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Lead, zinc, copper, and cadmium in fish and sediments from the Big River and Flat River Creek of Missouri's Old Lead Belt

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Abstract

The Old Lead Belt of Missouri was a major lead-producing region for over a century. Several large tailings piles and other industrial wastes remain behind, though mining operations in the region ceased in 1972. Samples of stream sediments and fish were collected from established sites on the Big River and Flat River Creek over a 3-year period from 1998 to 2000 to evaluate ongoing remediation efforts and determine the current impact of residual mining wastes. Benthic sediments and fish taken in the vicinity of inactive industrial sites were found to contain elevated concentrations of Pb, Zn, Cu, and Cd. Concentrations of Pb and Zn in fillets of suckers and sunfish, as well as in whole bodies of sunfish, correlate well with metal concentrations observed in surficial sediments. The results of analyses provide valuable quantitative information regarding specific sources, current levels of contamination, potential risk to public health, and will allow more accurate assessment of continuing remediation efforts.

Introduction

The Old Lead Belt of Missouri is located approximately 116 km southwest of St. Louis near the cities of Fredericktown, Farmington, Park Hills, Desloge, and Bonneterre. Mining and processing of galena occurred from the mid 1700s until 1972, when the last mine ceased operations. Peak production occurred during the first half of the 20th century, at which time, for several decades, the Old Lead Belt was the largest lead-producing region in the world. During most of its operations, there were few regulatory guidelines governing the disposal of mining wastes. For more than a century, waste rock containing varying amounts of residual metals was discarded in huge mounds of coarse chat and fine tailings, while slurries of very finely ground waste were allowed to settle in slime ponds. There are nine sites within the Old Lead Belt where accumulated mine wastes are recognised as major point sources of contamination of regional streams by fine sediments and vagrant metals. Seven of these tailings and chat disposal areas (Figure 1) have contributed to extensive benthic alteration and contamination of the Big River and its tributary, Flat River Creek by Pb, Zn, Cu and Cd (Gale *et al.* 1982, 1986, 2002; Wixson *et al.* 1982). These metals are potentially toxic if present and taken up by living organisms in excessive amounts from the environment. All four of these heavy metals have been shown to bind to soil and sediments. All tend to bind tenaciously to organic matter contained within soil, sediments, and suspended particulates within the water column. Organically bound metals may dissociate as free ions and participate in cation exchange reactions with various minerals and living organisms, depending on ambient pH, ionic strength, temperature, and in some cases, specifically interacting cations or anions. The organic matter of soils and sediments is known to play a major role in determining the bioavailability of heavy metals. Microorganisms and certain aquatic plants and animals often concentrate toxic metals from dilute aqueous environments. Pb, Zn, Cu and Cd, however, have not

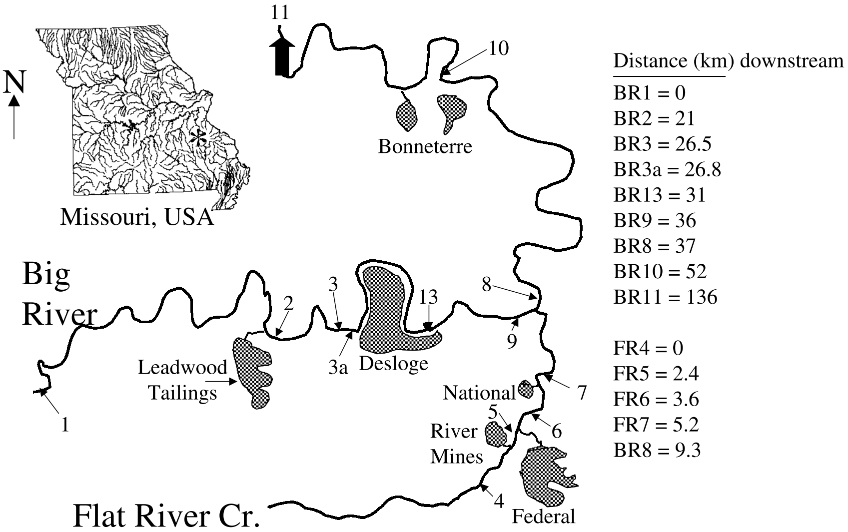

Fig. 1. Sampling sites on Big River and Flat River Creek in Missouri's Old Lead Belt. Not to scale. Concrete barriers immediately upstream of sites BR3a and BR11 prevent upstream migration under normal stream flow conditions.

Table 1. Screening values for metals in sediments ($\mu g\, g^{-1}$ dry weight) (EPA 1997).

Metal	ER-L[a]	ER-M[b]	AET-L[c]	AET-H[d]	TEL[e]	PEL[f]	FDA[g]
Pb	46.7	218	450	660	30.2	112	1.3
Zn	150	410	410	1600	124	271	–
Cu	34	270	390	1300	18.7	108	–
Cd	1.2	9.6	5.1	9.6	0.676	4.21	3.0

[a] Effects range – low value.
[b] Effects range – median value.
[c] Apparent effects threshold – low value.
[d] Apparent effects threshold – high value.
[e] Threshold effects level.
[f] Probable effects level.
[g] Food & Drug Administration Guidance/Action/Tolerance level for fish tissue concentration.

been found to be biomagnified in aquatic or terrestrial food chains (Kabata-Pendias & Pendias 1984; Agency for Toxic Substances and Disease Registry (ATSDR) 2002). Of the various heavy metals, Pb is reportedly the least mobile. Cu has also been shown to remain bound up as insoluble complexes in soil and sediment. Zn and Cd are considerably more mobile. They have greater tendency to dissociate from insoluble inorganic and organic complexes to form soluble ionic species that remain stable at neutral or slightly alkaline pH (see Kabata-Pendias & Pendias 1984).

Comprehensive reviews of the physical, chemical, and biological properties of these metals and many other potential environmental toxicants, as well as useful information regarding sources and routes of possible exposure, and current regulatory guidelines are available in the current literature (Kabata-Pendias & Pendias 1984; ATSDR 2002). The U.S. Environmental Protection Agency (EPA) in its National Sediment Quality Survey (1997) provided a number of guideline values for many recognised toxic chemicals, including Pb, Zn, Cu, and Cd (Table 1). It is important, however, to consider other site-specific conditions and the fraction of the sediments being analysed when making comparisons with these screening values.

