondale and in the Black River watershed (Appendix B).

Results of the sequential extraction procedure for Cd are presented in Fig. 11. An immediately noticeable feature of this graph is that the adjusted totals displayed beneath each bar for Irondale and for the three sites in the Black River watershed are higher than the concentrations listed in the preceding paragraph. This is an artifact of summing values for several fractions that were reported as equal to the lower limit of detectability ($0.02 \mu\text{g/g}$), but which were actually lower. The values for total Cd measured by conventional methods, listed above and in Appendix B, are better estimates of the total Cd concentrations at these sites than are the sums of the sequential fractions presented in Fig. 11.

At the Big River sites where Cd concentrations were measurable, several features of the sequential extraction results were similar to the results for Pb; however, there were also some noteworthy differences. As reported for Pb, sediment Cd concentrations at Desloge were higher than concentrations in the sample taken from the tailings pile (Fig. 11). This two-fold difference most likely resulted from the fact that Desloge samples were collected from a site immediately downstream of the confluence of Flat River Creek with the Big River (Fig. 1). Flat River Creek is known to be a source of tailings to the Big River; sediments in its lower reaches contained up to $35 \mu\text{g/g}$ in 1975 (Kramer 1976).

One difference between the results for Pb and Cd was the proportionally greater contribution of exchangeable Cd than of Pb in the

sediments at all sites affected by tailings (Fig. 11). Exchangeable Cd concentrations, where measurable, were fairly uniform, ranging from 0.9 $\mu\text{g/g}$ (15%) at Brown's Ford to 2.0 $\mu\text{g/g}$ (18.5%) at Washington State Park (Fig. 11). Concentrations were highest in silt-sized particles at Desloge; at Brown's Ford, they were highest in the clay fraction (Table 9b).

The higher exchangeable percentages for Cd than for Pb may be attributable to many factors, but the highly buffered, carbonate-bicarbonate dominated chemical system in the Big River and the sorption differential between Pb and Cd may be the most important. In the exchangeable section of the sequential extraction procedure, it was impossible to keep the pH neutral; the high carbonate-bicarbonate levels in the sediment-water mixtures tended to shift the pH toward 8.2 immediately after adjustment. When this occurred, some metals were probably re-adsorbed onto the surfaces of the solid material. Since Pb is much more rapidly and strongly adsorbed by inorganic ligands than is Cd (Vuceta and Morgan 1978), it is likely that some "exchangeable" Pb was actually adsorbed onto carbonate-rich sediment particles and extracted in Fraction 2. Tessier et al. (1979) raised this very question with regard to their own results for exchangeable vs. carbonate-bound metals, suggesting that the pH needed to be lowered to 5.0 in the procedure before some metals specifically adsorbed to carbonate (e.g., dolomite) particles would be released. In light of this discussion, then, the "exchangeable" concentrations and percentages for Cd probably reflect more accurately the amount of sorbed metal than do the values for Pb at those sites where the exchangeable Cd concentrations were high enough to measure.

Results for residual Cd also differed from those obtained for Pb; proportionally, the residual fraction was much more important for Cd in tailings and at Desloge (Fig. 11). Residual Cd concentrations averaged $19 \mu\text{g/g}$ (63%) in Desloge sediments, and $7.0 \mu\text{g/g}$ (47%) in tailings, but fell to $0.7 \mu\text{g/g}$ (6%) at Washington State Park and $0.5 \mu\text{g/g}$ (7%) at Brown's Ford (Fig. 11). Of the $15 \mu\text{g/g}$ difference in total Cd concentration between the tailings sample and the Desloge sediment sample, 80% ($12 \mu\text{g/g}$) of the difference was accounted for in the residual fraction. Residual Cd concentrations averaged only $0.04 \mu\text{g/g}$ (1.6%) in Mineral Fork (Fig. 11). Residual Cd concentrations were highest in the silt fraction at Desloge and in the clay fraction at Brown's Ford (Table 9b).

Results for the carbonate- and oxide-bound Cd fractions were more like the results obtained for Pb. Carbonate-bound Cd concentrations were $4.6\text{--}4.7 \mu\text{g/g}$ at Desloge and in the tailings sample, representing 16% and 31%, respectively, of the total Cd. At Washington State Park, the carbonate-bound Cd concentration was higher-- $6 \mu\text{g/g}$ (55%); at Brown's Ford, $2.9 \mu\text{g/g}$ (44%); and in Mineral Fork, $0.5 \mu\text{g/g}$ (20%) (Fig. 11). Carbonate-bound Cd concentrations were highest in the silt fraction at both Desloge and Brown's Ford (Table 9b).

Oxide-bound Cd concentrations were highest at Desloge ($3.5 \mu\text{g/g}$), but only represented 12% of the total; likewise, the $1.0 \mu\text{g/g}$ oxide-bound Cd in the tailings sample represented only 7% (Fig. 11). As reported for Pb, the relative importance of the oxide-bound fraction was greater downstream; at Washington State Park, oxide-bound Cd accounted for 16% of the total ($1.7 \mu\text{g/g}$), and at Brown's Ford, 23% ($1.5 \mu\text{g/g}$) (Fig. 11). Together, the carbonate- and oxide-bound fractions

represented 27% of the total Cd at Desloge; 38% in tailings; 71.3% at Washington State Park; and 67% at Brown's Ford. In Mineral Fork, carbonate- and oxide-bound Cd concentrations were $0.5 \mu\text{g/g}$ and $1.2 \mu\text{g/g}$, respectively, and together accounted for 67% of the total. Highest carbonate-bound Cd concentrations occurred in the silt fraction at both Desloge and Brown's Ford. Oxide-bound Cd levels were also highest in the silt fraction at both sites, but at Desloge they were nearly as high in the clay fraction; carbonate-bound Cd concentrations were lowest for clay-sized particles at Desloge (Table 9b).

Organically-bound Cd concentrations were low at all Big River sites, reaching a high of only $1.1 \mu\text{g/g}$ at Desloge. At Washington State Park and in Mineral Fork, the organic-Cd concentration was $<0.4 \mu\text{g/g}$, and at Brown's Ford, $0.7 \mu\text{g/g}$. Proportionally, organic Cd represented $<4\%$ of the total at Desloge, in the tailings sample, and at Washington State Park, and 11% at Brown's Ford (Fig. 11). Organic Cd concentrations were highest for clay-size particles at Brown's Ford and for sand-size particles at Desloge (Table 9b).

Although most Cd concentrations in samples from the Black River watershed were very low, some trends emerged that are worth noting. Total Cd concentrations averaged higher within ($0.62 \mu\text{g/g}$) and downstream ($0.37 \mu\text{g/g}$) than above ($0.09 \mu\text{g/g}$) Clearwater Lake. Total Cd concentrations were highest for silt-size particles within the lake, but were highest by far in the clay fraction downstream of the lake (Table 9b). It was the residual and oxide-bound fractions that contained the measurable concentrations both within and downstream of the lake (no fractions in the samples from upstream of Clearwater Lake contained enough Cd to warrant discussion). Based on these features of

the data, then, it appears that the mechanism of solubilization and re-precipitation with Fe and Mn hydrous oxides postulated as an explanation for the apparent increase in Pb concentration within and below Clearwater Lake may also describe the behavior of Cd in the Black River watershed.

Although the effects of differing particle size distributions between the samples from within the lake and downstream cannot be discounted, the concentration coefficients for total Cd (Table 9b) show that there is a marked difference in the particle-size association of the Cd between these two sites. Within the lake, the silt fraction accounted for nearly all of the Cd, with the lowest concentration in the clay fraction; below the lake, virtually all of the Cd was in the clay fraction (Table 9b). These results support the hypothesis of solubilization and subsequent reprecipitation, either directly as CdCO_3 or as Cd^{+2} sorbed onto hydrous oxides of Mn and Fe. Concentrations in the downstream sediments were too low to differentiate conclusively between carbonate- and oxide-bound fractions.

Total Zn concentrations in Big River sediments ranged from a low of 64.9 $\mu\text{g/g}$ at Irondale, rose to a high of 1658 $\mu\text{g/g}$ at Desloge, then declined with distance downstream to 704 $\mu\text{g/g}$ at Washington State Park and 485 $\mu\text{g/g}$ at Brown's Ford (Fig. 12). Total Zn levels in Mineral Fork sediments were surprisingly high--370 $\mu\text{g/g}$. In the Black River watershed, total Zn ranged from 21 $\mu\text{g/g}$ upstream of Clearwater Lake to 127 $\mu\text{g/g}$ within the lake and 115 $\mu\text{g/g}$ downstream (Fig. 12).

Examining the particle size coefficients for total Zn reveals that concentrations were highest in the silt fraction at Irondale and Desloge, and in the clay fraction at Brown's Ford and in the Black River

both upstream and downstream of Clearwater Lake (Table 9c). Within the lake, total Zn concentrations were lowest for clay-size particles and about equal for the silt and sand fractions. Total Zn concentrations were lowest in the clay fraction within the lake and highest downstream, as was described for Cd. Further examination of the particle-size coefficients reveals disagreement between the computed Zn distributions using the sum of the sequential fractions and the distribution using the conventionally-determined values for total Zn (Table 9c). For this reason, and because of the apparent imprecision at high concentrations of the sequential extraction technique (discussed earlier; Fig. 12), further interpretation of the coefficients for individual Zn fractions (Table 9c) should be done cautiously.

At the Big River sites upstream of Washington State Park (Desloge and Irondale), in the tailings sample, and at the three sites in the Black River watershed, at least 56% of the Zn in the sediments was in the residual fraction, and there was almost no exchangeable Zn (Fig. 9c). At Washington State Park, Brown's Ford, and in the Mineral Fork, carbonate- and oxide-bound Zn predominated (Fig. 9c). Organic Zn was relatively unimportant, accounting for 6.5% of the total at Mineral Fork, 5.7% at Brown's Ford, 5.4% in Clearwater Lake, 5.1% below Clearwater Lake, and <4% at the rest of the sites (Fig. 12).

When Cd and Zn concentrations in the lower Big River were examined relative to concentrations at Desloge, as was done previously for Pb (Table 11), a similar, but nonetheless different, pattern emerged. The results resembled those for Pb in that for both Cd and Zn, the residual fraction decreased the most, and the carbonate and oxide-bound fractions showed the least change (carbonate-bound and exchangeable Cd

Table 11. Concentrations of the five sequentially-extracted Cd and Zn fractions in sediments from Brown's Ford and Washington State Park as proportions of the concentrations at Desloge.

Metal Site	Fraction					Residual and Organic	Total
	Exchangeable	Carbonate	Oxides	Organic	Residual		
Cd							
Desloge	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Washington State Park	1.35	1.27	.49	.36	.04	.05	.34
Brown's Ford	.69	.61	.43	.62	.03	.06	.22
Zn							
Desloge	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Washington State Park	.42	.69	.89	.52	.17	.19	.37
Brown's Ford	.30	.34	.60	.63	.16	.18	.26

concentrations were actually higher at Washington State Park than at Desloge) (Table 11). The biggest difference among the three metals was in the magnitude of the decline in the residual fraction. Residual Pb at Brown's Ford was 24% of the concentration at Desloge (Table 10); for Zn, it was 18%; and for Cd, only 6% (Table 11). Repeating the "dilution exercise" performed earlier for Pb, using residual Cd and Zn concentrations in Mineral Fork as representative of the downstream "background" levels, residual Zn would have to be diluted by a factor of about 5.7 and residual Cd by 617 (for Pb, the residual dilution factor was about 7.5) to account for these changes by dilution alone. Furthermore, these results are not changed appreciably if organic and residual fractions are combined, indicating that the differences among the metals are not related to an inconsistency in the extraction procedure's ability to differentiate these two tightly-bound fractions.

The observed differences in the relative residual concentrations of Pb, Cd and Zn are probably related to three closely-related properties of the metals: sorption, solubility, and bioavailability. Pb, Cd, and Zn co-occur as metal sulfides in the old Lead Belt ores (USGS 1967), and all three sulfides are relatively insoluble. Pure galena (PbS) has a solubility of 0.86 mg/L (0.74 mg/L Pb); greenockite (CdS), 1.3 mg/L (1.01 mg/L Cd); and sphalerite (ZnS), 0.65 mg/L (0.44 mg/L Zn) in cold water (Weast and Astle 1978). Based on these solubilities and the relative abundance of the metal sulfides, one would expect dissolved concentrations of Cd>Pb>Zn. However, the data show dissolved Zn>Pb>Cd at all three Big River sites affected by Pb mine tailings (Table 4), which also corresponds to the abundance of the three metals in the tailings. A further explanation may lie in the differential

solubilities of the oxidized forms of the three sulfide minerals. It is widely known that the surfaces of galena crystals oxidize rapidly to $PbSO_4$ upon exposure to air, and that the material that is now tailings was mechanically processed--i.e., pulverized and rolled to its present texture in the presence of air, then mechanically sorted (Kramer 1976). Furthermore, Kramer (1976) presented evidence of bacterially-mediated oxidation of PbS , CdS , and ZnS within the Elvins tailings pile on Flat River Creek, as was also reported by Galbraith et al. (1972) for tailings heaps in the Coure d'Alene mining district in Idaho. It is therefore likely that much of what was originally PbS , CdS , and ZnS is now $PbSO_4$, $CdSO_4$ and $ZnSO_4$. The solubility of $PbSO_4$ is still relatively low--42.5 mg/L in cold water--but for $CdSO_4$ it is 7.5×10^5 mg/L, and $ZnSO_4$ is completely soluble. Note that for the metal sulfate solubilities, $Zn > Cd > Pb$ and that the correlations between dissolved metal concentrations and SO_4^{-2} concentrations in the Big River follow the same order as these solubilities: For dissolved Pb and SO_4^{-2} , $r=0.21$; for dissolved Cd and SO_4^{-2} , $r=0.47$; and for dissolved Zn and SO_4^{-2} , $r=0.80$ (Table 5).

Rickard and Nriagu (1978) describe a mechanism for the subaqueous oxidation of galena under alkaline conditions that is enhanced by the presence of Fe and Mn oxyhydroxides, which abound in the Big River. Under conditions typical of the Big River, some solubilized Cd, Pb, and Zn should be complexed by dissolved carbonates, and some should eventually precipitate as $CdCO_3$, $PbCO_3$ and $ZnCO_3$. Both phenomena would account for the higher percentages of carbonate-bound metals at Washington State Park than at Desloge. This process of carbonate precipitation, together with sorption by Fe and Mn hydrous oxides,

appear to be the dominant geochemical processes controlling Pb, Cd, and Zn distribution in the Big River. All three metals may also be complexed by other inorganic ligands, including phosphate and chloride, that are present in the Big River. However, these other species are usually unimportant compared to the carbonate species and the sorbed metals (e.g., Vuceta and Morgan 1978).

Biological processes may also be important in the solubilization of metals. In addition to the biologically mediated oxidation of sulfides discussed earlier, the abilities of many naturally-occurring and synthetic organic compounds to complex Pb, Cd and Zn are well known. Wixson and Bolter (1972) and Gale et al. (1973) reported that the attached stream microflora can remove significant quantities of metals from the water of Ozark streams receiving mine effluents; likewise, rooted aquatic plants can both extract some metals from the sediments and sorb metals from the liquid phase. However, the relatively low dissolved metals concentrations in filtered water samples and the proportionately low representation of organically-bound Pb, Cd, and Zn in sediment samples suggest that interactions with the biota are less important in the Big River than the geochemical mechanisms discussed earlier. Total organic carbon concentrations in Big River sediments were fairly low, ranging from 0.4-9.2 mg/g at Brown's Ford, 1.4-2.9 mg/g at Washington State Park, 0.1-4.0 mg/g at Desloge, 0.9-6.8 mg/g at Irondale, and 6.5-8.5 mg/g at Mineral Fork (Appendix B). In comparison, Kemp and Thomas (1976) surveyed the sediments of Lakes Ontario and Huron and found TOC concentrations in the range of 2-4% (20-40 mg/g) in uncontaminated, fine-grained sediments (mostly silts and clays), with concentrations as high as 6% (60 mg/g) where anthropogenic organic

material had accumulated. Likewise, Toth and Ott (1970) surveyed impoundments in Pennsylvania and found organic matter at 1.6-7.4% (16-74 mg/g)--considerably higher than in the Big and Black River systems. The uniformly low concentrations, even as far downstream as Brown's Ford, illustrate the dominance of the Big River sediments by inorganic material. It is therefore not surprising that organically-bound Pb, Cd, and Zn concentrations were also uniformly low.

