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Copper, Cadmium, and Zinc Concentrations in Aquatic Food Chains from the Upper Sacramento River (California) and Selected Tributaries

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Abstract. Metals enter the Upper Sacramento River above Redding, California, primarily through Spring Creek, a tributary that receives acid-mine drainage from a US EPA Superfund site known locally as Iron Mountain Mine. Waterweed *(Elodea canadensis)* and aquatic insects (midge larvae, Chironomidae; and mayfly nymphs, Ephemeroptera) from the Sacramento River downstream from Spring Creek contained much higher concentrations of copper (Cu), cadmium (Cd), and zinc (Zn) than did similar taxa from nearby reference tributaries not exposed to acid-mine drainage. Aquatic insects from the Sacramento River contained especially high maximum concentrations of Cu (200 mg/kg dry weight in midge larvae), Cd (23 mg/kg dry weight in mayfly nymphs), and Zn (1,700 mg/kg dry weight in mayfly nymphs). Although not always statistically significant, whole-body concentrations of Cu, Cd, and Zn in fishes (threespine stickleback, *Gasterosteus aculeatus;* Sacramento sucker, *Catostomus occidentalis;* Sacramento squawfish, *Ptychocheilus grandis;* and chinook salmon, *Oncorhynchus tshawytasch*) from the Sacramento River were generally higher than in fishes from the reference tributaries.

For over a century, fish kills from metal pollution have occurred in the Sacramento River at or below the mouth of Spring Creek (Figure 1), a small tributary that receives runoff from Iron Mountain Mine (Finlayson and Wilson 1979; CH2M Hill 1991). Major kills of ≥25,000 fish were documented in 1955, 1957, and 1967 (CH2M Hill 1991). The last recorded kill, which involved unknown numbers of trout (species not identified), occurred in Keswick Reservoir in January 1978 (CH2M Hill 1991).

In 1963, the Spring Creek Debris Dam (which forms Spring Creek Reservoir) was constructed partly to control the flow of acid-mine wastewater into Keswick Reservoir, an afterbay for Shasta Dam on the Sacramento River. Copper (Cu) cementation plants were also installed in the Spring Creek drainage to help remove this metal from the wastewater. Flow from the Debris Dam is regulated specifically to prevent acute toxicity from heavy metals in fish inhabiting the Sacramento River.

Efforts to alleviate the toxic effects of metals on fishes in the Sacramento River have focused primarily on chinook salmon *(Oncorhynchus tshawytscha)* and steelhead *(O. mykiss)* because these species are especially important to the socioeconomic welfare of people in California. Safe levels for total Cu were estimated initially in 1963 from 96-hr acute toxicity tests with chinook salmon fingerlings (Lewis 1963, cited by Hazel and Meith 1970). In 1978-80, the California Department of Fish and Game conducted additional tests that included cadmium (Cd) and zinc (Zn). The new tests employed embryos, larvae, and fingerlings of chinook salmon and steelhead, and were conducted for up to 83 days (see Finlayson and Ashuckian 1979; Finlayson and Verrue 1980, 1982; Finlayson and Wilson 1989). Based on these tests, the State of California adopted and the U.S. Environmental Protection Agency (USEPA) approved the following site-specific water quality objectives (standards) for the Sacramento River below Keswick Dam (values are dissolved concentrations for receiving waters where total hardness is 40 mg/L as $CaCO_3$): Cu, 0.0056 mg/L; Cd, 0.00022 mg/L; and Zn, 0.016 mg/L (Finlayson and Wilson 1989; CH2M Hill 1991).

The USEPA Superfund Program has implemented major pollution control measures at Iron Mountain Mine in an effort to reduce the volume of contaminated runoff entering Spring Creek (U.S. Fish and Wildlife Service and California Department of Fish and Game, USFWS-CDFG 1987). Despite these efforts, potentially toxic concentrations of dissolved metals still occur in the Sacramento River during heavy rainfall when re-