In October, 1992, the Desloge tailings pond/chat pile area was placed on the list of 'Superfund' sites and designated the 'Big River Mine Tailings Site' by the EPA. This huge pile of finely ground tailings is located in a horseshoe bend of the Big River, and has had a long history of severe erosion. In 1994, The Doe Run Company agreed to remediate this specific mine waste site and actual remediation work began in October, 1995. This steeply sloped pile has now been regraded, its slopes covered with coarse rock, and ripwrap was installed along its base to reduce further erosion into the adjacent Big River. The EPA also presented a schedule for the remediation of other mine waste sites in the Old Lead Belt. They include the Bonneterre tailings pond/chat piles, the Leadwood tailings pond/chat pile, and the Federal tailings pond, currently designated as St. Joe State Park. The latter area currently serves as a popular recreational area for swimming, fishing, horseback riding and off-road vehicles.

In order to assess the effectiveness of ongoing remedial activities, the University of Missouri–Rolla, the Missouri Department of Conservation, the Missouri Department of Natural Resources, and The Doe Run Company are cooperating to perform periodic analyses of metal concentrations in river sediments and selected fish species taken from specific sites along the Big River and Flat River Creek (Figure 1). The purpose of this study was to assess the current levels of metals contamination in the region and allow more accurate evaluation of potential risks to public health.

Methodology

Fish samples

Fish were collected during late August and early September of 1998, 1999, and 2000 using electrofishing techniques as authorised by the Missouri Department of Conservation. At shallow sites on Flat River Creek, a self-contained gas-powered, backpack-mounted electroshock unit was utilised to stun the fish (Coffelt Model BP-1CO). At other deeper sites, a larger Smith-Root Model 5 GPP 5000 W generator and shock box with accompanying Model SR-6 electrofishing tote barge was used. Attempts were made each year to collect fillets from at least five specimens of each of three groups of fish from each site:

Group A: Bottom-feeding Black Redhorse Sucker (*Moxostoma duquesnei*), Northern Hogsucker (*Hypentelium nigricans*) or Golden Redhorse Sucker (*Moxostoma erythrurum*).

Group B: Small sunfish which feed throughout the water column and commonly ingest considerable amounts of sediment. The abundant Longear sunfish (*Lepomis megalotis*) was the preferred species of this group.

Group C: Top-feeding Largemouth Bass (*Micropterus salmoides*) or Smallmouth Bass (*Micropterus dolomieui*).

In addition to fillets, whole body specimens of Group B (small sunfish) were also collected from all sites in 1999 and again at sites BR1 and BR3a in 2000 for total body analyses. All materials used in the fish collection and processing procedures were carefully chosen and maintained to avoid further contamination by heavy metals. Fish were filleted using a stainless steel knife and plastic fillet board. Fillets were rinsed carefully in flowing river water and double bagged in separate new plastic (Ziploc®) bags, sealed and labelled with a unique identifying number, then placed in an ice chest. Immediately upon return to the university laboratory, all specimens were frozen prior to delivery to the analytical laboratory.

Sediment samples

During 1999 and 2000, two or three composite samples of the suspendable particulates within the uppermost layers of benthic sediments were collected at each site in a sedimentation zone (SED), a riffle zone (RIF), and at random locations along the riverbed (RAN). A 500 ml polypropylene container was used to scoop up samples of benthic sediments to a depth of 3–4 cm. The plastic container was then covered with a lid and shaken vigorously. The liquid and light suspended particles were then decanted into a separate polypropylene container. The procedure was repeated several times resulting in a gravel-free sample of suspendable solids. After settling for 10–20 min, the solution above the composite sediment sample was carefully decanted off. The remaining sample in its closed plastic container was then held on ice during transport to the university laboratory. Upon arrival at the laboratory, each sediment sample was transferred to a clean conical centrifuge tube, capped and centrifuged at low speed for 2 min to dewater and concentrate the sample. Concentrated samples were then frozen and transferred to the analytical lab for digestion and analysis.

Chemical analyses

Chemical analyses of fish tissues and sediments were done in accordance with standard procedures established by the EPA (1991). Fish specimens collected in 1998 were analysed by the Environmental Trace Substances Laboratory at the University of Missouri–Rolla using nitric acid digestion and Inductively Coupled Plasma–Mass Spectrometry (ICPMS) for Pb, Cd, and Cu. Zn was determined on samples digested with a mixture of nitric and perchloric acids, followed by ICPMS analysis. Analyses of fish and sediment samples collected in 1999 and 2000 were performed by Midwest Research Institute–Florida Division, in Palm Bay, Florida, according to EPA Method 200.8, Determination of Trace Elements in Waters and Wastes by ICPMS. Fish samples were digested with tetramethylammonium hydroxide (TMAH), followed by acidification with nitric acid (EPA Method 200.11). Dried sediment samples were prepared and analysed using a mixture of hot nitric and hydrochloric acids, followed by ICP-Atomic Emission Spectrometry according to EPA Method 200.2. Results are expressed as ($\mu g\, g^{-1}$) wet weight for fish and $\mu g\, g^{-1}$ dry weight for sediments. Method Detection Limit (MDL) as defined by the EPA in 40 CFR Part 136 Appendix B were as follow: Pb, 0.01$\mu g\, g^{-1}$; Zn, 1.36 $\mu g\, g^{-1}$; Cu, 0.09 $\mu g\, g^{-1}$; Cd, 0.01 $\mu g\, g^{-1}$. Some reported values for Pb and Cd concentrations were below the stated MDL. Although not within the 99% confidence interval, these lower concentrations, as low as 0.002 and 0.001 $\mu g\, g^{-1}$, respectively, were above background noise levels. Any value reported below the calculated MDL should be considered with less confidence. For statistical and reporting purposes, those samples showing no apparent difference between signal and noise were assigned a value of 0.002 $\mu g\, g^{-1}$ for Pb and 0.001 $\mu g\, g^{-1}$ for Cd.