In the Black River-Clearwater Lake system, all the sulfide-originating metals were higher in sediments within and below the lake than above (Table 12). Our results generally agreed with the earlier results of Gale et al. (1976), who reported sediment concentrations near Clearwater Dam of up to 60 $\mu\text{g/g}$ Pb, 84 $\mu\text{g/g}$ Zn, 30 $\mu\text{g/g}$ Cu, and 0.5 $\mu\text{g/g}$ Cd. Organic carbon concentrations in the Clearwater Lake system were within the range reported for the Big River system--0.32-3.41 mg/g above the lake, 5.2-6.0 mg/g within the lake, and 2.6-5.3 mg/g below the lake. Although sediment concentrations of total Cd and total Zn were closely correlated with organic carbon, total Pb was not; total Pb was higher below than within Clearwater Lake even though organic carbon concentrations were higher within the lake. Although it is tempting to suggest that the apparent correlations between organic carbon and total Zn and total Cd indicate a biological mechanism of enrichment for these metals, the results of the sequential extractions point towards other pathways. For these metals, the seasonal cycle of Fe and Mn oxidation and reduction appear responsible for most of the differences between sites. Below the lake, Pb and Mn concentrations were both highest in silt fraction; Zn, Cd, and Fe concentrations were highest in the clay fraction. These slight

Table 12. Concentrations of Pb, Cd, and Zn in sediments from Clearwater Lake and from the Black River downstream of Clearwater Lake relative to upstream concentration.

Site	Pb	Cd	Zn
Upstream Clearwater Lake	1.00	1.00	1.00
Clearwater Lake	6.50	6.89	5.95
Downstream Clearwater Lake	6.97	4.16	3.02

differences suggest concomitant differences in the mechanisms involved, even among the three metals.

Some of the observed "enhancement" of Pb, Cd, and Zn in sediments within and below Clearwater Lake may result from the dissolution of more soluble sediment constituents during summer stratification. Dissolution of Fe and Mn hydrous oxides and of carbonates, and their subsequent transport downstream, would increase the relative concentration of the remaining, less-soluble sediment constituents, such as the residual metals. Likewise, scouring of fine-grained sediments by density currents and their subsequent downstream transport, which happens periodically at Clearwater Lake (Wixson and Bolter 1972), would also affect the relative concentrations of the metals because of the differences in concentrations among the size fractions. Within the lake, the clay-sized particles had the lowest Pb, Zn and Cd concentrations (Table 9a-c); loss of these low-concentration, fine-grained sediments would tend to increase the total metals concentrations in the remaining sediments. Likewise, the sediments in the Black River system above Clearwater Lake are substantially coarser than the sediments within and below the lake (Table 9f). Therefore, some of the observed differences in metals concentrations are probably an artifact of this textural inconsistency.

Divers collecting sediments in Clearwater Lake reported the presence of hydrogen sulfide (H_2S) upon disturbing the sediments. It is therefore likely that some reprecipitation of metal sulfides occurs within the anoxic lake sediments, as suggested by Rickard and Nriagu (1978).

Copper in sediments. Cu was the only metal other than Pb included in the sediment study that originated in tailings and was actually higher in the tailings sample than in the sediment sample from Desloge (Fig. 13). As Fig. 13 illustrates, total Cu declined from a high of 127 $\mu\text{g/g}$ in the tailings sample to 70 $\mu\text{g/g}$ at Desloge, 57 $\mu\text{g/g}$ at Washington State Park and 55 $\mu\text{g/g}$ at Brown's Ford. Concentrations were lower at the Big River sites not affected by tailings and in the Black River watershed (Fig. 13). Although the actual Cu concentrations differed, when the results from the traditional analyses for total Cu (Appendix B) were examined rather than the sum of the sequential fractions (Fig. 13), the trends were the same. In particular, Cu showed the same pattern of enhancement in sediments of Clearwater Lake and in the Black River downstream of the lake as that described for Zn and Cd, with most of the increase occurring among clay-sized particles (Table 9d).

Although the results of the sequential extraction procedure are somewhat questionable for Cu, the high percentage of Cu in the residual and organic fractions and low carbonate and oxide-bound percentages differentiate this metal from all others studied (Fig. 13). In particular, a higher percentage of Cu was organically-bound at all sites. This means either that the peroxide oxidation step in the sequential procedure attacked residual Cu to a greater extent than the residual fraction of other metals, or that more Cu was in fact bound to organic matter. Cu is more readily chelated than the other metals studied (Vuceta and Morgan 1978), so it would not be surprising to find that proportionally more Cu was tied up in biological systems or associated with organic coatings on sediment particles (e.g., Förstner

1981). Total Cu concentrations were highest in the silt fraction at Brown's Ford and at Irondale, in the sand fraction in Clearwater Lake, and in the clay fraction at the other sites (Table 9d).

Barium in sediments. Total Ba concentrations were highest in the sediments at Mineral Fork (2885 $\mu\text{g/g}$), Brown's Ford (1397 $\mu\text{g/g}$), and Washington State Park (1159 $\mu\text{g/g}$) (Fig. 14). Lowest concentrations occurred in the tailings sample (50 $\mu\text{g/g}$) and in the Black River above Clearwater Lake (91 $\mu\text{g/g}$). Concentrations within and below the lake were higher--344 $\mu\text{g/g}$ in lake sediments and 675 $\mu\text{g/g}$ downstream (Fig. 14).

Naturally-occurring barite (BaSO_4) is only slightly more soluble than CdS --2.22 mg/L (1.8 mg/L Ba) (Weast and Astle 1978). However, it is more soluble in acid, which suggests that it could be solubilized under reducing conditions. Results from the sequential extraction procedure, although they must be interpreted cautiously, show that residual Ba was the predominant form except within and below Clearwater Lake (Fig. 14). Ba concentrations in water, however, were about the same above, below, and within the lake during all three collection periods, ranging from 0.02 to 0.07 mg/L (Table 9c), indicating that any Ba solubilized from the sediments is rapidly re-precipitated, possibly as the insoluble BaCO_3 , or sorbed onto particulate material.

The sequential extraction procedure suggested little change in the distribution of Ba in the lower Big River (Fig. 14). Total Ba concentrations appear to show quite clearly the effects of sediment distribution, in this case from the opposite direction: Pb-rich mine

tailings from the Desloge area, low in Ba content, appear to dilute the Ba-rich sediments originating in the downstream areas of the watershed.

Metals in the Aquatic Biota

Bioavailability of heavy metals in the aquatic environment can be influenced by numerous variables including type of metal, length of exposure, oxidation state, pH, hardness, presence of organic compounds, and other chemical and physical characteristics of the aquatic system. Concentrations of metals in organisms are determined by a variety of factors including food habits, morphology, and physiological differences among organisms. Both biotic and abiotic factors must be considered in evaluating heavy metal accumulation in the biota.

Survey of Residue Levels in Aquatic Flora and Fauna

Metals in plants. Aquatic plants supply an intermediate reservoir through which trace metals from abiotic sources can enter and be retained within biological systems. They can influence the availability of metals by accumulation and by sorption from the water, and by secreting substances that can complex or chelate metals. For example, Morris (1971) observed dramatic decreases in dissolved Mn when the marine flagellate Phaeocystis bloomed, and Leland and McNurney (1974) found elevated Pb concentrations in algae collected near urban areas. The ability of algae to concentrate metals from the water has led to its use in removal of metals from mining and smelting effluents (Hassett et al. 1980). However, these authors also showed that algal species differed in their ability to accumulate metals, suggesting that differences were related to varying cell densities among species and to

age of a given culture. Therefore, a degree of caution must be observed when comparing metals concentrations in algae reported in the literature.

Highest residues of Pb, Cd, Cu, and Zn were found in algae from the Big River locations affected by mine tailings (Desloge, Washington State Park and Brown's Ford). Levels of Pb at Desloge (1210 $\mu\text{g/g}$) were twice as high as levels at Washington State Park (623 $\mu\text{g/g}$) and Brown's Ford (660 $\mu\text{g/g}$) (Table 13). Lowest concentrations of these four metals in the Big River Basin occurred at Irondale and Mineral Fork. Levels in the Black River Basin were also low, and there was no enhancement below Clearwater Dam. Concentrations of Pb, Cd, Cu, and Zn in water willow followed trends similar to algae with highest levels at Desloge, Washington State Park, and Brown's Ford and lowest levels at Irondale, Mineral Fork, and in the Black River Basin. Accumulations of these four metals were generally highest in the roots (Table 13).

Concentrations of Pb in roots, stems, and leaves of water willow were highly intercorrelated ($p < 0.01$) as were residues in macrophyte tissues and algae. Correlations for Cd levels among roots, stems, and leaves were also highly significant (Table 14), but there was no apparent relationship between water willow and algae for this metal. The observed interrelationships between metal concentrations in these plants may be explained in terms of possible mechanisms for the concentration of Pb and Cd.

In algae, Pb and Cd are concentrated primarily on surface adsorptive sites. Therefore, the degree to which different algal species concentrate metals depends on the number of surficial cells available for adsorption (Hassett et al. 1980). In higher plants, Pb

Table 13. Metals concentrations ($\mu\text{g/g}$, dry weight) in plants from the Big and Black Rivers. Algae, means of three samples; water willow, one sample each of roots, stems, and leaves from each location; and Ceratophyllum, one sample.

LOCATION Species tissue	Pb	Cd	Cu	Zn	Ag	Fe	Mn	Ba
MINERAL FORK								
Attached Algae	19.7	0.99	8.07	186.7	0.20	6100.0	1933.0	84.3
Water Willow roots	24.0	0.20	2.80	52.20	0.10	4300.0	440.0	400.0
stems	30.0	0.10	2.80	21.10	0.10	250.0	68.0	220.0
leaves	13.0	0.10	3.90	35.00	0.10	650.0	79.0	160.0
BROWN'S FORD								
Attached Algae	660.0	2.60	14.33	396.67	0.13	5133.0	2066.7	182.0
Water Willow roots	690.0	2.70	20.00	280.0	0.10	14000.0	2300.0	390.0
stems	220.0	0.90	8.70	110.0	0.10	1200.0	1100.0	210.0
leaves	180.0	0.78	8.40	110.0	0.10	1600.0	720.0	140.0
WASHINGTON STATE PARK								
Attached Algae	623.3	3.27	16.67	310.0	0.16	5333.3	1666.7	122.0
Water Willow roots	460.0	6.10	27.00	390.0	0.20	11000.0	2100.0	550.0
stems	290.0	2.00	14.00	80.0	0.10	1800.0	1100.0	220.0
leaves	320.0	1.90	15.00	180.0	0.10	2500.0	1100.0	200.0
DESLOGE								
Attached Algae	1210.0	2.40	18.56	758.33	0.10	8200.0	2133.3	65.3
Water Willow roots	1400.0	21.00	18.00	600.00	0.40	8800.0	2100.0	82.0
stems	310.0	6.40	12.00	600.00	0.10	1700.0	770.0	52.0
leaves	250.0	4.90	11.00	590.00	0.10	2800.0	580.0	52.0

Table 13 (cont'd)

	<u>Pb</u>	<u>Cd</u>	<u>Cu</u>	<u>Zn</u>	<u>Ag</u>	<u>Fe</u>	<u>Mn</u>	<u>Ba</u>
IRONDALE								
Attached Algae	16.3	0.73	11.45	46.50	0.10	8672.5	2635.0	187.5
Water Willow								
roots	11.0	0.30	7.60	26.00	0.10	2200.0	740.0	90.0
stems	2.2	0.10	3.70	14.00	0.10	320.0	200.0	58.0
leaves	1.7	0.10	6.90	24.00	0.10	540.0	210.0	44.0
UPSTREAM CLEARWATER LAKE								
Attached Algae	24.0	1.40	8.47	34.33	0.10	6200.0	290.0	620.0
Water Willow								
roots	8.9	0.30	24.00	33.00	0.10	3500.0	200.0	140.0
stems	12.0	0.20	21.00	29.00	0.10	2000.0	110.0	280.0
leaves	5.9	0.20	19.00	36.00	0.10	1500.0	120.0	270.0
DOWNSTREAM CLEARWATER LAKE								
Attached Algae	15.3	0.42	10.27	40.67	0.10	7833.3	14033.3	396.7
Water Willow								
roots	12.0	0.47	8.60	28.00	0.10	6500.0	5600.0	200.0
stems	7.6	0.20	4.50	18.00	0.10	2600.0	2200.0	130.0
leaves	9.8	0.20	7.80	32.00	0.10	3800.0	1500.0	64.0
<u>Ceratophyllum</u> sp.	14.0	0.88	8.60	52.00	0.10	5500.0	1200.0	290.0

Table 14. Product-moment correlation coefficients among metal concentrations in algae and roots, stems, and leaves of water willow.

Pb					Zn				
Cd	Roots	Stems	Leaves	Algae	Cu	Roots	Stems	Leaves	Algae
Roots	--	.88**	.77*	.99**	Roots	--	.99**	.99**	.93**
Stems	.99**	--	.98**	.95**	Stems	.87*	--	.99**	.92**
Leaves	.99**	.99**	--	.87*	Leaves	.87*	.97	--	.93**
Algae	.53	.54	.59	--	Algae	.52	.20	.18	--

Fe					Ba				
Mn	Roots	Stems	Leaves	Algae	Roots	Stems	Leaves	Algae	
Roots	--	.28	.40	-.55	Roots	--	.58	.45	-.35
Stems	.98**	--	.89**	-.02	Stems	--	--	.94**	.43
Leaves	.93**	.97**	--	.14	Leaves	--	--	--	.46
Algae	.90**	.82*	.74	--	Algae	--	--	--	--

*0.05 $\geq p > 0.01$

**0.01 $\geq p$

tends to be more concentrated in the roots than in the stems and leaves (Wallace and Romney 1977) where the roots are in direct contact with metal ions in the soil. In an aquatic system, emergent macrophytes such as water willow are completely submerged during high water events, thus exposing the plant's surface to metals in the water. Therefore, significant correlations for Pb concentrations in plants (Table 14) may indicate interrelationships between dissolved Pb and surficial adsorptive sites in both algae and water willow. When the plants were collected, the dissolved Pb concentration in the Big River at Desloge (0.02 mg/L) was at least twice as high as the concentrations at Washington State Park (0.009 mg/L) and at Brown's Ford (0.005 mg/L). This downstream decrease in dissolved Pb levels was reflected in an equivalent reduction in Pb concentrations (Table 13) in both algae and water willow roots. Pb concentrations in stems and leaves were also lower downstream from Washington State Park, but not as an apparent function of dissolved Pb. However, neither the duration nor the frequency of stem and leaf exposure to dissolved Pb during high water events has been evaluated.

Although Cd is concentrated on cell surfaces in algae, it is not readily adsorbed onto the surfaces of rooted plants. Cd has been shown to accumulate to a much greater degree than Pb through the roots and become incorporated into plant tissues (Reddy and Patrick 1977, Gambrell et al. 1980). Lack of a significant correlation between Cd concentrations in water willow and algae therefore suggests no relationship between the Cd adsorbed on the algal surfaces and that incorporated into the water willow tissue. Cd accumulation by water willow probably occurs by uptake through the roots from the sediment

rather than from the water. Highly significant correlations ($r > .99$) between Cd in water willow roots, stems, and leaves suggests a mechanism of direct Cd accumulation by the plant and distribution throughout the living organism.

Cu, like Cd, accumulates in the roots of plants and is transported through the vascular tissue into the stems and leaves. The correlation matrix for Cu (Table 14) indicates significant ($p < 0.01$) positive relationships among roots, stems, and leaves, but no significant correlation between rooted plant tissues and algae. Levels of Cu in algae decreased from Desloge to Washington State Park to Brown's Ford. Although highest concentrations in the Big River Basin in both algae and water willow occurred at these three sites, the small differences between concentrations in plants from these locations and the even lower concentrations at Irondale and Mineral Fork are probably not biologically significant. Algae and water willow collected below Clearwater Lake and algae collected from the Black River upstream of Clearwater Lake had concentrations similar to plants at Irondale. Water willow collected at the upstream site had a higher mean Cu concentration than any samples from the Big River.

Although highest concentrations of Zn in algae and water willow also occurred at the three contaminated Big River sites, Zn behaved differently from Pb, Cd, or Cu within the water willow tissue. Zn was uniformly distributed throughout the plant tissues; Pb, Cd, and Cu were more highly concentrated in the roots (Table 13). As a result, all possible relationships among roots, stems and leaves were highly significant ($p < .01$) for Zn.

Concentrations of Ag, Fe, Mn, and Ba in the plants were not related to the presence of mine tailings in the Big River. Ag was detectable in the roots of water willow at Desloge and Washington State Park and in the algae at Washington State Park, Mineral Fork, and Brown's Ford. Highest concentrations of Fe, Mn, and Ba in algae occurred at Irondale. In water willow, highest mean concentrations of Fe occurred at Brown's Ford with highest concentrations of Mn and Ba at Washington State Park.