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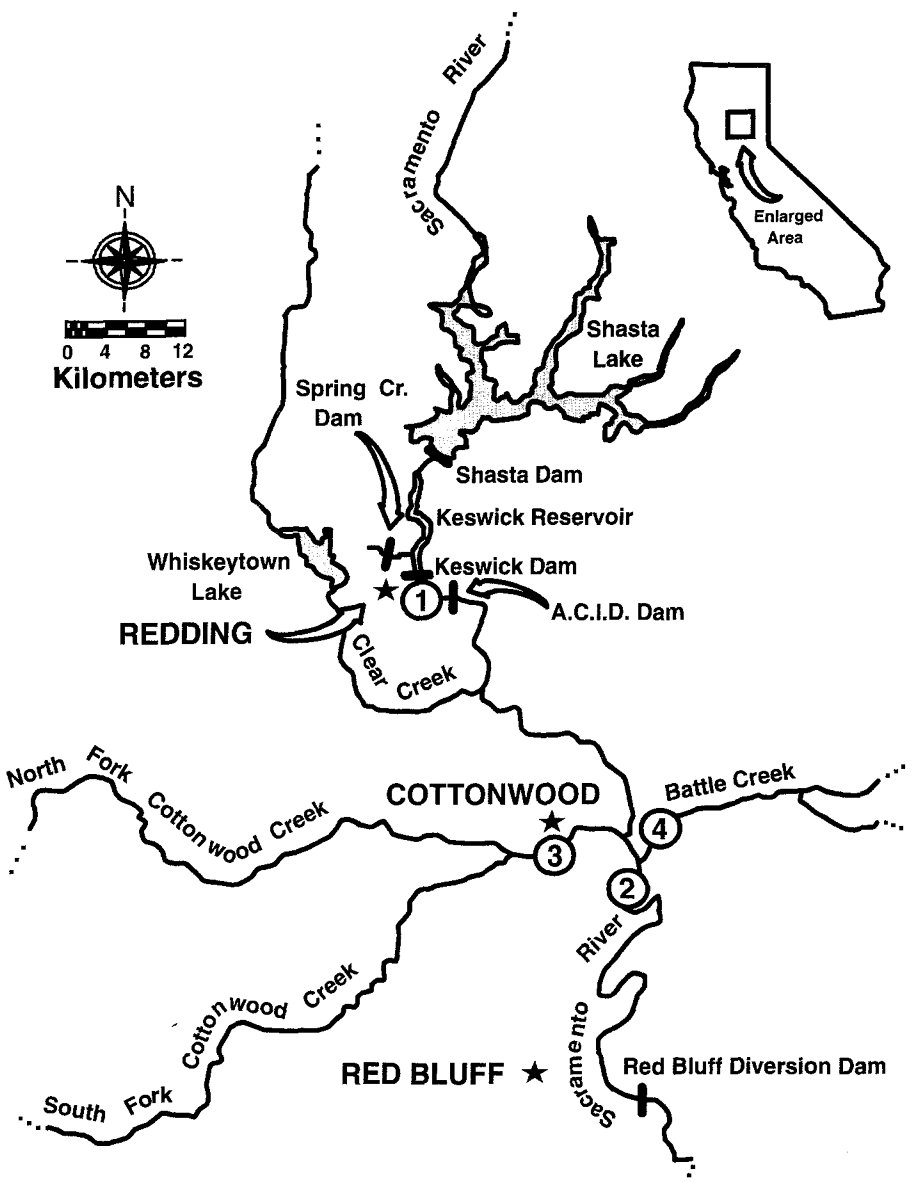

Fig. 1. Locations of sampling sites. Site names and abbrevations are as follows: (1) SRLR, Sacramento River at Lake Redding; (2) SRJF, Sacramento River near Jelly's Ferry Road; (3) CC, Cottonwood Creek at the Interstate 5 bridge; and (4) BC, Battle Creek at the Jelly's Ferry Bridge

leases from Shasta Dam and the Spring Creek Power Plant are inadequate for diluting uncontrolled flood-stage flows that overtop the Spring Creek Debris Dam (USFWS-CDFG 1987; Finlayson and Wilson 1989).

Dallinger *et al.* (1987) reported that heavy metal pollution in aquatic ecosystems is often more markedly reflected by high metal levels in sediments, macrophytes, and benthic animals than by elevated concentrations in water. Under these circumstances, fish could be endangered if they ingest sediment-dwelling invertebrates. According to Zanella (1982), caddisfly (Trichoptera) larvae and "mixed invertebrates" collected from the Sacramento River between Anderson and Red Bluff in 1976 and 1980 contained "very high" concentrations of Cu (74-403 mg/kg air-dried weight) and Zn (92-1,096 mg/kg air-dried weight), and "relatively high" concentrations of Cd (<2.0-8.9 mg/kg air-dried weight). However, prior to chemical analysis, the invertebrates were preserved and stored for 0.5-4.5 years in 10% buffered formaldehyde, with unknown effects on the measured metal concentrations.