Results and discussion

Zn and Cu are recognised as essential elements, required by a wide variety of enzymes and other cell components having vital functions in all living things. The recommended dietary allowance (RDA) for zinc in humans is 15 mg day^{-1} for men, 12 mg day^{-1} for women, 10 mg day^{-1} for children, and 5 mg day^{-1} for infants (ATSDR 1999). Harmful health effects generally begin at levels from 10 to 15 times the RDA. The National Research Council (1999) listed the estimated safe and adequate daily intake of Cu for adults as 1.5–3 mg; children 11 years and older as 1.5–2.5 mg; 1–2 mg for children between 7 and 10; 1–1.5 mg for children between 4 and 6; 0.7–1 mg for children between 1 and 3 and 0.4–0.7 mg for infants.

There are no known physiological requirements for Pb or Cd. The World Health Organization (1972) has recommended that dietary Pb should not exceed 0.3 $\mu g\, g^{-1}$ (wet weight basis), with a recommended limit of 450 μg of Pb day^{-1} for adults. The United Kingdom (1979) has a legislated permissible level for Pb in food at 1.0 $\mu g\, g^{-1}$ (wet weight basis). The U.S. Food and Drug Administration's Total Diet Study (1993) suggests a mean lifetime exposure to dietary Cd (excluding shellfish) of 10 μg person^{-1} day^{-1}. That study reported that the World Health Organization/Food and Agricultural Organization (WHO/FAO) has determined a maximum tolerable weekly intake of 7 μg Cd kg^{-1} (about 60 μg person^{-1} day^{-1} for a 60 kg person). A maximum tolerable daily intake of 55 μg person^{-1} day^{-1} has been suggested by ATSDR (2002).

Lead in water, fish and sediments

The hard, alkaline water of Old Lead Belt rivers and streams is a major factor in determining speciation, solubility, mobility, bioavailability, and toxicity of the heavy metals of concern (Kabata-Pendias & Pendias, 1984). In the Big River and Flat River Creek, the typical range for total hardness is 200–275 mg L^{-1}. That for Ca hardness is 105–155 mg L^{-1}, and total alkalinity is approximately 170–200 mg L^{-1} (values expressed as mg L^{-1} $CaCO_3$), with pH values of 7.7–8.0. Equilibrium calculations show that at pH > 5.4, the total solubility of Pb is approximately 30 $\mu g\, L^{-1}$ (ppb) in hard water (ATSDR 2002). Sediments are known to contain considerably higher levels of Pb than corresponding surface waters. Average concentrations of Pb in river sediments in the U.S.A. have been reported to be between 27 and 267 $\mu g\, g^{-1}$ (Fitchko & Hutcheson 1975; EPA 1980, 1982). The STORET database of Eastern and Midwestern river basins reports maximum Pb concentrations in river sediments of 440–1000 $\mu g\, g^{-1}$. Typical concentrations of lead in meat, fish, and poultry reported by the EPA (1986) range from 0.002–0.159 $\mu g\, g^{-1}$. The U.S. Fish and Wildlife Service performed a study of metals in a total of 315 composite samples of whole fish sampled from 109 stations nationwide from late 1994 to early 1995. The geometric mean Pb concentration was 0.11 $\mu g\, g^{-1}$ (wet weight), while the reported maximum was 4.88 $\mu g\, g^{-1}$ (Schmitt & Brumbaugh 1990).

Results of analyses for Pb in fish and sediments collected in 1998, 1999, and 2000 from Missouri's Old

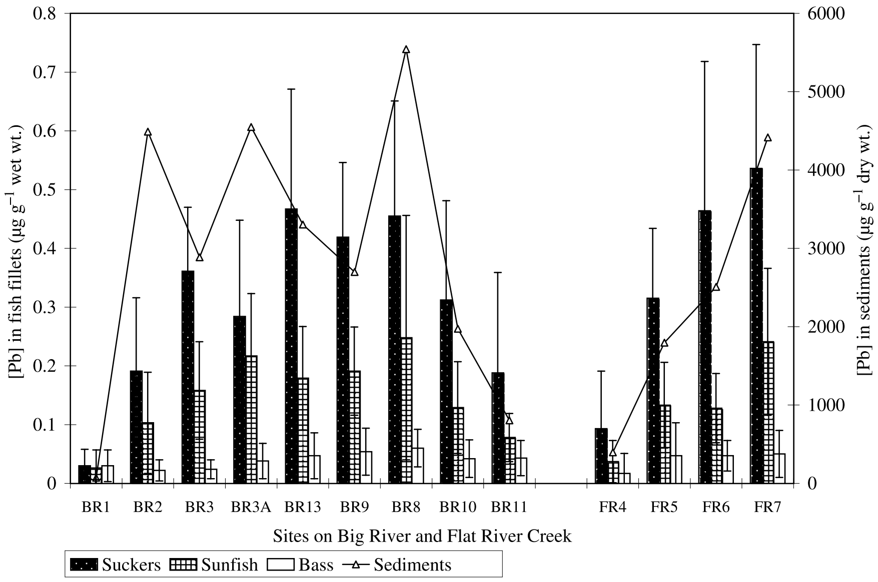

Fig. 2. Lead concentrations in fish fillets and sediments.

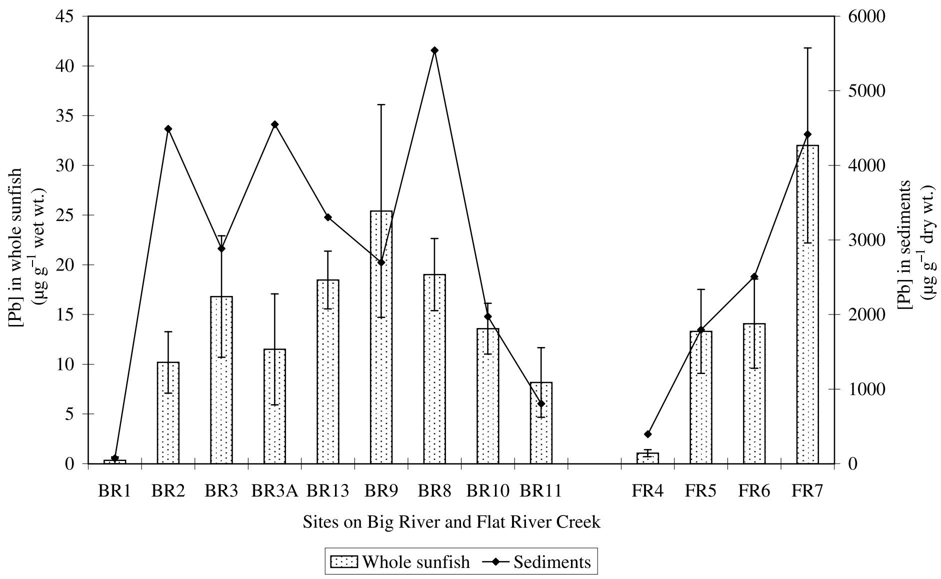

Fig. 3. Lead concentrations in whole sunfish and sediments.