Comparison of the Black River locations upstream and downstream of Clearwater Lake revealed that Fe was slightly higher and Ba was slightly lower in plants below Clearwater Dam. Levels of Mn upstream of Clearwater Lake were lower than concentrations at any Big River locations. However, the Mn concentrations in algae below the reservoir increased by a factor of 48.4 and concentrations in water willow increased by a factor of 21.7. The availability of Mn below Clearwater Lake is strongly influenced by the presence of the reservoir. A more detailed discussion of mechanisms responsible for elevated concentrations of Mn below the lake was presented in the water section. The importance of these mechanisms in altering the availability of Mn to the biological system is unquestionable.

In general, metals in the Big River and Black River watersheds tended to accumulate on surface adsorptive sites of algae. For water willow, Pb was probably bound to surfaces, with highest concentrations in the roots; Cd, Cu, and Fe concentrated in the roots but a substantial portion was passed into stem and leaf tissue; and Zn was more or less uniformly distributed throughout the plant. The heavy metal tolerance exhibited by these plants may involve specialized internal distributions

so that potentially toxic metals are deposited on the cell wall and not retained within the intercellular spaces of the tissue. Regardless of the ultimate location of the metal within the plant, metals bound by plants will be further incorporated into the aquatic system. Higher trophic level organisms will ingest the metals associated with plants, either as detritus or as leaf and stem material, regardless of whether the metals are sorbed or incorporated. Plants can also have a tremendous indirect impact on the availability of metals to other ecosystem components through modification of pH, release of organic agents, and extraction of metals from highly stable chelates.

Metals in crayfish. Crayfish feed on aquatic macrophytes and detritus and can accumulate sediment-bound toxicants. Knowlton (1981) showed that a high percentage of total body Pb in crayfish is loosely bound to the exoskeleton and suggested that the mechanisms for concentration of Pb involved direct accumulation from contaminated sediments.

In the survey, Orconectes luteus was collected at every Big River site. Levels of Pb and Cd were elevated at all locations affected by mine tailings, with highest concentrations at Desloge (140 $\mu\text{g/g}$) (Table 15). Lower levels of Pb at Irondale (1.4 $\mu\text{g/g}$) and Mineral Fork (2.7 $\mu\text{g/g}$) were comparable to levels in uncontaminated, laboratory-raised crayfish of the same genus from Knowlton's (1981) study. O. punctimanus was only found at one Big River site, Brown's Ford, where residues in this species and O. luteus were similar (Table 15). Concentrations of Pb in crayfish increased with sediment Pb concentrations (Fig. 15). Because the substrate is the primary habitat of crayfish, this

Table 15. Metals concentrations ($\mu\text{g/g}$, dry weight) in crayfish from the Big and Black Rivers. Single composite samples of 10-15 specimens each.

LOCATION Species	Pb	Cd	Cu	Zn	Ag	Fe	Mn	Ba
MINERAL FORK								
<u>Orconectes luteus</u>	2.7	0.04	61.0	93.0	0.60	190.0	200.0	700.0
BROWN'S FORD								
<u>Orconectes luteus</u>	110.0	1.3	140.0	120.0	0.70	430.0	480.0	560.0
<u>Orconectes punctimanus</u>	84.0	1.6	190.0	120.0	0.58	580.0	260.0	590.0
WASHINGTON STATE PARK								
<u>Orconectes luteus</u>	130.0	1.2	150.0	130.0	0.64	460.0	520.0	400.0
DESLOGE								
<u>Orconectes luteus</u>	140.0	1.5	96.0	200.0	0.78	1700.0	420.0	180.0
IRONDALE								
<u>Orconectes luteus</u>	1.4	0.42	95.0	87.0	0.73	290.0	380.0	440.0
UPSTREAM CLEARWATER LAKE								
<u>Orconectes punctimanus</u>	1.2	0.39	94.0	95.0	0.70	200.0	110.0	230.0
DOWNSTREAM CLEARWATER LAKE								
<u>Orconectes punctimanus</u>	17.0	0.58	130.0	95.0	0.76	330.0	520.0	285.0

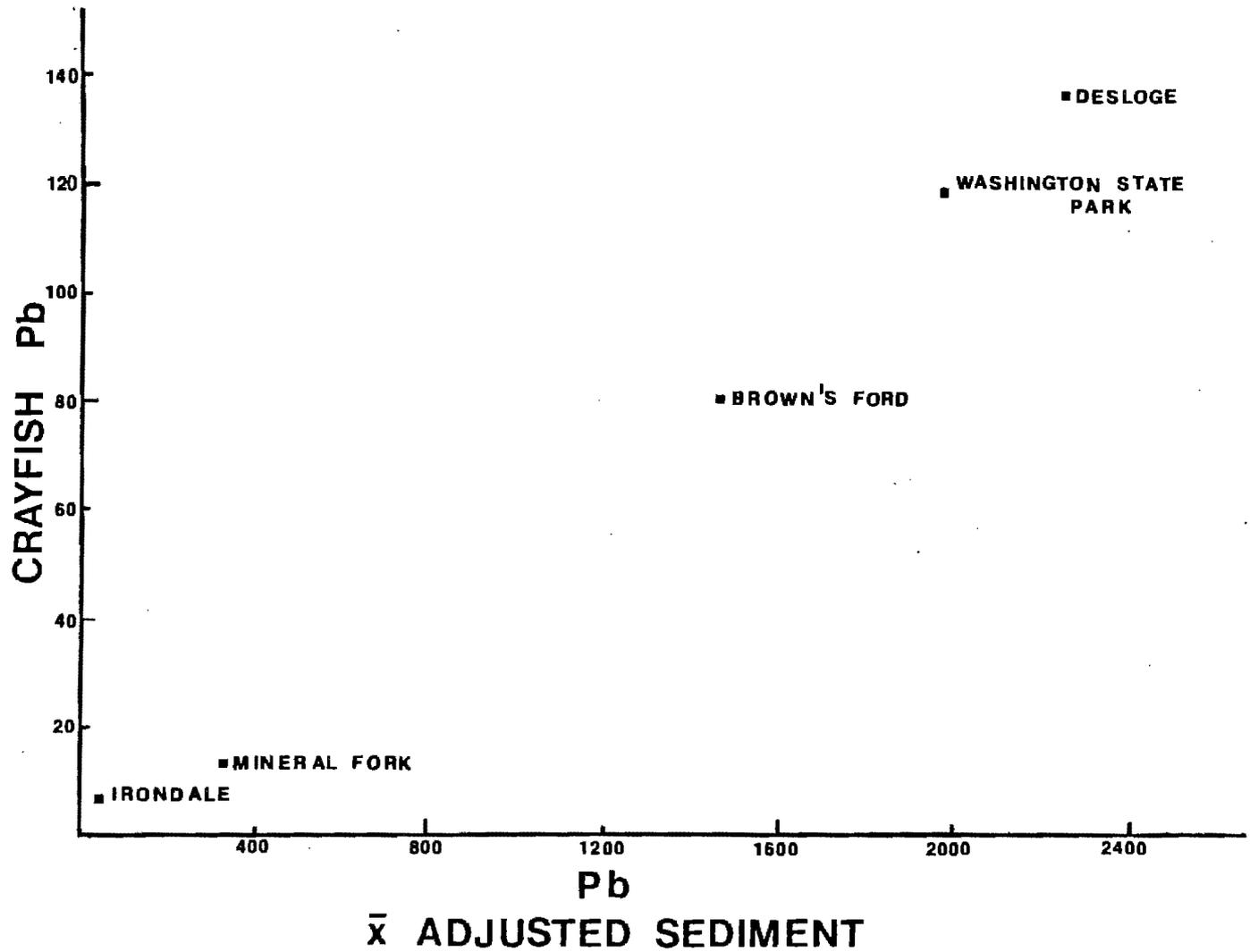


Figure 15. Pb concentrations ($\mu\text{g/g}$, dry weight) in crayfish (*O. luteus*) and in sediments from five sites on the Big River.

relationship may be a response to direct contact with the substrate as well as to ingestion of contaminated particles of sand, detritus, plants, and other organic material. Zn and Fe concentrations in crayfish were also highest at the three locations affected by mine tailings. Cu and Mn concentrations were highest at Washington State Park and at Brown's Ford (Table 15). Concentrations of Cu and Mn at Desloge were similar to concentrations at Irondale. Levels of Ag ranged from .58 $\mu\text{g/g}$ at Brown's Ford to .78 $\mu\text{g/g}$ at Desloge with no differences between control sites and contaminated sites. Ba was highest at Washington State Park, Brown's Ford and Mineral Fork, where active barite mining now occurs. At Brown's Ford, O. punctimanus had slightly lower levels of Pb and Mn and higher concentrations of Cd, Cu, Fe, and Ba than O. luteus. Zn concentrations were the same for both species.

In the Black River drainage, levels of Pb in crayfish (O. punctimanus) collected upstream of Clearwater Lake were similar to concentrations at Irondale. Crayfish downstream of the lake had Pb levels 14 times higher than those collected upstream. Levels of Cd, Cu, Fe, Mn, and Ba also increased below the reservoir. No change occurred in Zn concentration. The observed enhancement of Pb in crayfish collected below the reservoir may result from the increased Pb levels in sediments downstream. The calculated enhancement factor of 14 must be evaluated with caution because both upstream and downstream concentrations represent single composite samples of 10 to 15 crayfish. However, it is realistic to assume that some enhancement did occur given the habitat and food habits of the crayfish and the increased levels of Pb in the downstream sediments.

Metals in freshwater mussels. The sediment also provides habitat for freshwater mussels. These organisms actively filter small-diameter particulate material from the water and have been shown to accumulate heavy metals in both soft tissue and shell. Because they are primarily sessile organisms, they can indicate contaminant availability within a relatively limited area, and because of their longevity, indicate average conditions over an extended period. Within a species, smaller mussels tend to accumulate metals at higher rates than larger mussels (Boyden 1974) and concentrations in the soft parts are often higher than concentrations in the shell (Graham 1972).

Pocketbook mussels were collected at all Big River locations except Desloge, where an intensive search yielded none. Mussels were collected approximately 6 mi upstream of Desloge at Leadwood, a site that is also contaminated by Pb mine tailings (from erosion of the Leadwood tailings pile). Mussels collected at Leadwood, Washington State Park, and Brown's Ford were of similar size and had elevated levels of Pb, Cd, Cu, and Zn relative to uncontaminated sites (Table 16). Brown's Ford mussels had the highest mean Pb concentrations, with levels ranging from 310 to 490 $\mu\text{g/g}$ in the soft tissue and from 18 to 19 $\mu\text{g/g}$ in the shell. Pb levels at Washington State Park were lower, ranging from 200 to 310 $\mu\text{g/g}$ in the soft tissue and from 8 to 22 $\mu\text{g/g}$ in the shell. Mussels collected at Leadwood had soft tissue concentrations of 99 to 250 $\mu\text{g/g}$ and shell concentrations of 4.2 to 19 $\mu\text{g/g}$. Lowest Pb concentrations occurred at Irondale and Mineral Fork (Table 16). All mussels collected at these two sites were smaller than those collected at other Big River locations, but because tissue Pb concentrations were 46 to 179 times lower than at contaminated sites, effects of size were not apparent.

Table 16. Mean concentrations of metals ($\mu\text{g/g}$, dry weight) in the soft tissue and in the shells of freshwater mussels from Big River and Black River locations.

Tissue Location	Pb	Cd	Cu	Zn	Fe	Mn	Ba
SHELL							
MINERAL FORK	1.20	0.16	2.70	8.00	49.5	115.0	480.0
BROWN'S FORD	18.5	0.70	2.50	35.50	88.5	385.0	335.0
WASHINGTON STATE PARK	15.0	0.30	4.20	17.00	89.33	206.7	176.7
IRONDALE	0.76	0.11	2.93	4.67	75.66	403.3	163.3
UPSTREAM CLEARWATER LAKE	0.36	0.12	1.35	5.50	125.0	195.0	84.5
DOWNSTREAM CLEARWATER LAKE	0.75	0.09	1.77	4.67	97.0	1066.7	350.0
LEADWOOD	11.6	0.51	4.10	61.40	140.0	250.0	130.0
SOFT TISSUE							
MINERAL FORK	3.75	2.50	8.90	410.0	2050.0	4600.0	175.0
BROWN'S FORD	386.67	32.67	61.33	5966.7	1653.3	11366.7	193.3
WASHINGTON STATE PARK	245.00	19.67	54.83	1676.7	510.0	4066.0	320.0
IRONDALE	2.16	0.47	6.64	218.0	968.0	3520.0	448.0
UPSTREAM CLEARWATER LAKE	1.04	1.02	7.33	326.7	1200.0	8233.0	183.3
DOWNSTREAM CLEARWATER LAKE	4.35	0.61	5.05	1100.0	3150.0	10950.0	1025.0
LEADWOOD	174.50	35.50	28.50	5200.0	865.0	6950.0	460.0

Pb levels in mussels from Brown's Ford and Washington State Park did not appear directly related to total sediment Pb concentrations. At Brown's Ford, where sediment Pb concentrations were lower, mussel Pb concentrations were highest. Little difference was observed in the distribution of different chemical forms in the active surficial sediment between Brown's Ford and Washington State Park; however, the particle size distribution of the bottom sediments differed. The mean concentration of silt size material in bottom sediments at Brown's Ford was approximately 19 times higher than at Washington State Park (Table 9f), and the multiple regression coefficients presented in Table 9a indicate that most of the sediment Pb is associated with the silt fraction. Availability of this smaller particulate material would greatly influence the accumulation of metals in freshwater mussels. Silt concentrations did not vary as dramatically in water samples. The concentration of silt in unfiltered water samples collected at low and medium flow from Brown's Ford was only slightly higher than at Washington State Park, and at high flow the silt concentration at Washington State Park exceeded the concentration at Brown's Ford. Estimation of the actual Pb levels in the microhabitat of a freshwater mussel would require understanding the effects of tailings input from barite mining operations, the dilution of Pb-contaminated silt particles by relatively less contaminated particles from Big River tributaries such as Mineral Fork, and the possible mobilization and incorporation of Pb into the biological system. Total sediment metal concentrations alone cannot accurately reflect the availability of metals to all

organisms in a river such as the Big River where physical, chemical, and biological changes occur between upstream and downstream locations. Computation of total metal transport in the river, especially bedload transport, might provide the best indication of metal availability in the mussel's microenvironment.

Concentrations of Cd, Cu, and Zn in mussels followed the same pattern as Pb concentrations; highest levels in mussels did not occur in locations with highest total sediment concentrations. As was true for Pb, highest Cu, Cd, and Zn levels occurred in mussels from Brown's Ford and lowest concentrations were at Irondale and Mineral Fork. Ba was highest at Irondale and was therefore not related to barite mining. Mn concentrations were likewise not related to levels in water or in sediment; Mn concentrations in mussels were high at every location.

In the Black River Basin, mean soft tissue and shell Pb concentrations were higher in mussels collected below Clearwater Lake than above (Table 16). Tissue concentrations ranged from 0.37 to 1.6 $\mu\text{g/g}$ upstream and from 3.8 to 4.9 $\mu\text{g/g}$ downstream of the reservoir. Zn concentrations in the soft tissue were 3 times higher at the downstream location. Cd and Cu concentrations were slightly lower below the dam. Differences in Fe concentrations were more apparent, with values upstream of the lake ranging from 3100 to 3200 $\mu\text{g/g}$ and downstream values of 1000 to 1500 $\mu\text{g/g}$. Mean Mn concentrations above and below the reservoir were not significantly different ($p > 0.05$); however, Ba concentrations were approximately 6 times higher at the downstream location.

Metals in fish. Highest Pb, Cd, Zn, Mn, and Ba concentrations in edible fish tissue occurred in flathead catfish (Pylodictis olivaris) from Washington State Park (Table 17). This specimen's Pb concentration (12.0 $\mu\text{g/g}$) was over 12 times higher than any other fish sample collected. This 25 yr-old fish was also considerably older and larger than any other catfish collected. Because this was the only catfish from Washington State Park, size and age relationships with concentration could not be evaluated. Mean Pb concentrations in edible portions of catfish at other Big River locations ranged from lows of 0.06 $\mu\text{g/g}$ at Irondale to a high of 0.29 $\mu\text{g/g}$ at Brown's Ford. Concentrations in catfish from Desloge and Mineral Fork were identical (0.13 $\mu\text{g/g}$).

With the exception of the one large catfish at Washington State Park, Pb concentrations in fish from the Big River were highest in redhorse suckers at all locations affected by mine tailings (Table 17). Concentrations decreased from Desloge to Washington State Park but were higher downstream at Brown's Ford. All redhorse suckers at Brown's Ford, Washington State Park and Desloge exceeded the World Health Organization standard (0.3 $\mu\text{g/g}$) for allowable Pb levels in tissue for human consumption. Significantly lower levels occurred in redhorse suckers from Irondale and Mineral Fork. Concentrations in suckers from this study agreed closely with levels reported for suckers collected at Irondale, Desloge and Washington State Park by the Missouri Department of Conservation (Czarneski 1980).