In 1979-80, Wilson *et al.* (1981) surveyed the concentrations of metals in adult (3-year-old) rainbow trout (the nonmigratory form of steelhead) from the Sacramento River below Keswick Dam. Although mean concentrations (mg/kg wet weight) of metals in flesh were similar to published background levels (Cu, <0.20; Cd, <0.021; Zn, 4.24), those in liver (Cu, 287; Cd, 4.0; Zn, 57) were higher than background levels. As part of the Toxic Substances Monitoring Program, the State of California annually monitors metal concentrations in liver of rainbow trout from the Sacramento River at Lake Redding. Between 1980 and 1990, Cu concentrations varied from 120 to 330 mg/kg wet weight; Cd, from 0.92 to 4.60 mg/kg wet weight; and Zn, from 20 to 36 mg/kg wet weight (Rasmussen and Blethrow 1990, 1991; Rasmussen 1992).

The purpose of this study was to determine if metals from acid-mine drainage had contaminated aquatic food chains in the upper Sacramento River. To accomplish this purpose, the concentrations of Cu, Cd, and Zn were measured in selected fish-forage organisms and fishes from the Sacramento River below

Table 1. Comparison of water quality variables from the Upper Sacramento River and two tributaries during July–September 1990. Triplicate samples were collected from each site on nine occasions[a,b]

	Physical			Chemical				
Site[c] or statistic	Conductivity (μmhos/cm @ 25°C)	Temperature (°C)	Turbidity (NTUs)	Dissolved oxygen (mg/L)	pH	Total alkalinity (mg/L as $CaCO_3$)	Total dissolved solids (mg/L)	Total hardness (mg/L as $CaCO_3$)
SRLR	68.5 C	13.0 D	3.0 A	10.4 A	7.3 D	52.1 C	86.1 B	46.4 C
SRJF	66.2 C	14.9 C	3.3 A	10.9 A	7.6 C	52.6 C	79.5 B	47.0 C
CC	126.8 A	27.1 A	2.0 B	11.0 A	8.1 B	93.9 A	125.3 A	92.5 A
BC	86.0 B	20.7 B	2.6 AB	10.2 A	8.6 A	73.9 B	115.8 A	58.6 B
χ^2	17.207**	31.414**	9.669*	4.273	27.427**	28.282**	23.917**	29.675**

[a] Codes: *P ≤ 0.05; **P ≤ 0.01
[b] Within a column, arithmetic means followed by the same capital letter are not significantly different ($P > 0.05$, least significant difference test based on ranked values)
[c] See Figure 1 for names and locations of sampling sites

Keswick Dam and from nearby tributaries not exposed to acid-mine drainage.

Study Area

Four sampling sites were established on the Upper Sacramento River system in Shasta and Tehama counties (Figure 1). Two sites exposed to acid-mine drainage were located on the Sacramento River (upstream at Lake Redding, SRLR, and downstream near Jelly's Ferry Road, SRJF), whereas two reference sites not exposed to acid-mine drainage were located on nearby tributaries (Cottonwood Creek at the I-5 bridge, CC, and Battle Creek at the Jelly's Ferry Bridge, BC). The two tributaries enter the Sacramento River between SRLR and SRJF. We did not establish a sampling site on Keswick Reservoir above the mouth of Spring Creek (source of acid-mine drainage in the Sacramento River) because this reservoir and Shasta Lake (formed by Shasta Dam) inundated upstream reaches on the Sacramento Valley floor, leaving nothing comparable to the shallow lotic conditions in the four sampling sites.

The flow at SRLR, which is regulated by Keswick Dam, consists of water released from Shasta Dam and, to a lesser extent, from Spring Creek Debris Dam and the Spring Creek Power Plant (the power plant receives water from Whiskeytown Lake). At the downstream-end of SRLR, a portion of the Sacramento River is diverted by the Anderson-Cottonwood Irrigation District (ACID) Dam into the ACID Canal for irrigating the west side of the Sacramento Valley. Flow in Cottonwood Creek is influenced by several small diversions for irrigation and by irrigation return water from the ACID Canal. Flow in Battle Creek is regulated by five small powerplants, several small reservoirs, at least one small diversion for irrigation, and diversion and return water from the Coleman National Fish Hatchery. Flow at SRJF is similar to that at SRLR, with some influence from diversions for irrigation (primarily the ACID Canal) and inflows from tributaries such as Cottonwood and Battle creeks.

Water-quality data collected concurrently with this study indicated that sites on the Sacramento River were much cooler, slightly less turbid, less well buffered, and contained lower concentrations of dissolved salts than sites on the tributaries (Table 1). Compared to SRLR, the water at SRJF was somewhat warmer and more alkaline.