Table 2. Overall means and ranges for Pb in fish and sediments (samples collected 1998–2000).

Sample type	n	Mean [Pb] $\mu g\, g^{-1} \pm$ SD	Range $\mu g\, g^{-1}$ (min–max)
Sunfish fillets	186	0.140 ± 0.115	0.003–0.960
Whole sunfish	75	13.05 ± 9.80	0.134–42.09
Bass fillets	197	0.040 ± 0.034	0.002–0.185
Sucker fillets	280	0.309 ± 0.220	0.002–1.070
Control sediments	11	219 ± 175	64–477
Other sediments	63	3189 ± 2294	158–12406

Lead Belt are shown in Figures 2 and 3. Overall averages and ranges for [Pb] in fish and sediments analysed during the present study are shown in Table 2. With few exceptions, differences in metal concentrations from year to year were not significant. Pb concentrations were highest in sediments with the following order of decreasing levels:

sediments > whole body sunfish > sucker fillets > sunfish fillets > bass fillets.

Mean sediment Pb concentrations at all sites, including control sites, were higher than some of the screening values presented by the EPA. Concentrations of Pb in fish fillets are of specific concern because the fillet is the portion of the fish that is typically consumed by humans. However, whole body Pb concentrations are significant when considering possible impact on various other piscivorous animals within local food webs.

Group A fish

Of all the varieties of fish collected during this and previous studies conducted in Missouri's Old Lead Belt, suckers were found to contain the greatest concentrations of Pb in their muscle tissue samples. This is consistent with their recognised bottom-dwelling and bottom-feeding habits and likelihood of both dietary and contact exposure to Pb-laden sediments. Suckers also have numerous small bones embedded within their muscle tissue which may serve as repositories for Pb. Biological accumulation coefficients (BAC) for Pb in sucker fillets ranged from 0.43 to 4.2×10^{-4}. Of the total 239 sucker fillets collected from industrially affected sites and analysed over the 3-year study, 133 (56%) exceeded the WHO guideline of $0.3\,\mu g\,g^{-1}$ (WHO 1972). Two (<1%) exceeded the UK limit of $1.0\,\mu g\,g^{-1}$ (1979), and none exceeded the USFDA guidance level of $1.3\,\mu g\,g^{-1}$ (USEPA, 1997). All sites except the control site BR1 had at least one sucker fillet that exceeded the WHO guideline. At 9 of the total 13 sites, the mean Pb level in sucker fillets exceeded the WHO guideline in at least one year. The Missouri Department of Conservation has issued warnings against consumption of suckers taken from streams of the Old Lead Belt.

Group B fish

The Longear Sunfish and other closely related species are known to feed throughout the water column, and often tend to follow other bottom foraging animals in search of insect larvae, crayfish, etc. They are also likely to ingest and contact considerable sediment material. Highest absolute whole-body Pb concentrations were found at sites FR7 and BR9, though small sunfish collected from all industrially affected sites showed significantly higher body burdens of Pb than those specimens taken from control sites. BAC values for Pb in whole body sunfish ranged from 2.3 to 10.1×10^{-3}. In sunfish fillets, there was no significant trend for Pb over the 3-year period at any specific site although some significant annual differences were observed. At both control sites, samples collected in 1999 had higher Pb concentrations than those in 1998 and 2000, though the difference was not significant at site BR1. The results show that there were greater Pb concentrations observed in sunfish fillets at all industrially affected sites compared with control sites, though the differences were not always significant. BAC values for Pb in sunfish fillets ranged from 2.3 to 36×10^{-5}. The sunfish fillet Pb concentrations showed a longitudinal pattern very similar to that shown by sucker fillets, except that the average concentrations were on the order of half as great in the sunfish. The overall mean Pb concentrations in sunfish fillets collected over the 3-year period did not exceed the WHO guideline of $0.3\,\mu g\,g^{-1}$ at any of the 13 sites on the Big River and Flat River Creek. However, fillets of sunfish taken from Sites BR3A and BR8 in 1998 and from Site FR7 in 2000 showed means slightly above the WHO guideline. Of the total 156 specimens of small sunfish collected from industrially affected sites over the entire 3-year period, 14 (9%) were above the WHO guideline. None exceeded the UK limit or FDA guideline. However, one anomalous specimen taken from site BR8 in 1998 ($0.960\,\mu g\,g^{-1}$) resulted in a mean Pb concentration at that site that was slightly higher than the WHO guideline. In 1999, the mean Pb concentration at site BR3A was $0.306\,\mu g\,g^{-1}$ and in 2000 at site FR7 the mean Pb concentration was $0.302\,\mu g\,g^{-1}$. The Missouri Department of Conservation has also issued a warning to avoid consumption of small sunfish taken from the rivers of the Old Lead Belt.

Group C fish

In bass fillets, Pb concentrations were much lower than those found in small sunfish or suckers. The top-feeding bass are known to be in a higher trophic level and thus consume little benthic sediment. Even at sites with elevated concentrations of Pb in sediment, sucker fillets, sunfish fillets, and whole sunfish, the average Pb concentration in bass fillets never exceeded the

WHO guideline of 0.3 $\mu g\,g^{-1}$ in any of the 3 years. The highest individual Pb concentration in a bass fillet was 0.185 $\mu g\,g^{-1}$ from site BR9 in 1998. Of the 164 total specimens of bass fillets taken from industrially affected sites in and downstream of the Old Lead Belt, only 13 (8%) showed Pb concentrations above 0.1 $\mu g\,g^{-1}$. One out of a total of 33 taken from control sites (3%) was also above 0.1 $\mu g\,g^{-1}$. There were significant annual differences in Pb concentrations found in fillets of bass. For example, Pb levels in 1999 were significantly greater than in 2000 at all but three sites (BR8, FR6 and FR7). The reason for this is not clear. Mean values for sunfish tend to follow the same trend (though with less statistical significance). BAC values for Pb in fillets of bass ranged from 0.48 to 42×10^{-5}.