Elevated Pb levels were present in smallmouth bass collected at Washington State Park, Brown's Ford and Mineral Fork (Table 17). Concentrations in bass from Desloge were not higher than levels in bass

Table 17. Metals concentrations ($\mu\text{g/g}$, wet weight) in edible portions of fish from the Big and Black Rivers. Means of two samples (individual fish) unless otherwise indicated.

Location Species	Pb	Cd	Cu	Zn	Fe	Mn	Ba
Mineral Fork							
Smallmouth bass	0.19	0.01	0.42	13.97	12.15	0.63	1.75
Yellow bullhead	0.13	0.02	0.51	5.67	6.27	0.38	1.61
Redhorse sucker	0.08	0.01	0.22	13.42	3.00	0.64	1.81
Brown's Ford							
Smallmouth bass	0.21	0.01	0.32	4.50	4.87	0.29	0.62
Flathead catfish	0.29	0.02	0.66	12.24	8.44	0.26	0.18
Redhorse sucker	0.63	0.01	0.22	11.67	2.65	0.97	1.03
Washington State Park							
Smallmouth bass	0.27	0.01	0.26	9.49	5.14	0.46	0.68
Flathead catfish ⁴	12.00	0.34	0.69	23.00	10.00	4.90	3.20
Redhorse sucker	0.43	0.01	0.22	9.38	2.75	0.73	0.60
Mixed suckers ²	0.38	-	-	-	-	-	-
Desloge							
Smallmouth bass	0.05	0.01	0.32	11.73	3.90	0.13	0.04
Channel catfish	0.13	0.03	0.43	5.12	2.52	0.18	0.03
Redhorse sucker	0.57	0.03	0.28	16.15	2.81	0.36	0.16
Mixed suckers ²	0.79	-	-	-	-	-	-
Irondale							
Smallmouth bass	0.01	<0.01	0.27	13.28	3.90	0.23	0.15
Flathead catfish	0.06	0.06	0.44	6.75	8.26	0.57	0.13
Redhorse sucker	0.02	0.01	0.33	9.32	3.16	0.52	0.50
Mixed suckers ²	0.07	-	-	-	-	-	-

Table 17 (cont'd)

	Pb	Cd	Cu	Zn	Fe	Mn	Ba
Black River, upstream							
Smallmouth bass	0.04	0.01	0.32	7.46	4.36	0.11	0.03
Channel catfish	0.05	0.01	0.46	7.04	3.90	0.24	0.04
Redhorse sucker	0.03	<0.01	0.26	7.50	3.77	1.17	0.21
Black River, downstream							
Spotted bass	0.04	0.01	0.24	7.75	1.15	0.11	0.01
Channel catfish	0.04	0.01	0.21	5.73	2.30	0.26	0.01
Redhorse sucker	0.01	0.01	0.22	8.15	3.01	1.03	0.19
Leadwood Northern hogsucker ³	0.44	-	-	-	-	-	-

¹Edible portions were boneless samples of tissue and skin (without scales) for all species except catfish. Catfish tissue was analyzed without skin.

²Mixed suckers include northern hogsuckers and redhorse suckers. Mean concentrations are calculated from 10 samples of edible portions prepared and analyzed by the Missouri Department of Conservation.

³Only northern hogsuckers were available at this site.

⁴Concentration is based on 1 tissue sample.

from Irondale. Generally, in locations affected by mine tailings, Pb residues in suckers were higher than residues in catfish, which had higher levels than smallmouth bass.

Lead levels in all species collected at Irondale were low (<0.07 $\mu\text{g/g}$) relative to other Big River sites, but levels in individual species did not vary consistently with sediment concentrations. This inconsistency could be related to several factors. First, accumulation of Pb by a species can vary with resource utilization differences among the populations. For example, suckers are bottom-dwelling fish that may ingest detritus and sediments along with benthic invertebrates, but are also in frequent physical contact with the sediments. Whelan (MS, in preparation) has detected from 2200 to 7700 $\mu\text{g/g}$ Pb associated with detritus from Big River locations affected by mine tailings as compared to 21 to 22 $\mu\text{g/g}$ at Irondale. Ingestion of detritus, coupled with surface adsorption of Pb onto the mucus and skin of the fish could account for some of the high Pb levels in redhorse suckers. Higher concentrations of Pb were found in suckers and in mussels at Brown's Ford than at Washington State Park; sediment concentrations were higher at Washington State Park. This implies that measurement of total sediment Pb may not accurately reflect the availability of metals to organisms directly associated with the sediment-water interface.

With the exception of the large flathead catfish from Washington State Park, Pb concentrations in catfish increased from Desloge to Brown's Ford. Pb concentrations were also higher in smallmouth bass, which represent the highest trophic level collected in the survey, at downstream locations. However, from the survey data it is impossible to interpret the elevated concentrations of Pb in fish collected from the

Mineral Fork. Because only bass in Mineral Fork had Pb concentrations comparable to the levels detected in the downstream section of the Big River, elevated levels in fish from Mineral Fork may be related to fish mobility; the Mineral Fork collection site may have been too close to the Big River to be considered a control site for fish collection. However, the higher than expected metals levels in Mineral Fork sediments cannot be discounted.

Cd concentrations were extremely low or below detection thresholds in all edible portion fish samples except for the large flathead catfish from Washington State Park. Concentrations of Cu, Zn, Fe, and Mn did not vary directly with location in the Big River. Ba was highest at Washington State Park, Brown's Ford, and Mineral Fork, where active barite mining occurs.

In the Black River Basin, Pb, Cd, Cu, Zn, Mn, and Ba concentrations in fish collected upstream and downstream of Clearwater Lake were similar. Levels of Fe were consistently lower below the reservoir in all species.

Because edible portions may include metal-contaminated skin and mucus and may also be contaminated during tissue preparation, an effort was made to process a clean sample of muscle from each fish. Pb concentrations in these clean-processed samples were consistently lower than concentrations in edible portions of smallmouth bass and catfish from Mineral Fork, Brown's Ford and Washington State Park, and in catfish from Desloge (Table 18). Clean processing did not reduce Pb levels in those edible portions with low Pb concentrations. Levels of Pb in clean-processed redhorse suckers were higher from all locations affected by mine tailings. Because extreme care had been taken during

Table 18. Metals concentrations ($\mu\text{g/g}$, wet weight) in clean-processed fish tissues from the Big and Black Rivers. Means of two samples (individual fish) unless otherwise indicated.

Location Species	Pb	Cd	Cu	Zn	Fe	Mn	Ba
Mineral Fork							
Smallmouth bass	0.09	<0.01	0.20	4.33	6.71	0.34	0.82
Channel catfish	0.04	0.01	0.31	4.14	2.70	0.23	0.26
Redhorse sucker	0.09	<0.01	0.21	6.49	2.10	0.63	1.26
Longear sunfish ¹	0.02	<0.01	0.29	4.59	-	-	0.11
Brown's Ford							
Smallmouth bass	0.03	<0.01	0.13	3.30	1.50	0.12	0.01
Flathead catfish	0.06	0.01	0.17	4.32	0.92	0.28	0.04
Redhorse sucker	0.85	0.01	0.17	5.09	1.00	1.35	0.90
Longear sunfish ¹	0.24	0.03	0.27	6.33	-	-	0.10
Washington State Park							
Smallmouth bass	0.06	<0.01	0.17	4.05	1.84	0.18	0.10
Redhorse sucker	0.24	0.01	0.18	4.01	2.83	0.42	0.23
Longear sunfish ¹	0.20	0.02	0.25	5.63	-	-	0.06
Desloge							
Smallmouth bass	0.07	<0.01	0.15	5.80	1.40	0.11	0.01
Yellow bullhead	0.08	0.03	0.56	4.70	2.13	0.19	0.01
Redhorse sucker	0.52	0.01	0.16	10.46	0.69	0.38	0.13
Longear sunfish ¹	0.44	0.02	0.17	6.51	-	-	0.05
Irondale							
Smallmouth bass	0.06	<0.01	0.22	4.06	1.89	0.13	0.02
Yellow bullhead	0.06	0.05	0.28	3.83	3.85	0.60	0.11
Redhorse sucker	0.02	<0.01	0.24	4.37	1.20	1.35	0.37
Longear sunfish ¹	0.03	<0.01	0.27	5.24	-	-	0.11

Table 18 (cont'd)

	Pb	Cd	Cu	Zn	Fe	Mn	Ba
Black River, upstream							
Smallmouth bass	0.01	<0.01	0.18	4.34	1.95	0.08	0.01
Channel catfish	0.05	0.01	0.40	6.05	3.72	0.22	0.02
Redhorse sucker	0.03	<0.01	0.17	5.55	2.02	1.80	0.24
Longear sunfish ¹	0.05	<0.01	0.42	6.13	-	-	0.14
Black River, downstream							
Spotted bass	0.02	0.01	0.21	5.70	1.42	0.12	0.06
Channel catfish	0.02	<0.01	0.13	4.18	1.65	0.38	0.02
Redhorse sunfish	0.01	<0.01	0.18	4.24	2.28	1.01	0.07
Longear sunfish ¹	0.02	<0.01	0.31	5.40	-	-	0.05

¹Mean concentrations in longear sunfish are based on tissue samples of 9 to 28 fish.

sample preparation to exclude small bones from sucker tissue, the presence of high Pb levels in both edible portions and clean-processed samples suggests that suckers may accumulate a larger percentage of Pb in muscle tissue than either bass or catfish. Only clean-processed tissues were prepared for sunfish, but at Desloge Pb levels in these sunfish exceeded concentrations in edible portions of smallmouth bass. Pb concentrations in sunfish from Washington State Park and Brown's Ford were comparable to smallmouth bass from these locations (Table 17).

Pb and Cd levels in whole fish were highest in all species from locations affected by mine tailings (Table 19). Residues in these species include not only the levels in the fish tissue but any metal ingested by the fish immediately before collection. Residues in the whole body reflect the concentrations of metals to which higher trophic levels (piscivores) would be exposed, but does not indicate the availability of the metals to these predators.

Blood Enzyme Assay

The activity of the enzyme ALA-D is depressed by the presence of Pb in the blood (Hodson 1976). In humans, ALA-D activity is so sensitive that it is used to detect a harmful exposure to Pb before toxic symptoms appear (Secchi et al. 1974). Hodson (1977) found that the minimum concentration of Pb in the water that would cause enzyme inhibition in rainbow trout was 10 $\mu\text{g}/\text{l}$ (ppb) and that the recovery of enzyme activity upon exposure to clean water took approximately 2 months. Measurement of ALA-D activity has, under laboratory conditions, provided a short-term indication of long-term, sublethal effects of Pb in fish.

Table 19. Mean metals concentrations ($\mu\text{g/g}$ wet weight) in whole fish from the Big River and Black River.

Site Species	Pb	Cd	Cu	Zn	Fe	Mn	Ba
Mineral Fork							
Smallmouth bass	1.6	<.07	3.3	58	49	9	46
Channel catfish	6.4	.34	1.8	62	70	18	13
Redhorse sucker	5.5	.28	2.3	64	160	110	30
Brown's Ford							
Smallmouth bass	15.0	.30	4.7	66	80	14	41
Flathead catfish	12.0	.55	4.0	64	112	49	38
Redhorse sucker	30.0	.92	3.2	88	183	63	40
Washington State Park							
Smallmouth bass	10.0	.27	3.7	70	70	12	27
Channel catfish	12.0	.57	5.8	69	97	23	16
Redhorse sucker	52.0	.56	2.5	80	258	66	37
Desloge							
Smallmouth bass	10.0	.65	2.1	74	74	9	11
Channel catfish	24.0	.99	2.0	142	80	29	16
Redhorse sucker	44.0	1.25	1.4	173	75	48	11
Irontdale							
Smallmouth bass	5.0	.16	3.2	79	74	14	13
Flathead catfish	4.0	.41	4.8	62	130	21	14
Redhorse sucker	1.0	.06	1.9	70	348	104	20
Upstream, Black River							
Smallmouth bass	1.3	.10	4.3	63	150	11	25
Flathead catfish	2.2	.19	7.2	62	88	18	15
Redhorse sucker	.7	.10	1.5	68	115	53	13
Downstream, Black River							
Smallmouth bass	1.1	<.07	3.0	76	89	14	16
Channel catfish	18.0	.70	2.8	71	135	34	26
Redhorse sucker	.5	.13	1.9	68	157	163	13

An attempt to utilize this technique with longear sunfish under field conditions was impaired by the small volume of blood that could be collected from the specimens. Of the 107 fish collected from 7 locations, only 54 samples had the volume of blood required to perform both the ALA-D assay and the blood-Pb analysis. Sample size ranged from 4 fish at Washington State Park and Mineral Fork to 9 at Brown's Ford, 10 at Desloge, 12 at Irondale, 9 above Clearwater Lake and 6 below the lake. A log-log transformation of ALA-D and blood-Pb plotted in Fig. 16 shows the wide scatter of individual data points. Location means (Fig. 16) indicate an obvious difference in fish collected from the Black River and the Big River, as well as a negative relationship between blood-Pb and ALA-D among the Big River sites. However, there was a low correlation between blood-Pb and muscle-Pb and between muscle-Pb and ALA-D. Because of unexplainable low levels of ALA-D in fish from the Black River locations, these samples were deleted from consideration and attention was focused on Big River locations. Analysis of variance of sunfish from the Big River followed by Duncan's multiple range test indicated that ALA-D activity and blood-Pb concentrations at Mineral Fork and Irondale were significantly different from sunfish at Brown's Ford and Desloge ($p < 0.05$). Because of high sample variance and small sample size, Washington State Park was not significantly different from either control or contaminated sites. For sunfish in the Big River, the multiple regression model that explained the highest percentage of the variation (80%) in the ALA-D vs. blood-Pb relationship consisted of 15 variables, many of which were not biologically meaningful.

A second effort to test the ALA-D procedure under field conditions was attempted with redhorse suckers, a species that facilitated

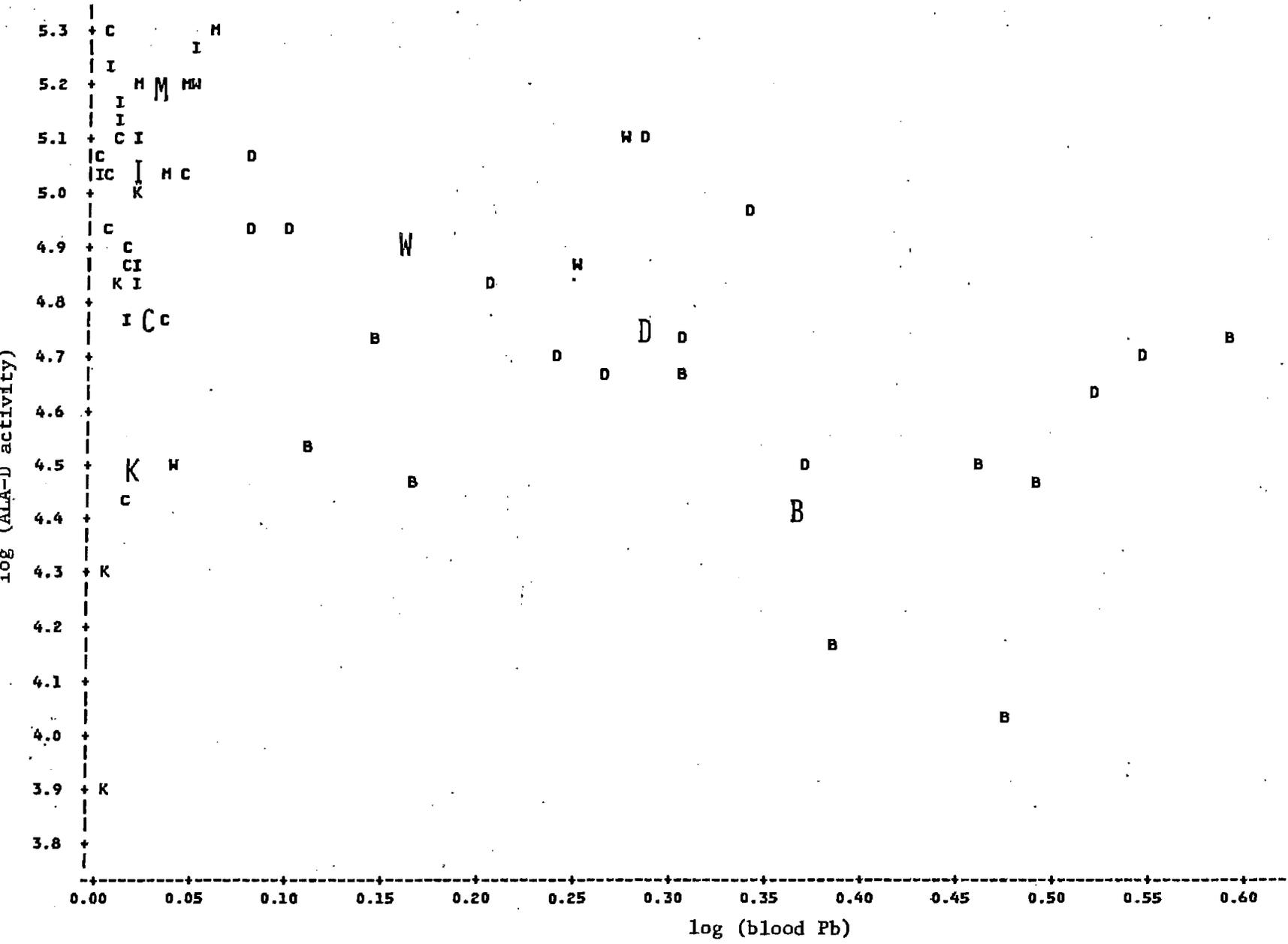


Figure 16. Log-log plot of the relationship between ALA-D activity and blood Pb concentration in longear sunfish from Brown's Ford (B), Washington State Park (W), Desloge (D), Irondale (I), Mineral Fork (M), upstream of Clearwater Lake (K), and downstream of Clearwater Lake (C). (Data from [unclear])

collection of large volumes of blood. Fish were collected at Irondale, Leadwood, Washington State Park and Desloge. Tissue concentrations are listed in Table 17 as "mixed suckers." A product-moment correlation matrix indicated that blood-Pb concentrations were highly correlated with both ALA-D activity ($r=-0.93$) and ALA-D activity expressed per mg of DNA ($r=-.97$). Correlations with muscle tissue Pb concentrations were again poor ($r=.26$). Within location sample variance for suckers was lower than for sunfish and a decrease in ALA-D activity with an increase in blood-Pb levels was observed (Fig. 17). Mean ALA-D activity and blood-Pb concentrations at Irondale were significantly different from all locations affected by mine tailings. Among the contaminated sites, the mean blood-Pb concentration was significantly higher at Desloge than at Washington State Park and Leadwood.