Materials and Methods

From July 10 to September 6, 1990, samples of filtered and unfiltered water, sediment, particulate organic detritus (detritus), waterweed *(Elodea canadensis)*, midge larvae (Chironomidae), mayfly nymphs (Ephemeroptera, mostly Baetidae), threespine stickleback *(Gasterosteus aculeatus)*, and fingerlings of Sacramento sucker *(Catostomus occidentalis)*, Sacramento squawfish *(Ptychocheilus grandis)*, and fall-run chinook salmon were collected for analysis of Cu, Cd, and Zn. This period coincided with the dry (low rainfall) season, resulting in little outflow from Spring Creek and minimal concentrations of dissolved metals in the Sacramento River. In addition, flows in the Sacramento River and other tributaries (including Cottonwood and Battle creeks) were relatively low during this period, reducing the effort needed to collect samples.

Biological taxa (matrices) were selected because they occurred in the study area and were believed to be important links in the aquatic food chain of fishes. Moyle (1976) reported that threespine stickleback, juvenile Sacramento sucker, and juvenile Sacramento squawfish consume mostly bottom-dwelling organisms or organisms living on plants (e.g., midge larvae), although the Sacramento sucker also eats algae and detritus and the Sacramento squawfish includes surface insects in its diet. By comparison, juvenile chinook salmon are opportunistic drift feeders that take a wide variety of terrestrial and aquatic insects (Moyle 1976). Shaffter *et al.* (1983) found that juvenile chinook salmon from the Sacramento River between Red Bluff and Colusa fed almost entirely on drifting insects, especially midges, mayflies (Baetidae), and aphids (Aphidae). According to Pennak (1978), midge larvae and baetid mayfly nymphs are chiefly herbivorous and feed on algae (midge larvae may also consume vascular plants) and organic detritus. Some midge larvae are carnivorous and feed on other insect larvae and oligochaetes (Pennak 1978).

Sample Collection and Storage

Water samples were obtained weekly from each site. Each sample was collected within 15 cm of the surface as a composite of three grab samples (one each from the left and right banks, and one in mid-channel), then about 500 mL was filtered under pressure through a 0.40-μm polycarbonate membrane. About 500 mL of unfiltered water was also collected from each site. All samples were placed in acid-rinsed polyethylene bottles, then acidified with ultrapure nitric acid (HNO_3) to pH <2.0 and chilled on ice for transport to the laboratory.

We attempted to collect triplicate samples of sediment, detritus, and the various biological matrices from each site. Sediment samples (250-300 mL each) were collected by hand with a polyethylene scoop or with a stainless steel Peterson dredge (if the water was too deep to wade), passed through a 2.0-mm (mesh size) polyethylene sieve, then placed in acid-rinsed 500-mL polyethylene bottles and chilled on ice for transport to the laboratory. Detrital samples were collected by straining sediments through a 3.2-mm-mesh dip net, then hand-sorting the materials retained in the net. Stems and leaves of waterweed were collected by hand or with a dip net. Aquatic insects were collected with 3.2-mm-mesh dip nets. Fishes were collected with a 3.2-mm-square-mesh beach seine measuring 23 m long × 1.2 m deep with a bag measuring 1.2 m × 1.2 m × 1.2 m, and with a backpack fish electroshocker. All biota were sorted from debris and rinsed in site water immediately after collection, then wrapped and double-bagged in polyethylene and chilled on ice for transport to the laboratory.

In the laboratory, all samples were stored at −10°C. Within 4 months of collection, biological samples were partially thawed, weighed, measured for total length (TL; fishes only) and weight, re-wrapped, and re-frozen until they were prepared for chemical analysis.

Except for fishes, each biological sample was composited from an unknown number of individuals with a combined biomass varying as follows (sample matrix, damp-dry biomass): detritus, 40.8–46.9 g; waterweed, 40.5–43.1 g; midge larvae, 10.2–16.4 g; and mayfly nymphs, 25.1–26.1 g. Statistics for composite whole-body samples of fishes were as follows (species, minimum-maximum number of individuals per composite, minimum-maximum TL of individuals per composite, minimum-maximum combined biomass of each composite): threespine stickleback, 15-15, 17-60 mm, 9.3-11.9 g; Sacramento sucker, 3-5, 23-128 mm, 1.0-34.0 g; Sacramento squawfish, 5-5, 25-118 mm, 9.7-14.9 g; and chinook salmon, 4-5, 63-81 mm, and 16.2-17.3 g.

Metal Determinations

Copper, Cd, and Zn were determined in unfiltered and filtered water samples. Unfiltered samples were digested with HNO_3, hydrogen perioxide, and heat from a hotplate. Filtered samples were analyzed without digestion. All analyses of water samples were performed by graphite furnace atomic absorption spectroscopy with deuterium arc background correction.