Correlations

Concentrations of Pb in fillets of suckers, fillets of sunfish, and whole body sunfish appear to correlate well with Pb concentration of the sediments ($r = 0.65$, 0.85, and 0.64, respectively). Correlation analysis of only those fish samples taken from sites with background sediment Pb concentrations up to approximately 4000 $\mu g\,g^{-1}$, yielded correlation coefficients of 0.86 ($p < 0.0001$), 0.82 ($p < 0.0001$), and 0.92 ($p < 0.0004$) for sucker fillets, sunfish fillets, and whole body sunfish. At higher sediment concentrations (>4000 $\mu g\,g^{-1}$), Pb concentrations in fish did not increase further. The reason for this is unknown. The uptake of Pb by these aquatic animals exposed to Pb-laden sediments appears to follow a pattern similar to that described for plants exposed to Pb in soils and nutrient solutions (Kabata-Pendias & Pendias 1984). No apparent correlation was observed between Pb in fillets of bass and Pb in sediments ($r = 0.29$, $p = 0.23$), probably due to their higher position in the food web and less contact with stream sediments.

Zinc in fish and sediments

Results of analyses for Zn in fish and sediments are shown in Figures 4 and 5. Overall averages and ranges for [Zn] in fish and sediments analysed during the present study are presented in Table 3. For comparison, the ATSDR Toxicological Profile for Zinc (2002) cites evidence that concentrations of zinc in Hamilton Harbour, Lake Ontario, sediments ranged from 1050 to 2900 $\mu g\,g^{-1}$ (Mayer & Manning, 1990). Those in sediments of the upper Columbia River in British Columbia ranged from 45 to 51 $\mu g\,g^{-1}$, and those in sediments from Lake Roosevelt, Washington, were 60–26,840 $\mu g\,g^{-1}$ (Johnson *et al.* 1990). The latter lake receives discharges from a lead–zinc smelter and a refinery.

Animals have been found to contain more zinc than most plants (ATSDR 2002). The FDA Total Diet Studies program reported an average concentration of Zn in dietary meat, fish, and poultry estimated at 29.2 $\mu g\,g^{-1}$ (Gartrell *et al.* 1986). The National Contaminant Biomonitoring Program reported a geometric mean concentration of Zn in various whole fish of 21.7 $\mu g\,g^{-1}$ (wet weight) (Schmitt & Brumbaugh 1990). Of all fish tested (bloaters, suckers, white perch, bass, catfish, etc.), common carp showed the highest concentrations of Zn. The concentration of Zn in yellow perch (*Perca flavescens*) from six acidic lakes in northwestern New Jersey ranged from 26.1 to 66.2 $\mu g\,g^{-1}$ (dry weight) (Sprenger *et al.* 1988).

Zinc in sediments

The current study clearly indicates a marked increase in Zn concentration in stream sediments in the vicinity of inactive industrial sites of Missouri's Old Lead Belt. With possible exception of control sites and the downstream site at BR11, Zn concentrations at most sites were generally higher than the screening values presented by the USEPA (1997). Highest values were found in sediments near the Desloge tailings pile (sites BR3A and BR13) and the River Mines tailings pile (FR5). The small stream of seepage entering Flat River Creek just upstream of site FR5 has long been recognised for its elevated concentrations of dissolved Zn (Whitton *et al.* 1981).

Zinc in fish fillets

Concentrations of Zn in fillets of both suckers and small sunfish are similar in magnitude, with similar ranges and mean values, and show some correlation with sediment ($r = 0.64$ and 0.59, respectively). Concentrations of Zn in bass fillets are somewhat lower and demonstrate less correlation with sediment Zn ($r = 0.41$). None of the fillet samples analysed contained sufficient (Zn) to pose a threat to public health.

Whole body analyses

Whole body analyses for Zn in small sunfish show significantly higher [Zn] than those observed in fillets of the same species. This is consistent with the known tendency for Zn to accumulate in liver, kidneys, and other internal organs. Significantly higher levels were found at sites near old industrial areas, especially

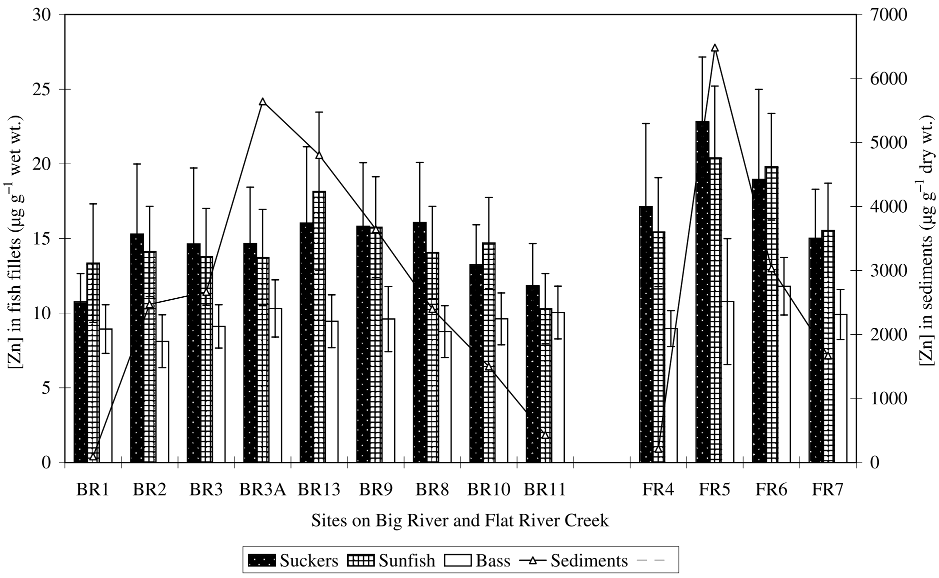

Fig. 4. Zinc concentrations in fish fillets and sediments.