Using a stepwise regression analysis, the relationship $Y = 1.134 - 1.832 \log_{10}x_1 + 0.057 \log_{10}x_2 + 0.625 \log_{10}x_3 - 0.796 \log_{10}x_4$ where $Y =$ ALA-D; $x_1 =$ wet weight blood-Pb (mg/L); $x_2 =$ (wet weight blood-Pb)²; $x_3 =$ wet weight Zn (mg/L); and $x_4 =$ hemoglobin (mg/mL) proved to be the best model, accounting for 82% of the variability. The intercept and all regression coefficients were highly significant ($p < 0.01$).

A variable for blood-Zn concentration was included because of the known enhancement of ALA-D activity by Zn. Pb inhibits ALA-D activity; Zn, however, is a required metal for activation of the enzyme (Finelli 1977). Zn^{+2} and Pb^{+2} compete for the same binding sites in the blood and, therefore, the activity of ALA-D depends not only on the blood-Pb level but also on the concentration and availability of Zn. The positive response for the Zn coefficient, with a negative quadratic response for Pb, supports this hypothesis.

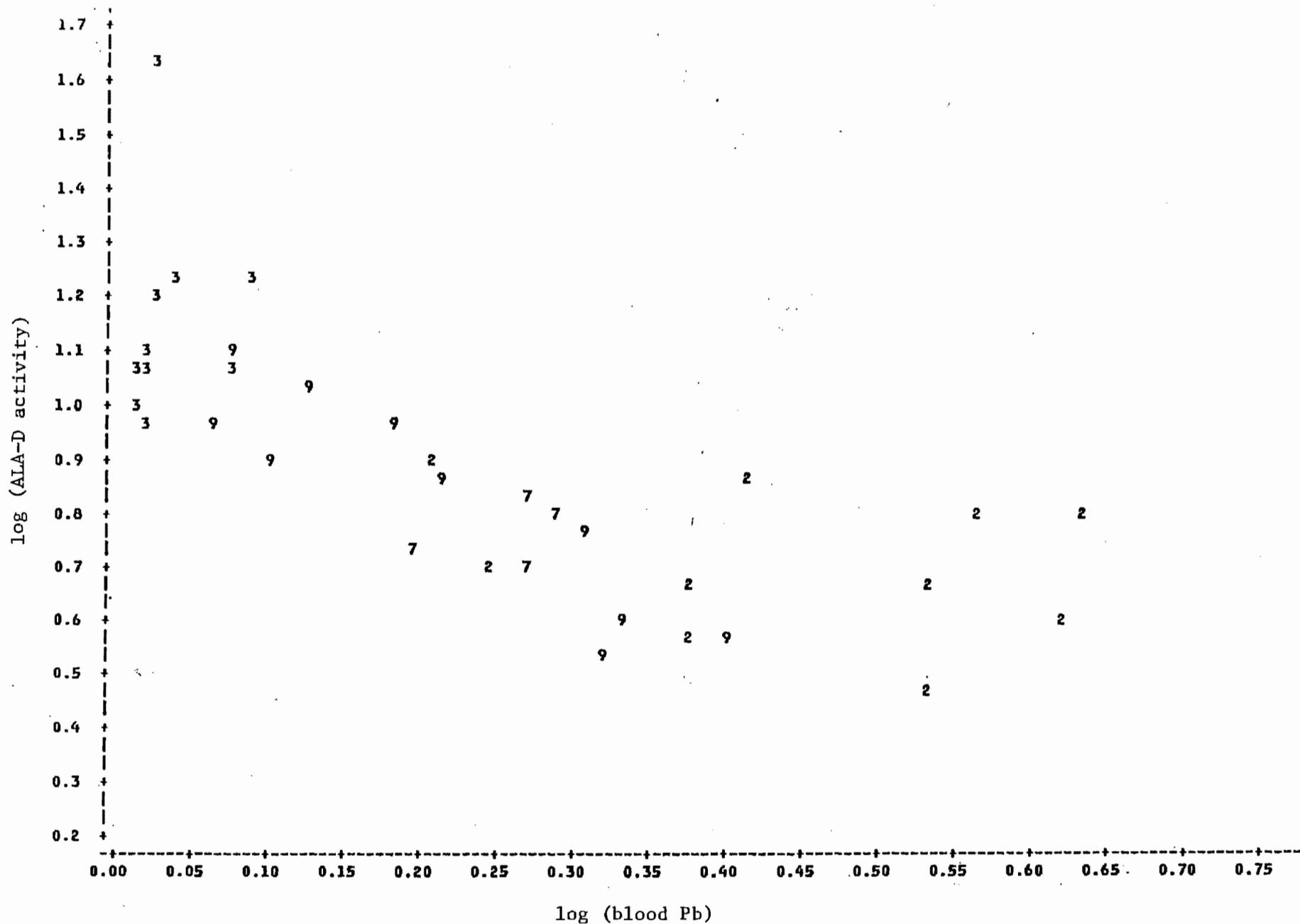


Figure 17. Log-log plot of the relationship between ALA-D activity and blood Pb concentration in several species of suckers from the Big River at Desloge (2), Washington State Park (9), Leadwood (7) and Irondale (3).

The relationship between blood-Pb, blood-Zn and ALA-D activity might be further improved by slight alteration in the time of field collection. At the time of collection, suckers were reproductively active and because of increased mobility, the samples may have included fish from poorly defined areas of the river. Collection at a different time of year could therefore better delineate the range of stream sampled. And, if possible, only one species should be used. Although an effort was made to collect blood from only black or golden redbreasted suckers, northern hogsuckers were used to supplement sample size at most locations and were the only sucker species available at Leadwood. Deletion of hogsuckers from the data set did not improve the relationship. In fact, variation among the northern hogsuckers at Leadwood (Fig. 17) was extremely low. Mean concentrations of Pb for 10 fish in the mixed sucker sample (Table 17) were similar to survey levels for redbreasted suckers, with high concentrations at Desloge and low concentrations at Irondale. And, as the plot of ALA-D vs. blood-Pb (Fig. 17) indicated, the points representing the Leadwood hogsuckers ("7") do not deviate markedly from the overall relationship.

The overall significance of the observed ALA-D response cannot be overstated. Analysis of environmental samples for Pb residues, especially fish samples, is notoriously difficult; contamination during collection, storage, handling, and sample preparation are extremely difficult to avoid (Patterson and Settle, 1976), and there is a high degree of sample-to-sample variability caused by the inhomogeneous distribution of Pb among the tissues of the fish (Phillips and Russo 1978). As such, the possibility of contamination and Type-II interpretive errors is always present when only residue data are

available for evaluation. The blood study results remove some of this uncertainty from the survey of residues in fish. Blood samples were drawn with sterile, heparinized syringes from the caudal artery of individual fish; placed immediately into sterile, heparinized vials; sealed; and quickly frozen until analyzed. There was little opportunity for contamination, and the clearly-defined, dose-response relationship would not have been observed had such contamination occurred; the variability would have been far greater than <20% unexplained variance in the response for suckers, especially considering that this rather hastily conducted field study included three species collected at the worst possible time of year.

Uptake of Metals by Caged Mussels

The question of metal bioavailability was addressed further in the mussel exposure studies conducted during October 1980 and again in July 1981. Pocketbook mussels for both studies, all about the same size, were collected from the Bourbeuse River and had relatively low metal concentrations compared to levels in mussels from affected reaches of the Big River (Table 16). Metals concentrations ($\mu\text{g/g}$) in the soft tissues of Bourbeuse River mussels were Pb, <0.1 to 1.5; Cd, <0.20; Zn, <900; Cu, <7.7; Fe <4400; Mn, 8800-22000; and Ba, 80-720.

Between the 2-wk and 4-wk collection periods in the October 1980 exposure study, water temperature at all Big River sites dropped below 12° C and continued to decrease to a low of 2° C by the end of the study. Feeding by mussels decreases dramatically below 12 °C, thus eliminating metal accumulation. Samples were collected through December, but metal analyses revealed no increases in metal levels after

the first 2-wk period. The highest Pb level detected was 11 $\mu\text{g/g}$ at Desloge. Mussels at Brown's Ford accumulated 3 $\mu\text{g/g}$. No accumulation occurred at Irondale, at Clearwater Lake, or at either Black River location.

The study was attempted again in August 1981; earlier initiation was prevented by repeated high water events from May through July. Results of this second study are presented in Fig. 18.

Transportation of mussels from the Bourbeuse River to new locations apparently had no inhibitory effects on feeding activity. After 2 weeks in the Big River, Pb concentrations in mussels at Desloge had increased by a factor of 143, at Washington State Park by a factor of 109, and at Brown's Ford by a factor of 77. Cd concentrations also increased substantially at all Big River locations affected by mine tailings. Concentrations of both metals continued to increase for the duration of the study (Figure 18). The highest mean Pb concentration attained after an 8-wk exposure was 121 $\mu\text{g/g}$ at Desloge. Final mean concentrations at Washington State Park and Brown's Ford were 85 $\mu\text{g/g}$ and 44 $\mu\text{g/g}$, respectively. Cd reached a mean concentration of 22.2 $\mu\text{g/g}$ at Desloge, 14.1 $\mu\text{g/g}$ at Washington State Park, and 5.0 $\mu\text{g/g}$ at Brown's Ford. For every 2-wk exposure period, concentrations of Pb and Cd at Desloge were higher than levels at Washington State Park, which were higher than concentrations at Brown's Ford. No increases in Pb or Cd occurred at Irondale.

Although mussels at Brown's Ford and Washington State Park for both the survey and exposure study were of similar size, no Pb or Cd concentrations in the exposure study at either location were as high as concentrations found in the survey (no mussels were found at Desloge for

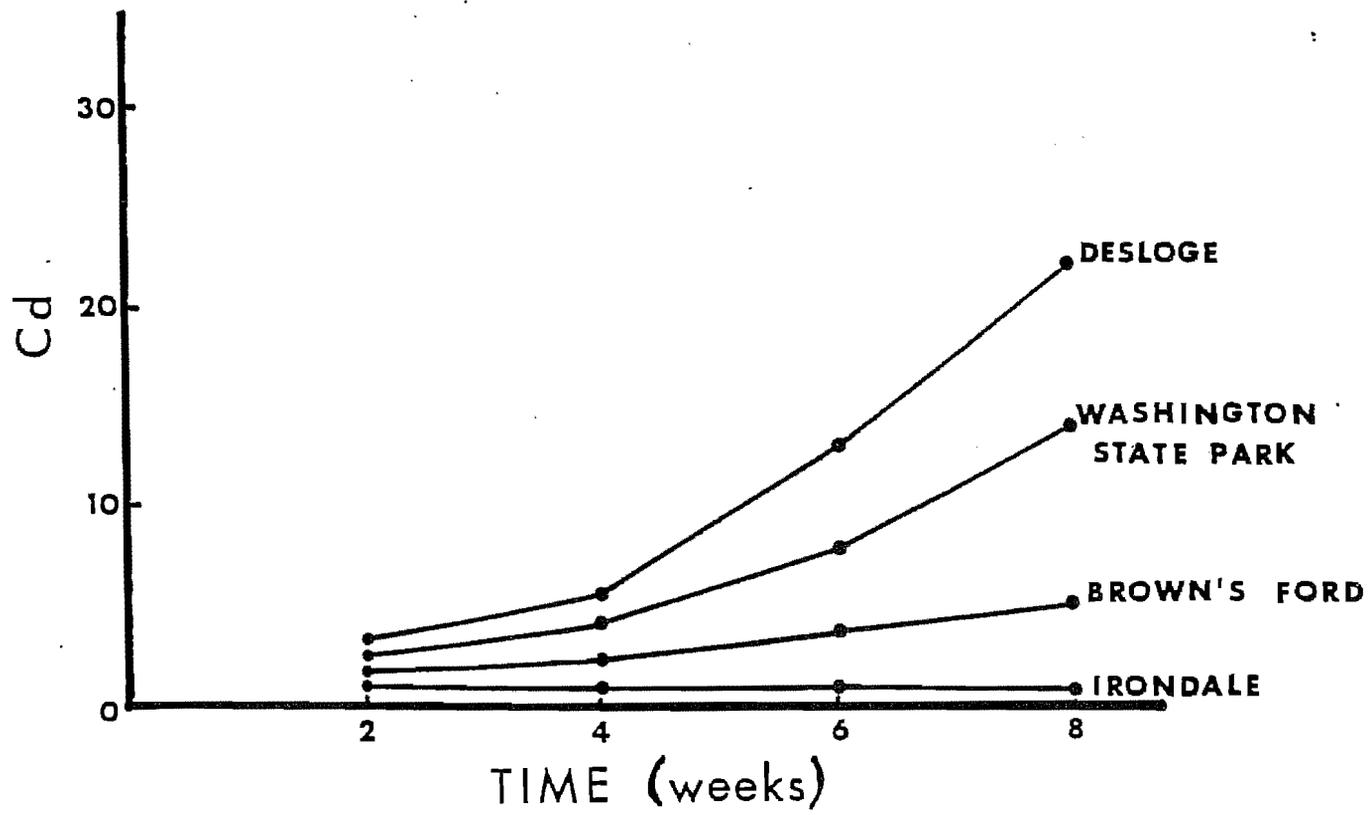
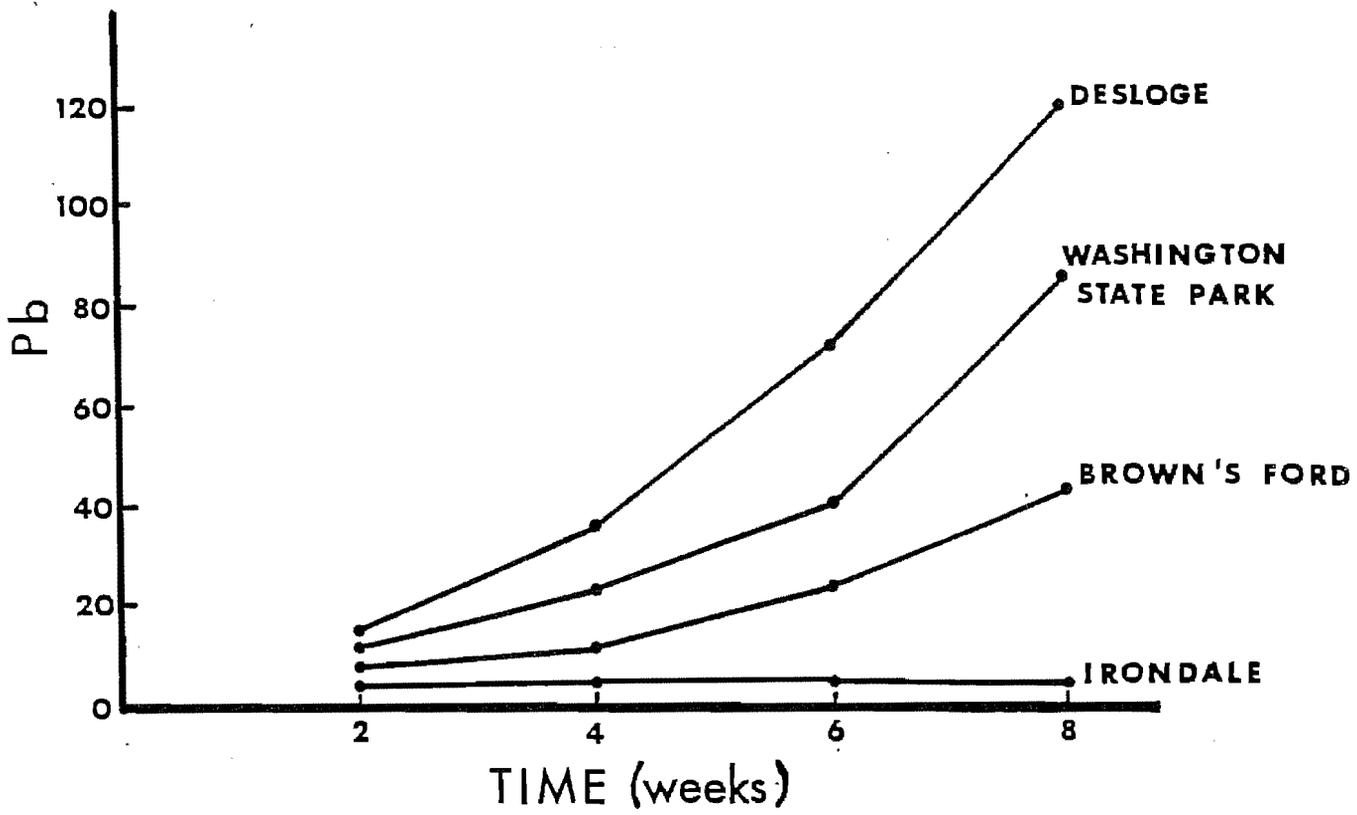