Samples of sediment, detritus, and biota were lyophilized to facilitate digestion and to determine moisture content. Dried samples were homogenized by grinding, then digested with HNO_3 (hydrochloric acid, HCl, was also added to sediment samples) and microwave heating. Digestates were diluted with 1% HCl, then analyzed for Cd and Cu by Zeeman furnace atomic absorption spectroscopy, and for Zn by flame atomic absorption spectroscopy. Concentration results were expressed as "total recoverable."

Quality Control

Digestion spikes of unfiltered samples yielded recoveries of 104% for Cu, 94% for Cd, and 109% for Zn. Analysis spikes of unfiltered samples yielded recoveries of 96% for Cu and 95% for Cd, whereas filtered samples yielded recoveries of 110% for Cu and 95% for Cd. Reference materials used in the analyses included National Institute of Standards and Technology (NIST) trace elements in water, NIST standard reference materials, and USEPA water pollution quality control check samples. Except for three analyses whose concentrations were below the limits of detection (LOD), all measurements from reference materials were within recommended ranges. Reagent and procedure blanks were analyzed for contamination and to calculate the LOD for each element within each group of samples; all were below the LOD. Calculated LODs (mg/L) for unfiltered water were 0.00156 for Cu, 0.00010 for Cd, and 0.00288 for Zn. For filtered water, LODs (mg/L) were 0.00098 for Cu, 0.00014 for Cd, and 0.00174 for Zn.

Pre-digestion sample spike recoveries for samples of sediment, detritus, and biota varied from 87% to 117%. Post-digestion spikes, analyzed as matrix suppression or enhancement checks, varied from 92% to 105% recovery. The accuracy of chemical determinations was assessed by analyzing research and reference materials from the International Atomic Energy Agency, National Institute for Environmental Studies-Japan, Marine Research Council of Canada, NIST, and Midwest Science Center. Recoveries of elements from these materials were within 15% of recommended or certified concentration ranges. Method precision was measured by analyzing samples in duplicate (relative percent difference, RPD) or triplicate (percent relative standard deviation, %RSD). Duplicate analyses yielded RPD values of <17 (mostly <4), whereas triplicate analyses exhibited %RSD values of 0.5-23 (mostly <10). For all analytes, mean blank equivalent concentrations were less than the LODs. Method LODs (mg/kg dry weight) varied with element and matrix as follows: Cd, 0.009 for sediment, 0.009-0.010 for detritus and waterweed, 0.04-0.05 for aquatic insects, and 0.009-0.013 for fish; Cu, 0.35 for sediment, 0.38-0.40 for detritus and waterweed, 0.24-0.72 for aquatic insects, and 0.38 for fish; and Zn, 2.2 for sediment, 1.6-2.1 for detritus and waterweed, 6.1-6.4 for aquatic insects, and 1.2 for fish.

Statistical Comparisons

Nonparametric tests (*e.g.*, Mann-Whitney-Wilcoxon rank sum [two-sample] test, Kruskal-Wallis test, Spearman rank correlation) were used for all statistical comparisons. A multiple means comparison test described by Conover (1980), where pairwise t tests (equivalent to Fisher's least-significant-difference test in the case of equal cell sizes) were performed with ranked values, was used only if significant ($P \leqslant 0.05$) chi-square (χ^2) values were computed by the Kruskal-Wallis test. If a metal concentration fell below the detection limit, a value of half the detection limit was used to facilitate the computation of arthmetic means (Schmitt and Brumbaugh 1990).

Results and Discussion

Mean moisture content of samples varied as follows (minimum-maximum in parentheses): sediment, 37% (28-54%); detritus, 76% (52-89%); waterweed, 91% (89-92%); midge larvae, 83% (81-85%); mayfly nymphs, 79% (78-81%); Sacramento sucker, 77% (74-79%); threespine stickleback, 72% (71-74%); Sacramento squawfish, 78% (77-78%); and chinook salmon, 78% (76-79%). Median values for moisture differed significantly among food-chain matrices ($\chi^2 = 77.509$, df = 8, $P = 0.0001$). To standardize the moisture content of sediment, detritus, and biological samples, all concentrations of metals from these matrices are hereinafter reported on a dry weight basis, unless indicated otherwise.

In general, median concentrations of Cu (3 of 4 comparisons), Cd (4 of 4 comparisons), and Zn (4 of 4 comparisons) did not differ significantly ($P > 0.05$, Mann-Whitney-Wilcoxon rank sum tests) between filtered and unfiltered water samples at the four sites. The sole exception was Cu at BC, where none of the filtered samples contained detectable concentrations, whereas the unfiltered samples contained a maximum concentration of 0.00367 mg Cu/L. Consequently, all references to water will refer to filtered samples.