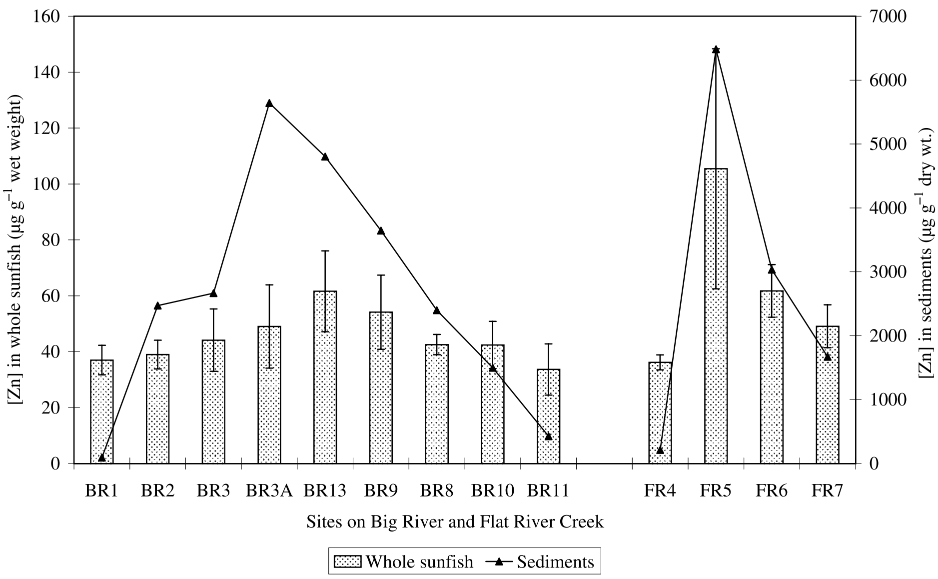

Fig. 5. Zinc concentrations in whole sunfish and sediments.

Table 3. Overall means and ranges of zinc concentrations in fish and sediments (samples collected 1998–2000).

Sample type	*n*	Mean [Zn] $\mu g\, g^{-1} \pm SD$	Range $\mu g\, g^{-1}$ (min–max)
Sunfish fillets	186	15.3 ± 4.4	7.6–29.8
Whole sunfish	75	49.5 ± 21.8	23.6–173
Bass fillets	197	9.66 ± 2.15	4.8–22.7
Sucker fillets	280	14.9 ± 4.9	6.3–31.3
Control sediments	11	147 ± 72	80–278
Other sediments	63	3210 ± 2098	293–9619

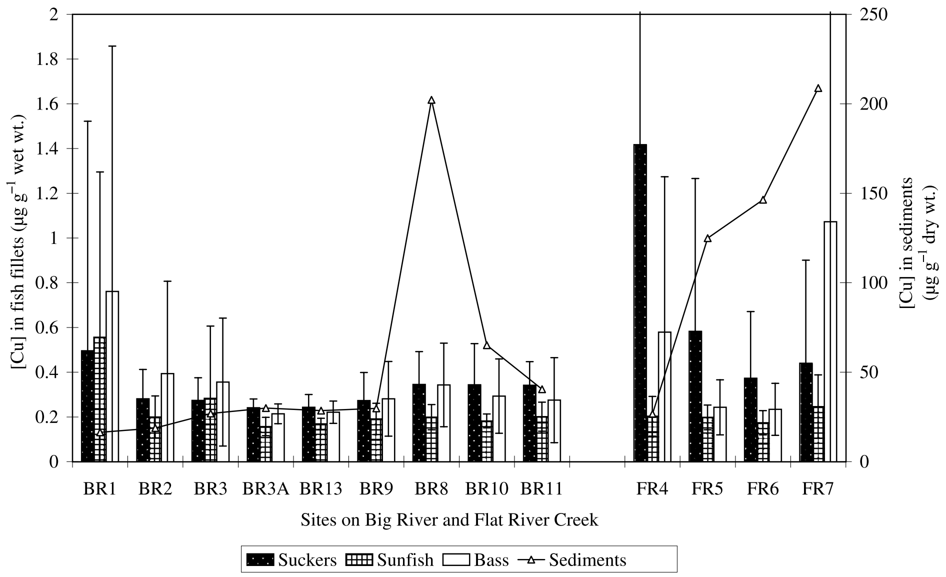

Fig. 6. Copper concentrations in fish fillets and sediments.

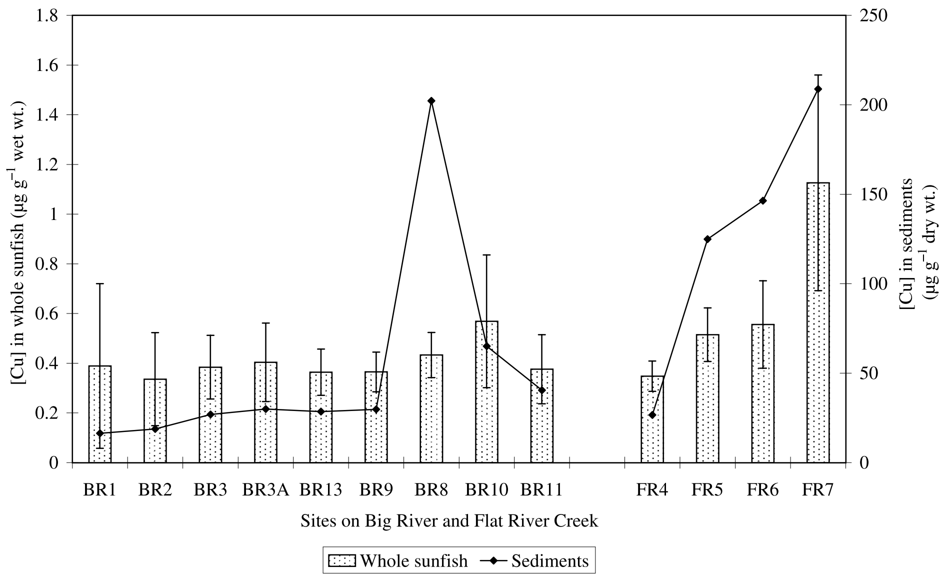

Fig. 7. Copper concentrations in whole sunfish and sediments.

Table 4. Overall means and ranges of copper concentrations in fish and sediments (samples collected 1998–2000).

Sample type	*n*	Mean[Cu] $\mu g\, g^{-1} \pm SD$	Range $\mu g\, g^{-1}$ (min–max)
Sunfish fillets	186	0.234 ± 0.260	0.087–2.2
Whole sunfish	75	0.464 ± 0.273	0.22–1.62
Bass fillets	197	0.392 ± 0.647	0.091–6.72
Sucker fillets	280	0.390 ± 0.573	0.111–5.86
Control sediments	11	21.06 ± 6.17	14.3–31.9
Other sediments	63	81.14 ± 84.93	11.8–446

those on Flat River Creek (FR5), and much greater correlation was evident with sediment [Zn] ($r = 0.79$).