Figure 18. Uptake of metals (mean concentrations, $\mu\text{g/g}$) by mussels exposed for eight weeks at four Big River locations.

comparison). Because levels from the survey represent an equilibrium concentration for resident mussels of a given size, mussels from the exposure study may have attained similar concentrations with longer exposure. Although mussels held at Desloge had highest concentrations after 8 weeks, results from the survey suggest that Pb concentrations in soft tissues at Brown's Ford would, after prolonged exposure, exceed the levels at Desloge, possibly indicating a greater degree of Pb availability. Concentrations of other metals indicated no general trends with time of exposure.

Unlike Pb and Cd, Cu is an essential component of respiratory pigment in the circulatory system of mussels. Although some increase in Cu occurred at Brown's Ford and Desloge, mussels held at Washington State Park and at Irondale showed no change. Zn increases were highest at the locations affected by mine tailings, but no pattern related to length of exposure or to distance downstream was evident. Fe, Mn, and Ba also varied considerably and seemed to follow no pattern with location. High sample-to-sample variability precluded further interpretation of the results for Zn, Fe, Mn and Ba.

In the Black River Basin, Pb and Cd levels were highest in mussels held below Clearwater Lake (Fig. 19). Pb levels here reached a mean of $3.5 \mu\text{g/g}$, which is only slightly less than the concentrations measured in survey mussels (Table 16). Based on the Bourbeuse River mussel mean Pb concentration of $0.12 \mu\text{g/g}$, Pb in mussels below the reservoir increased by a factor of 29. Cd concentrations also increased; levels were slightly higher than those detected in the survey, but appeared to plateau with no significant change between week 6 ($0.78 \mu\text{g/g}$) and week 8 ($0.74 \mu\text{g/g}$). No increases occurred in either Pb or Cd upstream of

BLACK RIVER

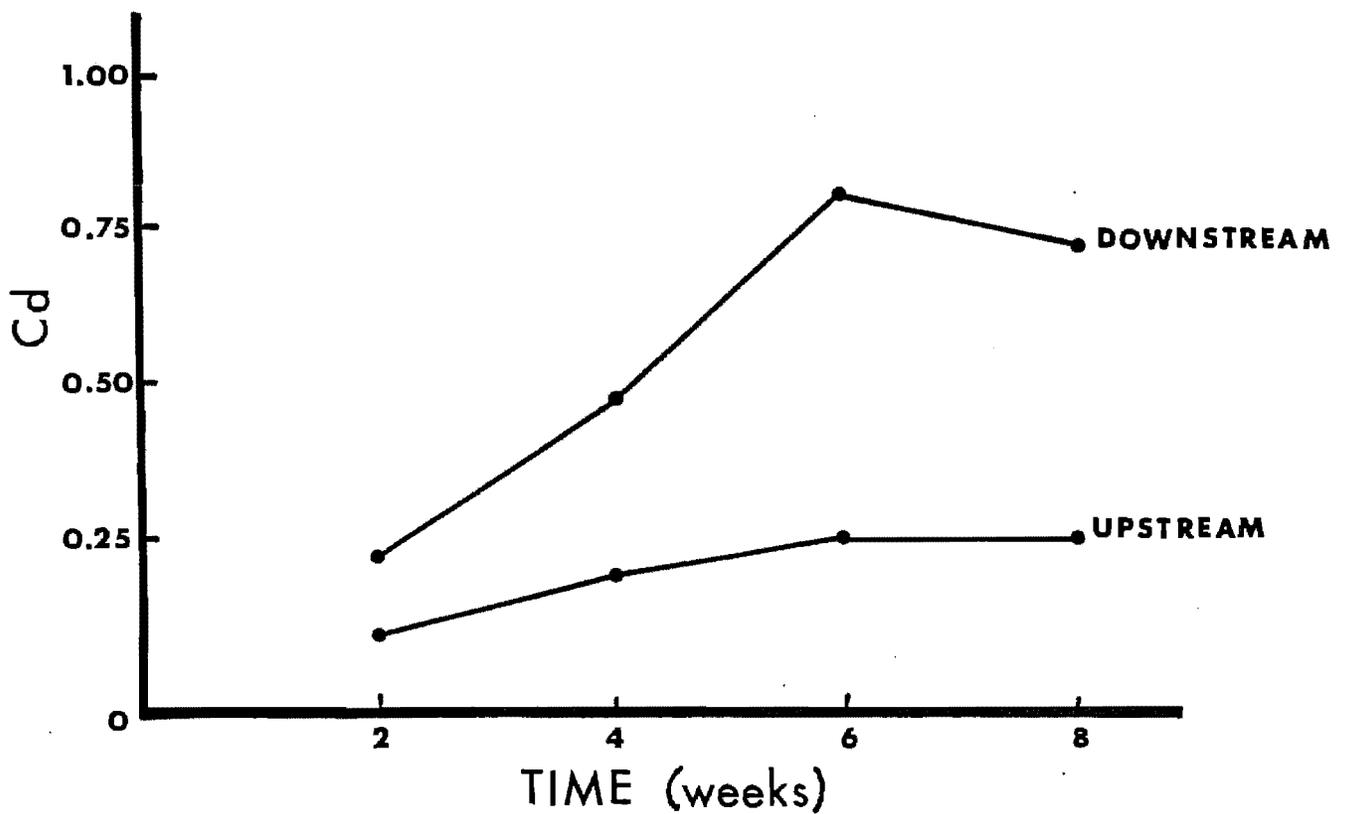
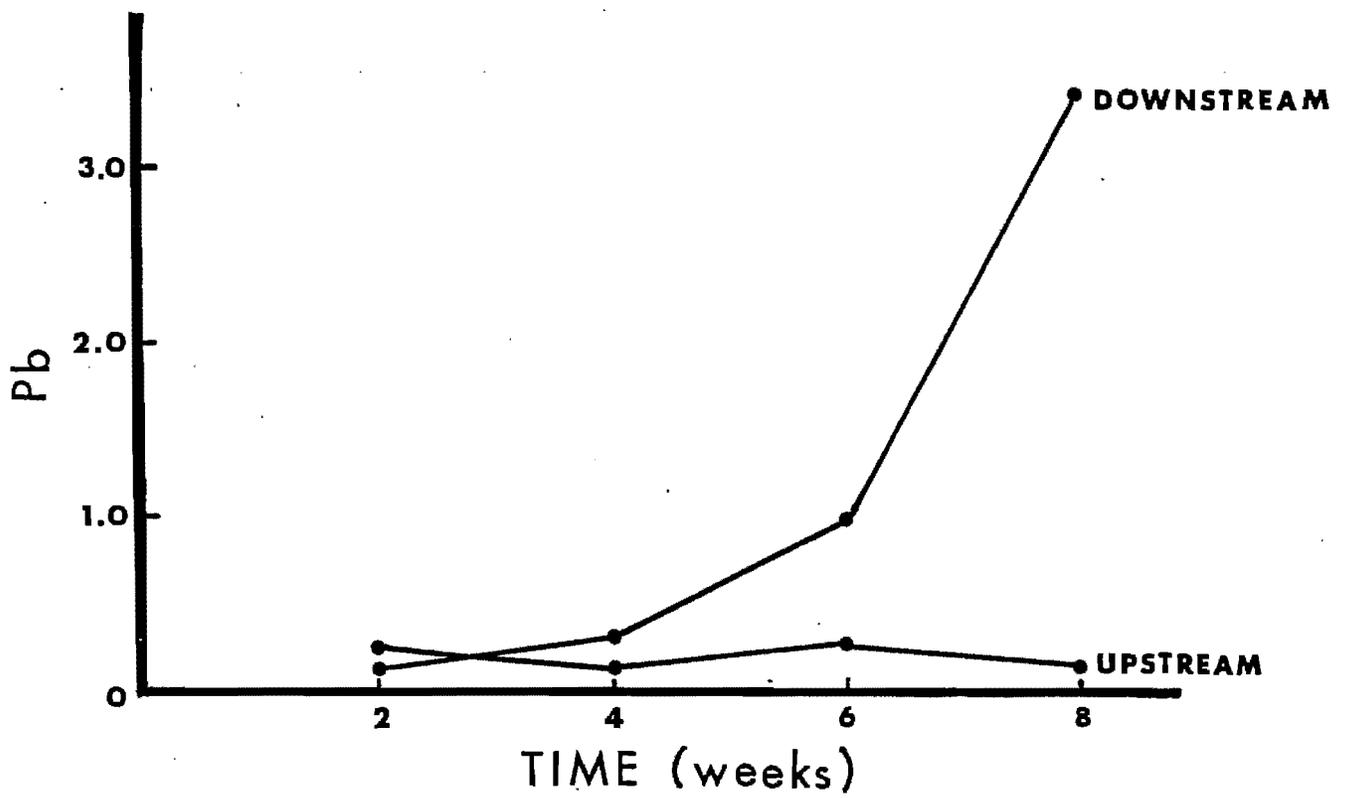


Figure 19. Uptake of metals (mean concentrations, $\mu\text{g/g}$) by mussels exposed for eight weeks at two Black River locations.

Clearwater Lake. This response is not unexpected given levels of Pb and Cd in water and sediments at this location. Accumulations downstream are important; they reflect an increase in available metals in hypolimnionic release waters.

SUMMARY AND CONCLUSIONS

This report represents an intermediate step in the study of trace metal dynamics in the Big and Black River watersheds. Some phases of the investigation have not yet been completed; the estimation of total sediment transport in the Big River, and detailed evaluation of the sequential extraction results relative to metal uptake rates by mussels will be forthcoming. Despite these limitations and the many obvious shortcomings of the data base, the investigation to date has yielded valuable insight into the distribution and bioavailability of metals from Old Lead Belt tailings in the Big River.

There should be no further question as to whether or not metals from tailings eventually find their way into the aquatic biota in reaches downstream of the former Pb mining area. Elevated residues of Pb, Cd and Zn were found in every biological form examined--algae, rooted plants, crayfish, mussels and fish. Furthermore, results of this survey corroborate the findings of the Missouri Department of Conservation--Pb residues in edible portions of some fish from affected reaches of the Big River presently exceed recommended levels for human consumption. Even though Pb contamination of fish during collection and processing may occur, the results of the clean room preparation study and the dose-response relationship observed in the ALA-D vs. blood-Pb investigation indicate that the Pb measured in Big River fish is not an artifact of collection and preparation procedures. Clean-processed fish from affected area had detectable Pb concentrations; ALA-D inhibition by blood-Pb could be predicted with 80% accuracy in suckers from the Big

River; and neither of these measurements should have been influenced by external contamination.

After documenting the distribution of trace metals in the Big River watershed, the investigation sought to identify mechanisms that would explain their distribution and estimate their bioavailability. Examination of historical records and the collection of water quality information under different flow conditions confirmed earlier suspicions; most of the metals derived from Pb mine tailings are transported in the solid phase, and concentrations (as well as mass) in the suspended load increase with flow. Although the analyses are not complete, these results highlight the importance of infrequently-occurring, high-flow events in the movement of solid-phase metals. Liquid-phase transport cannot be discounted; dissolved metals concentrations also increase with flow and must be included in consideration of mass transport. However, of the metals studied, only Ba appears to be transported in the liquid phase to any extent, and only Mn approached Missouri standards for drinking water in filtered samples. However, in unfiltered samples from affected sites on the Big River, residues of most metals exceeded drinking water standards at high flow.

The sequential extraction and caged mussel studies sought to determine the relative availability of metals to the biota at affected and unaffected sites. These investigations revealed that surprisingly little Pb remains in residual (unavailable) form, even in tailings, and that although proportionally more Cd than Pb is unavailable in tailings, it too is rendered available as a result of interaction with the aquatic environment. This was somewhat unexpected; conventional wisdom would assume the metal sulfides to remain insoluble under the highly-buffered,

alkaline, oxidizing environment typical of the Big River. Several mechanisms were postulated for the phenomenon, the most plausible of which center on the abilities of many constituents in the Big River to form stable complexes with the metals and the high concentrations of solid-phase material capable of adsorption. The data suggest that the formation of insoluble metal carbonates and adsorption by dolomite particles and hydrous oxides of Fe and Mn may be the most important of these mechanisms. Organically-bound metals were relatively unimportant in Big River sediments, which was also unexpected.

Investigations of Clearwater Lake revealed relatively low levels of most metals. Sediment concentrations within and downstream of the lake were generally higher than concentrations in the Black River upstream. Several mechanisms were postulated to explain this phenomenon. The most plausible of these includes: (1) differences in the particle-size composition of the sediments at the three sites; (2) selective dissolution and downstream export of certain sediment constituents; and (3) the dissolution and re-precipitation of Pb, Cd, and Zn in the annual cycle of Fe and Mn oxidation/reduction. Some re-precipitation of the metals within the sediments as sulfides also may occur, but metals in the surficial lake sediments are probably solubilized when carbonates are dissolved and hydrous oxides of Mn and Fe are reduced during summer stratification.

With respect to the proposed impoundment of the lower reaches of the Big River, there is no reason to suspect that limnological conditions in such a reservoir would be appreciably different than present conditions in Clearwater Lake. The proposed reservoir would certainly stratify, and reducing conditions would prevail for an

extended period every year. Results of the sequential extraction study suggest that most of the Pb and Cd present in sediments of the lower Big River--the exchangeable, carbonate-bound, and oxide-bound fractions--could be solubilized under such conditions. Leland et al. (1973), commenting on oxide-bound trace metals in Lake Michigan, concluded that "Such alternating conditions of reduction and oxidation result in the release and resorption of trace metals from hydrous oxide surfaces and may lead to a dynamic cycle of some trace elements in lake environments." Likewise, Förstner (1981) concluded that under reducing conditions, Fe and Mn hydrous oxides may represent significant sources of dissolved metals.

The sediments of an impoundment on the lower reaches of the Big River would undoubtedly sequester significant quantities of trace metals (even Clearwater Lake sediments show an enhancement of Pb, Cd, Zn and Cu relative to upstream concentrations). Rickard and Nriagu (1978) describe "...unidirectional flow of Pb into the aerobic sediments." However, the seasonal cycle of oxidation and reduction in the anaerobic environment, with concomitant mixing and distribution of re-precipitated, fine-particulate metals, would probably result in higher concentrations of sediment-bound, and hence, biologically-bound, metals than presently occur in the Big River. Considering that residues in the Big River biota, especially in fish, are already unacceptably high, any further increase in metals levels would only serve to exacerbate an already marginal environmental situation.

The study revealed relatively little about the behavior of Ba originating in the barite mining district except that it is widely dispersed in the lower Big River watershed; that it is transported in

both liquid and solid phases; and that it does not accumulate to any great degree in the biota. Concentrations in filtered water samples from Clearwater Lake were about the same as concentrations upstream and downstream, despite some apparent enhancement in lake sediments.