Variations in Metals Among Food-Chain Matrices

Concentrations of Cu, Cd, and Zn were lowest in water and much higher in other matrices (Tables 2–4). Considerable variation occurred among the concentrations of metals in sediments, detritus, waterweed, and aquatic insects. In the Sacra-

Table 2. Concentrations of copper (mg/L in water, mg/kg dry weight in other matrices) in water, sediment, detritus, and various aquatic biota from the Sacramento River and selected tributaries. N, sample size; $\bar{x}$, arithmetic mean; Min-Max, minimum-maximum[a,b]

Site or statistic	Filtered water N	$\bar{x}$	Min-Max	Sediment N	$\bar{x}$	Min-Max	Detritus N	$\bar{x}$	Min-Max	Waterweed N	$\bar{x}$	Min-Max	Midge larvae N	$\bar{x}$	Min-Max
BC	9	<0.00098 C	<0.00098–<0.00098	3	9.6 D	7.8–11.	3	16. C	16.–16.	3	6.3 D	6.3–6.4	3	17. D	16.–18.
CC	9	0.00089 B	<0.00098–0.0014	3	14. C	13.–15.	3	28. B	26.–29.	3	7.7 C	7.3–8.1	3	30. C	28.–32.
SRLR	9	0.0030 A	0.0015–0.0050	3	210. A	85.–300.	3	300. A	260.–350.	3	150. A	120.–190.	3	200. A	190.–200.
SRJF	9	0.0028 A	0.0012–0.0048	3	32. B	26.–36.	3	36. B	29.–42.	3	89. B	87.–91.	3	140. B	120.–160.
χ^2 or Z		27.894**			10.385*			9.974*			10.385*			10.385*	

Site or statistic	Mayfly nymphs N	$\bar{x}$	Min-Max	Sacramento sucker N	$\bar{x}$	Min-Max	Threespine stickleback N	$\bar{x}$	Min-Max	Sacramento squawfish N	$\bar{x}$	Min-Max	Chinook salmon N	$\bar{x}$	Min-Max
BC	3	18. D	17.–19.	3	3.3 C	3.1–3.7	3	4.1 A	3.7–4.7	3	6.2 A	4.3–7.3	0	---	---
CC	3	29. C	28.–29.	3	4.6 B	4.2–5.4	0	---	---	3	9.0 A	8.1–10.	0	---	---
SRLR	3	75. A	73.–79.	2	9.7 A	7.2–12.	3	9.8 A	8.2–13.	0	---	---	3	5.3 A	5.1–5.5
SRJF	3	48. B	47.–48.	3	11. A	9.0–12.	3	8.4 A	7.7–9.3	3	8.5 A	6.7–9.8	2	5.9 A	4.9–7.0
χ^2 or Z		10.385*			8.803*			5.804			3.467			0.289	

[a] Codes: * $P \leq 0.05$; ** $P \leq 0.01$

[b] Within a column, means followed by the same capital letter are not significantly different ($P > 0.05$, least significant difference test based on ranked values)

Table 3. Concentrations of cadmium (mg/L in water, mg/kg dry weight in other matrices) in water, sediment, detritus, and various aquatic biota from the Sacramento River and selected tributaries. N, sample size; $\bar{x}$, arithmetic mean; Min-Max, minimum-maximum[a,b]

Site or statistic	Filtered water N	$\bar{x}$	Min-Max	Sediment N	$\bar{x}$	Min-Max	Detritus N	$\bar{x}$	Min-Max	Waterweed N	$\bar{x}$	Min-Max	Midge larvae N	$\bar{x}$	Min-Max
BC	9	<0.00014 B	<0.00014–<0.00014	3	0.01 D	<0.01–0.02	3	0.10 D	0.08–0.11	3	0.10 D	0.10–0.11	3	0.20 D	0.14–0.27
CC	9	<0.00014 B	<0.00014–<0.00014	3	0.07 C	0.04–0.11	3	0.12 C	0.11–0.12	3	0.73 C	0.33–1.5	3	0.75 C	0.72–0.78
SRLR	9	0.00022 A	<0.00014–0.00080	3	1.5 A	0.82–1.9	3	11. A	9.9–13.	3	13. B	12.–14.	3	15. A	14.–16.
SRJF	9	0.00014 A	<0.00014–0.00041	3	0.61 B	0.53–0.67	3	1.4 B	1.0–1.7	3	16. A	16.–17.	3	8.3 B	6.1–12.
χ^2 or Z		12.134**			10.385*			10.238*			10.421*			10.385*	