Cu in fish and sediments

Results of analyses for Cu in fish and sediments are summarised in Figures 6 and 7. Overall averages and ranges for [Cu] in fish and sediments analysed during the present study are presented in Table 4. The current Toxicological Profile for Cu compiled by the ATSDR (2002) indicates that stream sediments from pristine areas generally contain $<50\,\mu g\,g^{-1}$ Cu. The level can reach several thousand $\mu g\,g^{-1}$ in polluted areas (Harrison & Bishop 1984). Surficial sediment of Penobscot Bay, ME was $14.1\,\mu g\,g^{-1}$ (dry weight) while sediments from estuaries and bays in other New England locations ranged from 4.4 to $57.7\,\mu g\,g^{-1}$ (Larsen *et al.* 1983). Cu levels from 24 sites along the New Jersey coast ranged from <1 to $202\,\mu g\,g^{-1}$ with a mean of $66\,\mu g\,g^{-1}$ (Renwick & Edenborn 1983). Cu in surficial sediments in lakes in the Sudbury region of northeastern Ontario, where several smelters operate, decreased rapidly with increasing distance from the smelters. Three lakes 10 km from the Sudbury smelters contained Cu concentrations in sediment approaching $2000\,\mu g\,g^{-1}$ (dry weight) (Bradley & Morris 1986).

Mean [Cu] in muscle tissue of 268 fish specimens in several surface water systems in eastern Tennessee ranged from 0.12 to $0.86\,\mu g\,g^{-1}$ (wet weight), with a maximum level of $2.2\,\mu g\,g^{-1}$ (Blevins & Pancorbo 1986). Eight species of freshwater fish collected at 112 stations in the US in 1978–1979 and 1980–1981 displayed a geometric mean [Cu] of 0.86 and $0.68\,\mu g\,g^{-1}$, with ranges from 0.29 to 38.75 and 0.25 to 24.1, respectively (Lowe *et al.* 1985). Mean [Cu] in 127 samples of edible fish from Chesapeake Bay and its tributaries were $1.66\,\mu g\,g^{-1}$ in 1978 and $1.85\,\mu g\,g^{-1}$ in 1979 (Eisenberg & Topping 1986).

Observed concentrations of Cu in fish and sediments from Old Lead Belt streams do not appear to be excessive, when compared to screening values promulgated by the USEPA (1997) and values reported in the literature (ATSDR 2002). However, sediment data from the current study indicate a pattern of increasing [Cu] all along Flat River Creek, from site FR5 downstream to the point of confluence with the Big River at site BR8. Little correlation is apparent between Cu concentrations in fish fillets and those in sediments (r values range from 0.05 to 0.29). Highest absolute concentrations of Cu in fillets were actually found at the control sites BR1 and FR4. Stronger correlation is apparent between Cu concentrations of whole bodies of sunfish and sediments ($r = 0.72$). This, too, is consistent with the known tendency for Cu to become concentrated in liver and other internal organs.

Cd in fish and sediments

The ATSDR review of the literature (2002) indicates that Cd may bioaccumulate in all levels of aquatic and terrestrial food chains. It accumulates largely in the liver and kidneys of vertebrates and not in muscle tissue (Sileo & Beyer 1985; Harrison & Klaverkamp 1990; Vos *et al.* 1990). Intestinal absorption of Cd is low and biomagnification through the food chain may not be significant (Sprague 1986). Thornton (1992) reported a range of Cd content in marine sediments from 0.1 to $1.0\,\mu g\,g^{-1}$. Surficial sediments collected from 18 locations in three major tributaries to Newark Bay, New Jersey, had a mean Cd concentration of $10 \pm 6\,\mu g\,g^{-1}$ (dry weight) (Bonnevie *et al.* 1994). In heavily industrialised areas, sediments contained $14–29\,\mu g\,g^{-1}$ Cd. In sediments of the Hudson River estuary, Cd concentrations in suspension were higher than in bottom sediments by a factor of 30 (Gibbs 1994).

The FDA Total Diet Study indicated a range of concentrations of Cd in meat, fish and poultry from trace amounts up to $0.014\,\mu g\,g^{-1}$, with an average of $0.0057\,\mu g\,g^{-1}$ (Gartrell *et al.* 1986). Shellfish, liver, and kidney meats generally have higher concentrations of Cd than other fish or meat (Elinder 1985; Schmitt & Brumbaugh 1990; IARC 1993). Cd concencentrations up to $8\,\mu g\,g^{-1}$ in oysters, $30–50\,\mu g\,g^{-1}$ in edible hepatopancreas of crabs and $3\,\mu g\,g^{-1}$ in salmon flesh have been reported (IARC 1993). A mean Cd concentration of $1.64\,\mu g\,g^{-1}$ was reported for redear sunfish living in stormwater ponds of Florida compared to $0.198\,\mu g\,g^{-1}$ for redear sunfish living in control ponds (Campbell 1994). The mean Cd concentration in largemouth bass living in stormwater ponds was $3.16\,\mu g\,g^{-1}$ (wet weight) compared to $0.241\,\mu g\,g^{-1}$ for largemouth bass living in control ponds.