Concentrations in filtered water samples from the lower Big River were about 50% of the present drinking water standard; the behavior of Ba under reducing conditions should therefore be evaluated more thoroughly.

In the short time span of this investigation, it was not reasonable to consider all possibilities with respect to the geochemistry of Pb. The approach selected--especially the sequential extraction procedure--was the one deemed to provide the most useful information in the shortest period of time. Even the originators of the procedure employed (Tessier et al. 1979), along with other authorities (e.g., Rickard and Nriagu 1978), recognize the obvious shortcomings of such an operational, non-theoretical approach. The aqueous chemistry of the metals in the real-world environment is far too complex to deal with in such a simplistic, one-time exercise. Future studies, if contemplated, should therefore focus on more detailed, thermodynamic investigations of the relationships among the metals and the many possible complexing, chelating, and adsorptive mechanisms that may be involved, and on more accurately quantifying solid-phase flux rates. Even without these refinements, however, the studies completed to date have shown that under present conditions, the metals in Pb mine tailings represent an available source of potentially toxic material to the downstream aquatic environment. These metals can in no way be considered benign or permanently sequestered in their present state. They are actively transported by the river and are accumulated by the biota.

As a final consideration, Kramer (1976), citing a report by Parsons (1947), reported that Pb mining activities in the Old Lead Belt produced some 227 million MT of tailings. Much of this material probably remains in the Big River watershed. Any proposed developments within the watershed--public works projects, major shifts in land-use patterns, and ameliorative actions included--must therefore be evaluated in terms of their potential effects on the distribution and availability of the significant quantities of toxic metals present in these tailings.

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Appendix A. Dissolved (D) and total (T) metals concentrations and concentrations of other water constituents (all in mg/L) in water samples from sites on the Big and Black Rivers and from Clearwater Lake.

 SITE=BROWN'S FORD

OBS	DATES	LOC	DEPTH	TEMP	DTEMP	TTEMP	DTEMP	TTEMP	DTEMP	TTEMP	DTEMP	TTEMP	DTEMP	TTEMP	DTEMP	TTEMP	DTEMP	TTEMP	DTEMP	TTEMP
22	APR 78	USACE	18700.0	0.006	1.3000	0.001	0.006	0.0170	0.760	0.004	0.082	-	-	-	-	0.005	0.058	0.120		
23	APR 78	USACE	20900.0	0.009	1.3000	0.001	0.006	0.0220	0.720	0.004	0.072	-	-	-	-	0.005	0.048	0.260		
24	APR 78	USACE	23500.0	0.013	1.2600	0.001	0.006	0.0470	0.710	0.005	0.068	-	-	-	-	0.005	0.057	0.220		
25	APR 78	USACE	27000.0	0.015	1.1800	0.001	0.005	0.0520	0.620	0.008	0.081	-	-	-	-	0.005	0.050	0.380		
26	APR 78	USACE	29200.0	0.011	1.2000	0.001	0.006	0.0270	0.660	0.005	0.075	-	-	-	-	0.005	0.048	0.220		
27	APR 78	USACE	30800.0	0.013	1.3000	0.001	0.006	0.0370	0.590	0.006	0.078	-	-	-	-	0.005	0.042	0.390		
28	APR 78	USACE	30900.0	0.009	1.2000	0.001	0.006	0.0220	0.600	0.004	0.064	-	-	-	-	0.005	0.036	0.150		
29	APR 78	USACE	31600.0	0.006	1.1600	0.001	0.006	0.0220	0.540	0.006	0.068	-	-	-	-	0.005	0.049	0.120		
30	APR 78	USACE	32400.0	0.019	1.1150	0.001	0.006	0.0600	0.535	0.010	0.059	-	-	-	-	0.005	0.042	0.240		
31	APR 78	USACE	33100.0	0.010	1.1600	0.001	0.006	0.0300	0.605	0.004	0.077	-	-	-	-	0.005	0.042	0.110		
32	APR 78	USACE	33500.0	0.007	0.9500	0.001	0.005	0.0300	0.600	0.010	0.068	-	-	-	-	0.005	0.047	0.090		
33	APR 78	USACE	34200.0	0.006	1.0350	0.001	0.006	0.0270	0.570	0.006	0.049	-	-	-	-	0.005	0.044	0.060		
34	APR 78	USACE	34000.0	0.004	1.0350	0.001	0.114	0.0200	0.790	0.005	0.057	-	-	-	-	0.005	0.043	0.080		
35	APR 78	USACE	34200.0	0.012	1.1600	0.001	0.010	0.0320	0.570	0.016	0.067	-	-	-	-	0.005	0.046	0.280		
36	APR 78	USACE	34300.0	0.006	1.2850	0.001	0.008	0.0340	0.605	0.006	0.068	-	-	-	-	0.005	0.048	0.110		
37	APR 78	USACE	34200.0	0.007	1.4100	0.001	0.009	0.0220	0.720	0.005	0.073	-	-	-	-	0.005	0.049	0.110		
38	APR 78	USACE	34200.0	0.008	1.4500	0.001	0.009	0.0450	0.670	0.005	0.066	-	-	-	-	0.005	0.052	0.130		
39	APR 78	USACE	34200.0	0.008	1.4500	0.001	0.009	0.0450	0.670	0.005	0.066	-	-	-	-	0.005	0.052	0.130		

OBS	TEMP	DTEMP	TTEMP	DEPTH	TEMP	DTEMP	TTEMP	DEPTH	TEMP	DTEMP	TTEMP	DEPTH	TEMP	DTEMP	TTEMP	DEPTH	TEMP	DTEMP	TTEMP	DEPTH	TEMP	DTEMP	TTEMP
22	26.20	0.0500	1.350	-	-	-	-	-	-	-	-	-	56	0.16	0.02	-	0.59	0.03	16.10	46.80	37.10	-	-
23	29.80	0.0500	1.500	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	7.00	38.20	54.80	-	-
24	29.20	0.0500	1.200	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	12.70	52.60	34.70	-	-
25	26.20	0.0500	1.400	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	7.00	58.30	34.70	-	-
26	24.90	0.0500	1.350	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	15.40	44.30	40.30	-	-
27	24.00	0.0500	1.350	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5.70	63.80	30.50	-	-
28	20.00	0.0500	1.250	-	-	-	-	-	-	-	-	-	58	0.23	0.02	-	0.55	0.04	5.20	77.90	16.90	-	-
29	23.00	0.0500	1.200	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	9.80	51.80	38.40	-	-
30	20.00	0.0500	1.070	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5.60	73.80	20.60	-	-
31	24.00	0.0500	1.170	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	14.80	46.90	38.30	-	-
32	23.80	0.0500	1.170	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	16.50	46.30	37.20	-	-
33	21.40	0.0500	1.120	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6.40	54.90	38.70	-	-
34	21.60	0.0500	1.200	-	-	-	-	-	-	-	-	-	58	0.21	0.02	-	0.54	0.06	5.50	87.90	6.60	-	-
35	23.00	0.0500	1.400	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	11.80	53.60	34.60	-	-
36	25.40	0.0500	1.525	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6.40	54.40	39.20	-	-
37	28.00	0.0500	1.830	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5.20	65.60	29.20	-	-
38	27.80	0.0500	1.675	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.90	59.60	35.40	-	-
39	27.80	0.0500	1.675	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.90	59.70	35.40	-	-

-----SITE=BROWN'S FORD-----

	D	F	D	D	D	D	D	D	D	D	D	D	D	D	D	D	D	D	D	D
O	A	L	L	P	P	T	C	C	Z	Z	C	C	B	B	A	A	A	A	A	F
S	E	B	W	H	B	B	D	D	N	N	U	U	A	A	G	G	S	S	S	E
40	APR	78	USACE	34200.0	0.007	1.1500	0.001	0.007	0.0220	0.580	0.007	0.057	-	-	-	-	0.005	0.045	0.150	
41	APR	78	USACE	34500.0	0.008	1.2450	0.001	0.008	0.0220	0.655	0.006	0.060	-	-	-	-	0.005	0.048	0.150	
42	APR	78	USACE	34300.0	0.010	1.1600	0.001	0.008	0.0270	0.635	0.005	0.039	-	-	-	-	0.005	0.046	0.170	
43	APR	78	USACE	33800.0	0.008	1.0350	0.001	0.007	0.0350	0.535	0.006	0.047	-	-	-	-	0.005	0.039	0.150	
44	APR	78	USACE	33100.0	0.011	1.0350	0.001	0.008	0.0350	0.600	0.006	0.048	-	-	-	-	0.005	0.038	0.200	
45	APR	78	USACE	29400.0	0.007	0.6600	0.001	0.005	0.0240	0.305	0.005	0.056	-	-	-	-	0.005	0.029	0.180	
46	APR	78	USACE	27000.0	0.014	0.8250	0.001	0.006	0.1550	0.410	0.012	0.080	-	-	-	-	0.005	0.028	0.240	
47	APR	78	USACE	24300.0	0.018	0.7850	0.001	0.004	0.0570	0.345	0.009	0.068	-	-	-	-	0.005	0.019	0.280	
48	APR	78	USACE	21600.0	0.007	0.7400	0.001	0.066	0.0350	0.675	0.008	0.071	-	-	-	-	0.005	0.021	0.110	
49	JUL	80	CNFRL	95.6	0.005	0.0425	0.001	0.001	0.0125	0.029	0.005	0.005	0.467	0.489	0.001	0.001	-	-	0.010	
50	APR	81	CNFRL	650.0	0.007	0.0840	0.001	0.001	0.0100	0.030	0.006	0.011	0.320	0.380	0.001	0.001	-	-	0.045	
51	MAY	81	CNFRL	11900.0	0.026	0.4400	0.001	0.001	0.0500	0.170	0.037	0.024	0.100	0.220	0.001	0.001	-	-	0.140	

	T	D	T	D	P	T	H	C	S	D	S	O	T	T	A	T	O	P	P	P	A				
O	T	D	T	D	P	T	H	C	S	D	S	O	T	T	A	T	O	P	P	P	A				
S	E	N	N	O	H	K	D	D	D	D	D	L	B	L	F	D	E	E	N	S	S				
40	23.20	0.0500	1.270	-	-	-	-	-	-	-	-	-	-	-	71	0.24	0.03	-	0.68	0.03	8.70	51.50	39.80	-	-
41	24.90	0.0500	1.450	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	10.50	49.90	39.60	-	-
42	23.00	0.0500	1.300	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.40	52.10	43.50	-	-
43	18.40	0.0500	0.945	-	-	-	-	-	-	-	-	-	-	-	48	0.19	0.02	-	0.47	0.02	7.70	53.30	39.00	-	-
44	18.60	0.0500	1.020	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	12.30	48.20	39.50	-	-
45	13.60	0.0500	0.845	-	-	-	-	-	-	-	-	-	-	-	42	0.18	0.02	-	0.40	0.02	7.20	53.20	39.60	-	-
46	13.80	0.0500	0.845	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	19.40	40.60	42.00	-	-
47	9.30	0.0500	0.690	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.20	49.10	46.70	-	-
48	10.40	0.0500	0.590	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	17.20	42.70	40.10	-	-
49	0.27	0.0305	0.070	6.2	7.4	236	274	489	298	9	2	3	5	44	4	0.11	0.01	0.01	0.03	0.01	0.00	87.86	12.14	27.0	24.0
50	0.61	0.0130	0.130	8.2	7.5	171	200	379	226	30	5	8	4	24	14	0.28	0.02	0.04	0.01	0.01	4.09	91.09	4.82	17.0	17.5
51	0.50	0.0470	0.340	8.4	7.6	70	88	178	128	145	25	72	8	19	32	0.37	0.01	0.08	0.21	0.03	23.18	49.25	27.57	11.5	11.9

----- SITE=BLK R UP -----

	D	L	F	D	T	D	T	D	T	D	T	D	T	D	T	D	T	D	T
OBS	DATE	TYPE	DEPTH	DEPTH	DEPTH	DEPTH	DEPTH	DEPTH	DEPTH										
58	JUL 80	CNFRL	-	0.005	0.005	0.001	0.001	0.01	0.01	0.005	0.005	0.047	0.0435	0.001	0.001	-	-	0.0175	0.025
59	APR 81	CNFRL	-	0.005	0.005	0.001	0.001	0.01	0.01	0.005	0.005	0.037	0.0340	0.001	0.001	-	-	0.0120	0.038
60	MAY 81	CNFRL	-	0.005	0.005	0.001	0.001	0.01	0.01	0.005	0.005	0.025	0.0260	0.001	0.001	-	-	0.0180	0.120

	D	T	D	P	A	A	O	L	L	S	U	C	U	C	A	I	M	H	H	A	I	L	E	M	P	
OBS	DATE	TYPE	DEPTH																							
58	0.0085	0.007	8.8	7.7	123	128	253	177	1	1	1	3	12	2	0.11	0.01	0.05	0.01	0.01	0	63.68	36.32	31.0	25.0		
59	0.0040	0.007	9.0	7.5	125	146	287	162	4	3	2	4	21	4	0.19	0.01	0.01	0.05	0.01	0	84.75	15.25	22.0	16.7		
60	0.0300	0.015	9.5	8.0	65	98	163	111	9	1	13	2	14	12	0.18	0.01	0.02	0.05	0.01	0	86.91	13.09	24.5	14.7		

----- SITE=BLK R DN -----

	D	L	F	D	T	D	T	D	T	D	T	D	T	D	T	D	T	D	T
OBS	DATE	TYPE	DEPTH	DEPTH	DEPTH	DEPTH	DEPTH	DEPTH	DEPTH	DEPTH									
61	JUL 80	CNFRL	200	0.005	0.005	0.001	0.001	0.01	0.01	0.005	0.005	0.0705	0.068	0.001	0.001	-	-	0.0145	
62	APR 81	CNFRL	1040	0.005	0.005	0.001	0.001	0.01	0.01	0.005	0.005	0.0370	0.038	0.001	0.001	-	-	0.0100	
63	MAY 81	CNFRL	160	0.005	0.005	0.001	0.001	0.01	0.01	0.005	0.005	0.0270	0.029	0.001	0.001	-	-	0.0900	

	D	T	D	P	A	A	O	L	L	S	U	C	U	C	A	I	M	H	H	A	I	L	E	M	P	
OBS	DATE	TYPE	DEPTH																							
61	0.105	0.207	0.274	7.6	7.4	120	122	236	145	6	2	3	3	12	2	0.06	0.01	0.05	0.02	0.01	0	82.22	17.78	34	26.0	
62	0.032	0.008	0.032	8.5	7.7	113	138	270	156	3	2	0	5	24	6	0.29	0.01	0.01	0.02	0.01	0	50.93	49.07	18	14.9	
63	0.120	0.007	0.032	8.8	8.0	72	91	186	101	4	1	2	2	14	6	0.31	0.01	0.06	0.02	0.01	0	81.77	18.23	22	15.0	

 SITE=DESLOGE

OBS	DATE	L	D	D F E		D	T	D	T	D	T	D	T	D	T	D	T	D	T
				LP	OT														
52	JUL 80	CNFR	45.3	0.0195	0.041	0.002	0.004	0.313	0.359	0.005	0.005	0.1465	0.137	0.001	0.001	-	-	0.0165	0.09
53	APR 81	CNFR	298.0	0.0110	0.085	0.001	0.001	0.060	0.110	0.005	0.005	0.0900	0.094	0.001	0.001	-	-	0.0420	0.42
54	MAY 81	CNFR	932.0	0.0120	0.110	0.002	0.004	0.100	0.160	0.005	0.006	0.0650	0.071	0.001	0.001	-	-	0.0450	0.63

OBS	DATE	L	D	P	A	L	R	N	I	O	L	B	L	F	D	E	N	S	P	P	P	A	C	I	C	R	W
52	0.070	0.078	8.7	8.3	202	336	651	454	4	3	1	9	144	2	0.81	0.02	0.09	0.06	0.03	0.00	97.08	2.92	27.5	25.0			
53	0.026	0.077	8.4	7.7	133	170	329	199	8	3	5	3	30	16	0.77	0.02	0.03	0.04	0.01	0.00	63.12	36.88	19.0	18.0			
54	0.054	0.120	8.8	7.6	95	126	245	147	31	7	12	2	26	15	0.80	0.01	0.08	0.07	0.02	18.76	55.60	25.64	21.0	14.4			

 SITE=IRONDALE

OBS	DATE	L	D	P	A	L	R	N	I	O	L	B	L	F	D	T	D	T	D	T	D	T	D	T	D	T
55	JUL 80	CNFR	7.1	0.005	0.005	0.001	0.001	0.01	0.01	0.005	0.005	0.153	0.154	0.001	0.001	-	-	0.018								
56	APR 81	CNFR	160.0	0.005	0.005	0.001	0.001	0.01	0.01	0.005	0.005	0.075	0.078	0.001	0.001	-	-	0.022								
57	MAY 81	CNFR	300.0	0.005	0.005	0.001	0.001	0.01	0.01	0.005	0.005	0.059	0.066	0.001	0.001	-	-	0.028								

OBS	DATE	L	D	P	A	L	R	N	I	O	L	B	L	F	D	T	D	T	D	T	D	T	D	T	D	T
55	0.318	0.023	0.115	5.8	7.8	196	210	381	225	10	2	4	3	16	3	0.12	0.01	0.02	0.02	0.01	0	72.01	27.99	26.0	25.2	
56	0.260	0.025	0.068	9.1	7.6	121	142	280	158	5	2	3	2	18	10	0.28	0.01	0.01	0.05	0.01	0	87.09	12.91	17.0	17.0	
57	0.230	0.018	0.065	8.8	7.7	100	124	245	141	11	5	4	2	17	8	0.77	0.01	0.01	0.04	0.01	0	65.02	34.98	14.5	13.6	

Appendix B. Metals concentrations in sequentially-extracted sediment fractions ($\mu\text{g/g}$, dry weight), particle size distributions for individual samples (%), and total organic carbon (TOC) concentrations (mg/g , dry weight). The following suffixes identify the fractions: E, exchangeable; C, carbonate-bound; OX, oxide-bound; O, bound to organic matter; and R, residual. T- prefixes indicate metals concentrations (total) determined by conventional acid digestion and AA analyses of separate sample aliquots.