Site or statistic	Mayfly nymphs N	$\bar{x}$	Min-Max	Sacramento sucker N	$\bar{x}$	Min-Max	Threespine stickleback N	$\bar{x}$	Min-Max	Sacramento squawfish N	$\bar{x}$	Min-Max	Chinook salmon N	$\bar{x}$	Min-Max
BC	3	0.46 D	0.44–0.48	3	0.04 C	0.03–0.04	3	0.02 A	0.01–0.02	3	0.03 C	0.03–0.04	0	---	---
CC	3	3.0 C	2.8–3.1	3	0.13 B	0.10–0.15	0	---	---	3	0.20 B	0.17–0.21	0	---	---
SRLR	3	21. B	21.–21.	2	0.96 A	0.72–1.2	3	1.4 A	1.3–1.6	0	---	---	3	1.1 A	1.1–1.2
SRJF	3	23. A	23.–23.	3	0.78 A	0.70–0.90	3	1.3 A	1.1–1.4	3	1.3 A	0.90–2.0	2	1.1 A	1.0–1.3
χ^2 or Z		10.385*			8.843*			5.956			7.200*			0.289	

[a] Codes: * $P \leq 0.05$; ** $P \leq 0.01$

[b] Within a column, means followed by the same capital letter are not significantly different ($P > 0.05$, least significant difference test based on ranked values)

mento River, concentrations of Cu, Cd, and Zn were higher in waterweed and aquatic insects than in fish. In Battle and Cottonwood creeks, however, only Cd concentrations followed a similar pattern. Copper concentrations in Battle and Cottonwood creeks were higher in aquatic insects than in waterweed and fish, whereas Zn concentrations were higher in aquatic insects and fish than in waterweed.

Baudo (1983), Wren *et al.* (1983), Mance (1987), and others reported that Cu, Cd, and Zn do not undergo biomagnification (i.e., a progressive increase in concentration from one trophic level to the next higher level) in the aquatic environment. In general, our results also indicated that these metals did not biomagnify in the Sacramento River. However, fishes from reference sites had Zn concentrations that were higher than those in one or both of the aquatic insects (especially midge larvae).

Although an assessment of mechanisms responsible for variations in metal concentrations among food-chain matrices was beyond the scope of this study, other investigators (e.g., Phillips 1980; Mance 1987; Timmermans *et al.* 1989) reported that metal concentrations are typically higher in sediment than in the overlying water because waterborne metals tend to be removed

Table 4. Concentrations of zinc (mg/L in water, mg/kg dry weight in other matrices) in water, sediment, detritus, and various aquatic biota from the Sacramento River and selected tributaries. N, sample size; x̄, arithmetic mean; Min-Max, minimum-maximum[a,b]

Site or statistic	Filtered water			Sediment			Detritus			Waterweed			Midge larvae		
	N	x̄	Min-Max	N	x̄	Min-Max	N	x̄	Min-Max	N	x̄	Min-Max	N	x̄	Min-Max
BC	9	0.0046 C	0.0020–0.013	3	26. B	21.–35.	3	59. B	54.–65.	3	54. C	54.–55.	3	72. D	65.–79.
CC	9	0.0063 C	0.0019–0.013	3	36. B	30.–41.	3	58. B	55.–61.	3	43. D	41.–45.	3	83. C	81.–86.
SRLR	9	0.056 A	0.0072–0.220	3	550. A	270.–740.	3	770. A	670.–840.	3	460. B	440.–490.	3	430. B	400.–460.
SRJF	9	0.026 B	0.0084–0.075	3	170. A	140.–200.	3	170. A	130.–200.	3	930. A	910.–950.	3	500. A	490.–520.
χ^2 or Z		20.295**			9.974*			9.359*			10.385*			10.385*	

Site or statistic	Mayfly nymphs			Sacramento sucker			Threespine stickleback			Sacramento squawfish			Chinook salmon		
	N	x̄	Min-Max	N	x̄	Min-Max	N	x̄	Min-Max	N	x̄	Min-Max	N	x̄	Min-Max
BC	3	130. D	130.–130.	3	94. A	80.–110.	3	130. B	120.–130.	3	140. B	130.–150.	0	---	---
CC	3	250. C	230.–260.	3	110. A	97.–120.	0	---	---	3	170. A	160.–170.	0	---	---
SRLR	3	1300. B	1300.–1300.	2	130. A	93.–180.	3	170. A	150.–210.	0	---	---	3	170. A	170.–170.
SRJF	3	1600. A	1600.–1700.	3	150. A	140.–160.	3	210. A	200.–210.	3	180. A	170.–190.	2	130. A	130.–130.
χ^2 or Z		10.421*			4.985			6.252*			6.489*			1.443	