Results of analyses for Cd in fish and sediments of Missouri's Old Lead Belt are shown in Figures 8 and 9. Overall averages and ranges for [Cd] in fish and sediments analysed during the present study are presented in Table 5. Cd concentrations in surficial sediments were elevated at all sites in the vicinity of old industrial areas, commonly approaching levels approximately an order of magnitude higher than USEPA screen-

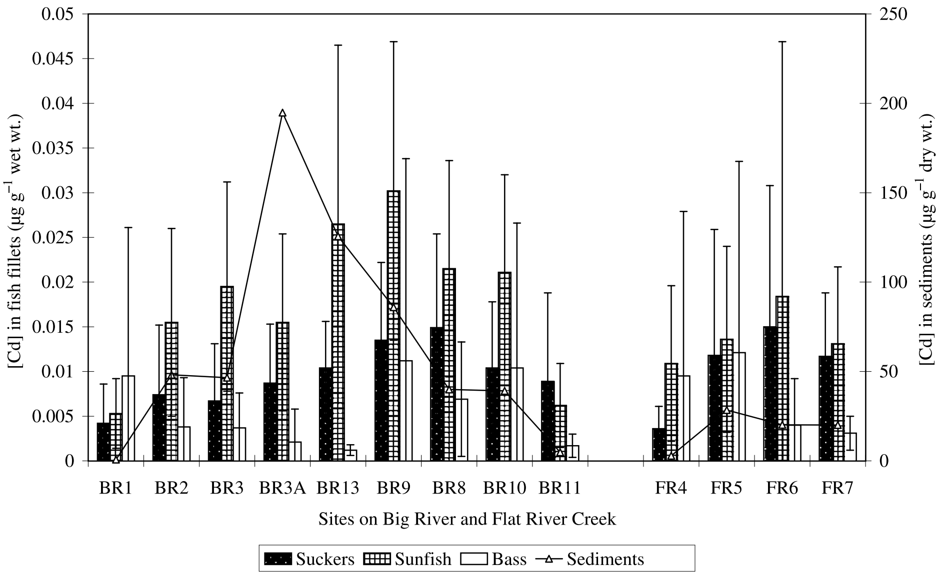

Fig. 8. Cadmium concentrations in fish fillets and sediments.

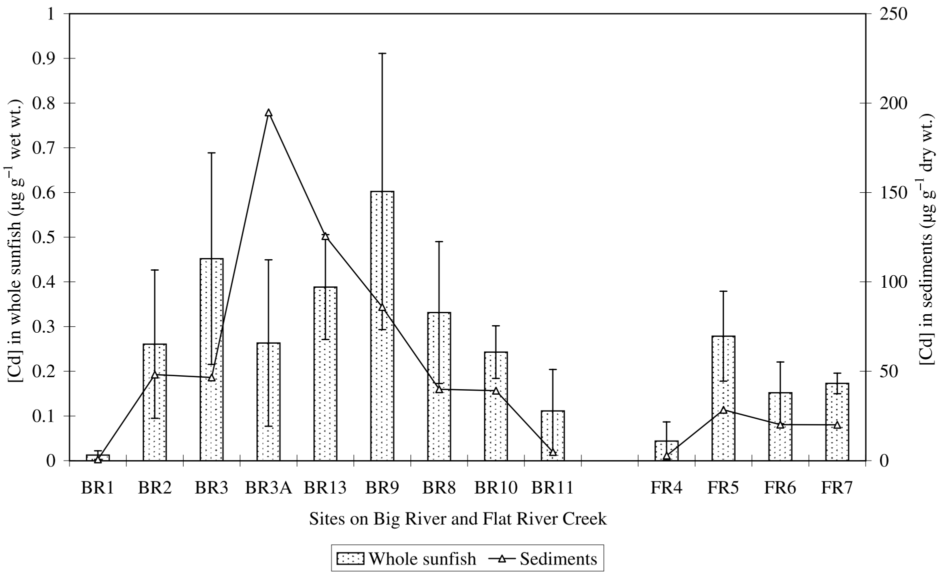

Fig. 9. Cadmium concentrations in whole sunfish and sediments.

Table 5. Overall means and ranges of cadmium concentrations in fish and sediments (samples collected 1998–2000).

Sample type	*n*	Mean [Cd] $\mu g\, g^{-1} \pm SD$	Range $\mu g\, g^{-1}$ (min–max)
Sunfish fillets	186	0.016 ± 0.015	0.001–0.118
Whole sunfish	75	0.239 ± 0.208	0.006–1.00
Bass fillets	197	0.006 ± 0.013	0.001–0.1
Sucker fillets	280	0.010 ± 0.009	0.001–0.076
Control sediments	11	1.72 ± 1.13	0.62–3.2
Other sediments	63	61 ± 71	3.4–403

ing values. Highest concentrations ranging from 70 to 403 $\mu g\ g^{-1}$ were observed in proximity to the Desloge tailings pile (BR3A, BR13) and the Park Hills sewage discharge (BR9). There were few significant differences and considerable variation among respective fish samples at most sites. Cd concentrations in fillets and whole bodies of small sunfish show rather weak correlation with sediment values ($r = 0.49$ and 0.51, respectively). Concentrations of Cd in whole bodies of small sunfish were generally an order of magnitude greater than those found in muscle tissue. In contrast to the other metals of concern, small sunfish generally contained higher [Cd] than either suckers or bass. From a public health standpoint, the amount of Cd in most fish fillets analysed in the current study would fall within acceptable human dietary limits. However, consumption of 85–130 g of those fillets having the highest observed Cd concentrations (Table 5) would provide the maximum recommended daily exposure or approximately 20% of the maximum tolerable daily intake.

Conclusions

The results of this study indicate that the historical mining activities of Missouri's Old Lead Belt continue to have a significant impact on the sediments and fish in the Big River and Flat River Creek. Concentrations of Pb, Zn, and Cd in superficial, suspendable sediment samples taken from sites within these streams were generally higher than USEPA screening values. Elevated concentrations of these metals in local sediments may represent a potential risk to the aquatic environment. There are few, if any, significant differences in observed concentrations of heavy metals in any species of fish collected at any given site during the current study and in earlier studies conducted in the 1980s. Concentrations of these metals in tissues and whole bodies of aquatic organisms frequently correlate well with concentrations observed in suspendable sediments, although there is no evidence of any biomagnification in higher trophic levels. Analytical results indicate that Pb concentrations in edible fillets of bass pose no apparent risk to public health. However, 56% of the fillets taken from suckers and 9% of the sunfish fillets contained elevated [Pb] in excess of the WHO guideline for Pb in Food (0.3 $\mu g\ g^{-1}$). Less than 1% of the sucker fillets and none of the small sunfish were found to exceed the UK guideline (1 $\mu g\ g^{-1}$) or FDA guideline (1.3 $\mu g\ g^{-1}$). Concentrations of Zn and Cu in fish from Old Lead Belt sites were within acceptable limits for human consumption, though Cd concentrations observed in a few of the most heavily contaminated samples approach maximum recommended levels. As remediation efforts continue and expand to include other areas of concern, continued surveillance of metal concentrations in sediments and fish should be conducted to provide effective assessment.

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