SEQUENTIAL EXTRACTION OF SEDIMENTS

OBS	LOC	DESCRP	PCTSAND	PCTSILT	PCTCLAY	TOC	PBE	PBC	PBOX	PBO	PBR	TPB	CDE	CDC	CDOX	CDO	CDR	TCD	ZNE
1	MIN FORK	RIFFLE	66.0854	20.2877	13.6269	6.53	4	87	86	30	38.4	200	0.4	0.6	0.9	0.4	0.02	1.60	0.4
2	MIN FORK	POOL	90.4875	7.1438	2.3687	8.46	4	149	111	42	42.5	330	0.4	0.4	1.5	0.4	0.06	0.84	0.4
3	BRN'S FD	RIFFLE	87.7358	7.8871	4.3771	1.66	4	508	874	105	140.0	900	2.7	4.9	1.7	1.4	0.70	7.50	9.6
4	BRN'S FD	RIFFLE	95.8835	2.9500	1.1665	0.41	4	215	376	50	42.4	630	1.4	1.4	0.6	0.4	0.50	3.30	5.4
5	BRN'S FD	RIFFLE	90.7609	4.1614	5.0778	2.52	4	143	197	23	44.6	420	0.6	0.6	0.4	0.4	0.02	2.90	3.6
6	BRN'S FD	POOL	72.4328	23.0532	4.5140	5.43	15	1261	770	83	105.2	1800	0.6	4.2	1.7	0.5	0.02	5.60	6.2
7	BRN'S FD	POOL	49.9588	36.6011	13.4401	9.16	17	1296	926	89	150.7	2200	0.7	4.2	2.4	0.5	0.82	7.20	5.6
8	BRN'S FD	POOL	42.6295	38.0557	19.3148	9.04	34	2332	1486	105	176.0	3900	0.6	4.7	3.3	1.2	1.20	9.30	7.3
9	DESLOGE	RIFFLE	92.1700	4.2725	3.5575	3.98	19	1023	1178	115	404.8	2800	1.9	1.0	6.4	1.0	4.41	18.00	16.9
10	DESLOGE	RIFFLE	94.2663	3.5604	2.1733	3.57	11	1509	1166	132	142.9	2900	3.1	9.0	4.4	1.0	27.30	57.00	35.7
11	DESLOGE	RIFFLE	92.6555	3.3197	4.0248	5.13	20	1444	994	80	101.5	2800	2.3	4.3	5.5	1.1	7.25	21.00	27.7
12	DESLOGE	POOL	99.8200	0.0577	0.1223	0.05	13	525	569	81	565.6	1600	1.0	5.6	2.1	0.8	27.22	44.00	16.2
13	DESLOGE	POOL	99.5512	0.2078	0.2410	0.12	25	616	618	117	1215.0	2200	0.8	5.8	2.2	1.0	44.70	56.00	17.8
14	DESLOGE	POOL	99.2413	0.4637	0.2950	0.19	24	652	580	138	830.8	2100	0.6	5.9	2.2	2.0	35.00	47.00	15.0
15	IRONDALE	RIFFLE	95.6703	3.5158	0.8139	2.14	4	4	16	4	18.0	33	0.4	0.4	0.4	0.4	0.02	0.20	0.4
16	IRONDALE	RIFFLE	96.2937	2.7327	0.9736	2.16	4	4	23	7	17.1	50	0.4	0.4	0.4	0.4	0.02	0.10	0.4
17	IRONDALE	RIFFLE	97.3109	1.8017	0.8874	0.86	4	4	25	4	11.3	29	0.4	0.4	0.4	0.4	0.02	0.09	0.4
18	IRONDALE	POOL	84.8437	12.6041	2.5522	6.00	4	6	34	10	10.7	53	0.4	0.4	0.4	0.4	0.02	0.20	0.4
19	IRONDALE	POOL	94.3333	4.9116	0.7551	5.08	4	7	23	7	8.3	35	0.4	0.4	0.4	0.4	0.02	0.10	0.4
20	IRONDALE	POOL	89.8758	8.8199	1.3042	6.77	4	7	19	7	8.1	39	0.4	0.4	0.4	0.4	0.02	0.20	0.4
21	BLK R UP	RIFFLE	98.5915	0.9317	0.4768	1.24	4	4	4	4	3.9	10	0.4	0.4	0.4	0.4	0.02	0.09	0.4
22	BLK R UP	RIFFLE	99.0805	0.3429	0.5765	0.32	4	4	5	4	4.2	10	0.4	0.4	0.4	0.4	0.02	0.09	0.4
23	BLK R UP	RIFFLE	99.1054	0.4249	0.4696	0.77	4	4	4	4	3.4	10	0.4	0.4	0.4	0.4	0.02	0.09	0.4
24	BLK R UP	POOL	97.6873	1.4068	0.9059	0.83	4	4	4	4	4.3	20	0.4	0.4	0.4	0.4	0.02	0.09	0.4
25	BLK R UP	POOL	98.5091	0.5644	0.9265	3.41	4	4	5	4	3.9	12	0.4	0.4	0.4	0.4	0.02	0.09	0.4

OBS	ZHC	ZNOX	ZNO	ZNR	TZN	CUE	CUC	CUOX	CUO	CUR	TCU	BAE	BAC	BAOX	BAO	BAR	TBA	FER	TFE	MNR	TMN
1	71.1	136.0	22.0	120	360	0.4	0.4	0.5	5.1	16.8	29	126.0	283.0	89.6	61.9	2400	3700	13600	15000	79	660
2	60.4	149.0	26.4	157	200	0.4	0.4	0.4	6.3	19.0	15	122.0	310.0	97.7	52.7	2231	1500	15702	11000	91	270
3	196.0	228.0	64.1	330	490	0.4	2.9	2.6	12.5	19.0	33	88.0	83.1	92.5	34.0	1653	1200	19834	14000	107	1200
4	74.4	125.0	28.9	149	220	0.4	1.7	2.4	4.5	7.5	10	50.8	30.0	66.3	24.8	891	460	13699	7100	65	430
5	40.1	84.0	6.7	44	440	0.4	0.9	1.5	2.0	0.2	21	28.9	38.7	42.5	27.9	1228	3400	5848	9200	36	600
6	192.0	217.0	22.2	145	420	0.4	0.8	1.0	19.1	36.2	48	82.6	67.8	85.7	29.2	1184	2900	14474	14000	92	1200
7	166.0	217.0	25.2	171	520	0.4	0.5	1.0	20.9	37.7	51	75.3	66.8	87.5	23.1	1164	1800	15068	12000	109	1300
8	190.0	286.0	58.8	200	660	0.4	0.4	1.2	39.0	41.6	76	110.0	70.7	89.9	27.7	1040	1600	16000	21000	104	1500
9	409.0	396.0	45.0	1429	970	0.4	4.1	0.5	18.9	113.1	47	12.9	19.1	105.0	12.8	250	160	39286	23000	2976	3300
10	957.0	489.0	53.4	452	3160	1.0	3.5	0.9	34.3	56.4	45	25.3	35.5	36.8	5.4	302	160	17460	21000	579	3100
11	659.0	413.0	45.1	507	1090	0.4	0.9	0.4	34.5	60.1	76	29.2	25.4	17.7	8.8	232	240	15942	29000	536	4500
12	209.0	222.0	26.2	1060	2700	0.4	2.6	0.4	6.6	27.8	27	4.9	4.6	23.4	1.9	59	74	13907	27000	927	4100
13	206.0	206.0	36.8	1301	3040	0.4	4.0	0.4	16.9	34.2	36	6.9	7.1	12.4	4.6	66	65	14384	29000	959	3700
14	193.0	177.0	65.7	1474	2440	0.4	1.3	0.4	14.4	32.7	32	1.9	6.8	16.6	4.2	56	60	12179	28000	769	3900
15	4.0	9.6	1.9	33	51	0.4	0.4	0.4	1.1	8.5	13	30.2	33.2	46.6	2.1	275	280	14504	12000	70	1200
16	7.5	21.7	2.3	43	66	0.4	0.4	0.9	1.5	12.4	18	42.5	49.0	64.6	15.6	349	330	17829	14000	101	1500
17	2.8	7.6	1.1	29	43	0.4	0.4	0.4	0.8	6.4	12	19.1	19.4	52.5	1.5	167	250	10000	9200	60	790
18	14.9	22.2	3.0	91	82	0.4	1.0	1.0	5.8	22.3	21	68.6	97.6	79.1	18.7	275	480	21667	20000	125	2300
19	7.0	13.4	2.0	41	65	0.4	0.7	0.4	1.8	13.1	19	57.2	65.1	50.9	17.8	204	300	17518	15000	109	1200
20	6.8	12.3	2.1	41	77	0.4	0.4	0.4	1.9	12.3	35	67.1	58.5	48.8	11.9	282	410	15217	18000	101	1600
21	2.1	3.7	0.8	14	28	0.4	0.4	0.5	1.0	4.1	9	3.3	2.7	1.1	1.0	71	85	3622	5400	18	200
22	2.5	5.8	1.0	14	26	0.4	0.4	2.4	1.6	5.1	11	8.9	6.2	2.4	1.0	83	78	4916	4600	25	210
23	1.2	3.5	0.6	11	26	0.4	0.4	0.7	0.7	3.8	5	5.2	2.1	1.3	1.0	63	87	3829	4700	22	170
24	1.8	4.5	0.5	12	32	0.4	0.4	2.6	1.2	4.2	9	6.9	4.9	1.2	1.0	80	89	4380	6800	19	260
25	2.7	5.0	0.8	15	30	0.4	0.4	0.5	1.3	5.2	9	7.7	3.3	2.2	1.0	74	79	5469	5700	30	170

SEQUENTIAL EXTRACTION OF SEDIMENTS

OBS	LOC	DESCRP	PCTSAND	PCTSILT	PCTCLAY	TOC	PBE	PBC	PBOX	PBO	PBR	TPB	CDE	CDC	CDOX	CDO	CDR	TCD	ZNE
26	BLK R UP	POOL	99.4671	0.3322	0.20065	1.26	4	4	5	4	4.7	10	0.4	0.4	0.4	0.4	0.02	0.09	0.4
27	BLK R DN	RIFFLE	94.1818	2.9250	2.89320	3.28	4	4	101	17	24.1	158	0.4	0.4	0.4	0.4	0.02	0.55	0.4
28	BLK R DN	RIFFLE	96.8326	1.4672	1.70021	4.26	4	4	22	16	29.5	55	0.4	0.4	0.4	0.4	0.12	0.47	0.4
29	BLK R DN	RIFFLE	94.3590	2.7879	2.85317	4.92	4	4	57	11	23.1	80	0.4	0.4	0.5	0.4	0.08	0.47	0.4
30	BLK R DN	POOL	93.1373	2.8478	4.01492	2.57	4	4	54	4	7.9	75	0.4	0.4	0.4	0.4	0.02	0.40	0.4
31	BLK R DN	POOL	84.5045	8.1899	7.30555	5.29	4	4	47	18	21.8	63	0.4	0.4	0.4	0.4	0.02	0.20	0.4
32	BLK R DN	POOL	93.8511	2.7637	3.38518	3.71	4	4	41	16	20.7	62	0.4	0.4	0.4	0.4	0.02	0.20	0.4
33	CW LAKE	POOL	87.1795	12.2645	0.55601	5.60	4	20	26	12	21.5	86	0.4	0.4	0.4	0.4	0.06	0.50	0.4
34	CW LAKE	POOL	89.8575	8.8834	1.25916	6.00	4	19	23	11	11.8	87	0.4	0.4	0.4	0.4	0.02	0.82	0.4
35	CW LAKE	POOL	97.9442	1.4700	0.58576	5.20	4	18	26	12	20.0	93	0.4	0.4	0.5	0.4	0.02	0.56	0.4
36	TAILINGS	.	99.4110	0.0640	0.52500	.	40	476	605	70	257.3	1500	1.8	4.5	0.9	0.7	6.50	10.00	18.0
37	TAILINGS	.	99.7750	0.0480	0.11700	.	36	539	734	57	219.5	1800	1.5	4.8	1.1	0.4	7.30	12.00	17.5
38	TAILINGS	.	98.9010	0.1360	0.96300	.	35	573	859	180	1103.0	2200	2.0	4.4	1.0	0.4	7.06	10.00	16.0
39	WS PARK	RIFFLE	93.3567	4.1464	2.49697	2.88	14	1038	775	90	112.8	1590	2.0	6.5	2.2	0.4	0.71	5.10	10.2
40	WS PARK	POOL	97.9474	0.8820	1.17057	1.44	4	705	825	74	86.9	1350	2.0	5.5	1.3	0.4	0.68	1.80	7.3

OBS	ZNC	ZNOX	ZNO	ZNR	TZN	CUE	CUC	CUOX	CUO	CUR	TCU	BAE	BAC	BAOX	BAO	BAR	TBA	FER	TFE	MNR	TMN
26	2.3	4.1	0.6	13	24	0.4	0.4	0.4	0.9	5.1	5	5.2	2.9	1.9	1.0	112	54	5176	4100	27	78
27	24.7	37.8	8.0	88	83	0.4	0.4	1.5	7.6	22.4	75	31.5	168.0	398.0	67.4	224	340	20690	13000	157	7400
28	25.5	34.5	6.8	95	84	0.4	0.4	1.4	6.4	31.1	32	103.0	175.0	386.0	57.9	410	420	32787	15000	213	8900
29	16.0	26.8	5.2	65	83	0.4	0.4	0.4	4.5	21.3	30	58.5	98.8	275.0	60.5	213	380	21296	14000	148	7700
30	18.2	31.5	5.1	66	100	0.4	0.4	2.3	5.8	18.9	49	56.6	130.6	237.0	27.8	216	360	17105	15000	105	7200
31	12.0	21.4	5.7	44	69	0.4	0.4	0.5	5.9	14.5	22	30.9	65.5	166.0	50.3	185	340	12097	12000	113	5800
32	6.5	22.0	5.0	45	83	0.4	0.4	1.0	6.3	16.5	42	23.5	66.5	160.0	49.0	140	280	14876	12000	115	4300
33	8.6	17.8	6.9	83	160	0.4	0.4	1.0	6.6	30.6	45	70.0	41.0	4.7	22.2	165	440	24793	35000	157	2100
34	8.2	16.1	7.1	95	160	0.4	0.4	0.9	6.5	29.1	42	64.2	42.0	3.7	23.7	268	450	27559	36000	181	1900
35	8.2	17.9	6.6	107	170	0.4	0.4	1.2	6.5	30.0	89	87.4	41.2	5.0	21.0	190	450	26446	34000	181	1900
36	167.0	84.2	9.5	397	720	0.4	17.4	0.4	22.2	117.6	178	2.2	9.4	12.4	3.0	29	280	11029	15000	882	5500
37	166.0	105.0	9.4	439	900	0.6	18.5	0.4	20.2	79.3	200	2.3	6.5	6.0	3.1	33	310	10976	17000	915	4200
38	158.0	94.9	7.0	408	700	0.5	16.5	0.4	10.7	81.5	198	2.2	3.5	3.6	4.6	33	290	13043	20000	1196	6000
39	260.0	295.0	27.0	187	370	0.7	3.7	1.8	19.8	29.7	23	63.5	60.4	67.6	20.5	827	290	17293	14000	120	580
40	240.0	234.0	19.6	137	200	0.9	4.8	1.7	19.1	32.0	10	58.9	68.2	61.5	23.0	1086	540	14493	11000	130	840