[a] Codes: * $P \leq 0.05$; ** $P \leq 0.01$
[b] Within a column, means followed by the same capital letter are not significantly different ($P > 0.05$, least significant difference test based on ranked values)

by adsorption onto particles or by chemical transformation into an insoluble form. By comparison, aquatic plants rooted in metal-enriched sediment tend to have higher concentrations than the sediment because there is active uptake not just from the sediment, but also from the water (Mance 1987). Among aquatic animals, variables such as water quality, diet composition and foraging behavior, physiological processes, and body weight or age of the individual can influence the body burden of metals. In addition, certain metals (e.g., Cu and Zn, but not Cd) are required by animals (including aquatic insects and fish) for growth and survival (National Research Council 1979, 1993; Roesijadi 1992). When ambient concentrations of Cu and Zn in water and food are low (but not below critical threshold concentrations that trigger symptoms of nutrient deficiency), physiological mechanisms may allow animals to accumulate required amounts of these essential micronutrients by decreasing excretion rates and increasing absorption efficiencies (National Research Council 1979). Conversely, when ambient concentrations are high, animals may reduce their body burdens of these metals by increasing excretion rates and decreasing absorption efficiencies. Exposure to very high concentrations of metals (including Cd) can also stimulate production of metallothioneins (metal-binding proteins) that protect cellular function until the metals are cleared from the tissue (Richards 1989; Roesijadi 1992).

Variations in Metal Concentrations Among Sampling Sites

Concentrations of Cu, Cd, and Zn in samples of water, sediment, detritus, waterweed, aquatic insects, and fish were generally higher in the Sacramento River than in the two reference sites (Tables 2–4). In the Sacramento River, metal concentrations in most matrices either declined or did not vary from upstream (SRLR) to downstream (SRJF). However, Cd concentrations in waterweed and mayflies and Zn concentrations in waterweed, midges, and mayflies were exceptional because they increased significantly ($P < 0.05$) from upstream to downstream. Metal concentrations in different matrices also varied between the two reference sites, with higher concentrations usually occurring in samples from CC than from BC.

General Discussion

Dissolved concentrations of Cu, Cd, and Zn in water samples from reference sites (Tables 2–4) were similar to average (or background) concentrations reported by Moore and Ramamoorthy (1984) for freshwater systems and did not exceed site-specific water quality objectives in the Sacramento River Basin Plan (as established by the State of California; CH2M Hill 1991). By comparison, dissolved concentrations of these metals in water samples from the Sacramento River (Tables 2–4) exceeded background concentrations, and in the case of Cd and Zn, several measurements exceeded the site-specific water quality objectives. Nevertheless, they were still far below acutely toxic concentrations reported by Moore and Ramamoorthy (1984) for freshwater fishes.

Concentrations of Cu, Cd, and Zn in sediment, waterweed, aquatic insects, and fish from reference sites (Tables 2–4) were similar to those from relatively unpolluted surface waters (Anderson 1977; Moore and Ramamoorthy 1984; Timmermans *et al.* 1989), whereas concentrations in samples from the Sacramento River (Tables 2–4) fell within the ranges for waters receiving industrial effluent or acid-mine drainage (Moore and Ramamoorthy 1984; Kiffney and Clements 1993). Although several published studies have attempted to delineate the toxic thresholds of these metals in fish diets (e.g., Koyama *et al.* 1979; Murai *et al.* 1981; Lanno *et al.* 1985; Gatlin *et al.* 1989; Wekell *et al.* 1989; Handy 1993) and fish tissues (e.g., Mount and Stephan 1967; Cardeilhac *et al.* 1981; Carbonell and Tarazona 1993; Handy 1993), none of the studies involved fish-forage organisms and fishes sampled during the present study.

Conclusions and Recommendations

Results from the present study indicate that aquatic food chains exposed to acid-mine drainage in the Upper Sacramento River have accumulated Cu, Cd, and Zn without evidence of biomagnification. Concentrations of these metals in water, sediment, detritus, and biota from the river are generally elevated compared to concentrations in similar matrices from nearby tributaries that do not receive acid-mine drainage.

Specific studies are needed to better assess the extent and severity of metal contamination in the Upper Sacramento River and to identify potential toxic effects on fishes. For example, feeding trials are needed to determine if metal-contaminated forage organisms in the river are toxic when consumed by fish. Field surveys that employ techniques for measuring biochemical or physiological indicators of stress (e.g., metallothionein levels) in wild fish may indicate the presence of sublethal toxic effects. Also, surveys of fish distribution and abundance could uncover community-level evidence of metal-associated stress. In addition, generic studies are needed to better predict toxic thresholds of metals ingested by different life stages and species of fish and to determine the importance of interactions among various mixtures and chemical forms of metals in the diet.

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