# FATE AND EFFECTS OF HEAVY METALS ON THE ARKANSAS RIVER

by

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Resources Research Institute

**Completion Report No. 163** 



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15 December, 1991

Grant No. 14-08-0001-G1551-04 Project No. 2

The research on which this report is based was financed in part by the U.S. Department of the Interior, Geological Survey, through the Colorado Water Resources Research Institute; the contents of this publication do not necessarily reflect the views and policies of the U.S. Department of the Interior, nor does the mention of trade names or commercial products constitute their endorsement by the United States Government.

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# ABSTRACT

This research examined fate and effects of heavy metals (Cd, Cu, Zn) in the Arkansas River, a Colorado stream receiving metals from historic mining operations. Benthic invertebrate communities were sampled at several stations located upstream and downstream from California Gulch, a U.S. EPA "Superfund" site in Leadville, CO. Impacted stations were characterized by reduced species richness, reduced abundance, and a shift in community composition from metal-sensitive taxa (e.g. Ephemeroptera) to metaltolerant taxa (Orthocladiini chironomids and Trichoptera). Multivariate analysis of benthic community composition indicated that differences among stations were dependent on season, as greatest effects were observed during spring runoff. Bioconcentration of heavy metals by periphyton and dominant invertebrate taxa was examined at several stations in the Arkansas River. Levels of metals were greatly elevated at stations immediately downstream from California Gulch. Differences in metal concentrations among functional groups were evident, as levels in collectors and grazers were much higher than those in predators. Metal concentrations in organisms remained elevated at stations located greater than 20 km downstream from California Gulch, despite greatly reduced levels in water. Metal concentrations were elevated in several taxa important in the diet of the brown trout, Salmo trutta. The implications of these findings for food chain transfer of metals from benthic invertebrates to S. trutta in the Arkansas River are discussed.

# INTRODUCTION

### **Background**

It is well established that heavy metals from historic mining operations have resulted in some of the most severe water quality problems in the state of Colorado. Numerous small streams and large rivers in the 'Front Range Mineral Belt' have been degraded by heavy metals. In particular, the upper Arkansas River Basin has been recognized as a site of extremely poor water quality for many years. Although several point and non-point sources of impact have been identified, past mining and metallurgical operations in the Leadville area (Leadville, CO) have received the most attention. The Yak tunnel, a U.S. EPA Superfund site, releases a large volume highly contaminated water into California Gulch, which flows directly into the Arkansas River. As a result, levels of cadmium, copper, and zinc are greatly elevated in the Arkansas River immediately downstream.

Previous investigations suggest that the potential exists in the Arkansas River to support a excellent brown trout fishery. Reduced populations and poor survival of adult brown trout observed in the Arkansas River have been attributed to heavy metal contamination. In particular, bioaccumulation of copper, cadmium, and zinc, either from water or from the food chain, may have contributed to the observed decline of <u>S. trutta</u> populations. Benthic invertebrates are the primary food of brown trout and readily accumulate heavy metals, thus providing a potential source of metals to fish in this system.

# Assessment of the Biological Integrity of Stream Ecosystems

The use of biological communities to assess the integrity of stream ecosystems has received considerable attention. The distribution and abundance of diatoms (Patrick 1954), protozoans (Cairns et al. 1972), macroinvertebrates (Winner et al. 1980; La Point et al. 1984; Hilsenhoff 1987; Clements et al. 1988; 1989; 1991) and fish (Karr et al. 1987; Fausch et al. 1990) have been examined in stream biomonitoring studies. Owing to taxonomic and other logistical difficulties, the use of protozoan and diatom communities for monitoring effects of contaminants is limited. Karr's 'Index of Biotic Integrity' (IBI) (Karr

1981), based on species composition and relative abundance of fish communities, has been used successfully in several ecoregions of the United States (Karr et al. 1987) to assess the biological conditions of streams. Because of low species diversity in Rocky Mountain streams, however, the IBI is of limited use in many western states (K.D. Fausch, personal communication).

Analysis of the distribution and abundance of benthic invertebrates is routinely employed in stream biomonitoring studies. Because of their wide variation in sensitivity to contaminants, benthic invertebrates are good indicators of water quality and useful for delineating among reference, impacted, and recovery sites in streams (Winner et al. 1980; La Point et al. 1984; Waterhouse and Farrell 1985; Wiederholm 1984; Chadwick et al. 1986; Clements et al. 1988; 1989; Clements, 1991). Typical indicators of impacted benthic communities include reduced abundance, lower species diversity, and shifts in community composition from sensitive to tolerant taxa.

#### **Bioaccumulation of Heavy Metals**

Metal bioavailability in sub-alpine and alpine streams is poorly understood because the biological communities of such systems are complex and difficult to sample. In addition, metal concentrations in the water show extreme seasonal variation, which may lead to erroneous predictions of the water quality at sites receiving heavy metals.

Feeding habits and size of benthic invertebrates are diverse and may be an important source of variation of metal concentrations of aquatic organisms. Levels of metals in aufwuchs (e.g. biotic and abiotic material accumulated on rock surfaces), can be extremely high as a result of surface adsorption and absorption by periphyton. These materials may represent an important source of metals to those groups associated with the aufwuchs, such as grazers and collectors.

We measured concentrations of heavy metals in the water, periphyton and benthic invertebrates at the Arkansas River to address the following questions: (1) Are there differences in metal concentrations between reference, polluted, and recovery zones? (2) Are there differences in metal concentrations between functional groups? (3) Is monitoring metal concentrations of benthic organisms an adequate monitor of water quality?

#### <u>Objectives</u>

This project examined fate and effects of heavy metals on biological communities in the upper Arkansas River Basin. **The principal objectives of this research were:** 

- 1) to measure the impact of heavy metals (Cd, Cu, and Zn) on benthic invertebrate communities in the Arkansas River;
- 2) to delineate zones of high impact, moderate impact, and recovery based on the distribution and abundance of these organisms;
- 3) to examine seasonal variation in effects of metals on benthic communities;
- 4) to examine the potential transfer of heavy metals from benthic invertebrates to brown trout, <u>Salmo trutta</u>.

# MATERIALS AND METHODS

#### Study Site

The Arkansas River flows in a high mountain basin between the Sawatch and Mosquito mountain ranges in central Colorado (Roline 1988). The river is a typical subalpine stream in the Rocky Mountain region of the western United States. Substrate consists of mainly cobble and pebble, with few boulders. Flow is dependent upon snowmelt, with peak flow occurring during spring runoff and gradually diminishing during late summer and fall. Riparian canopy is scarce consisting mainly of willow and pine.

# Sampling Benthic Invertebrates

To determine the impact of heavy metals on benthic invertebrate communities, quantitative samples were collected from November, 1989 to May, 1991 at stations located throughout the upper Arkansas Basin above and below California Gulch, a U.S. EPA Superfund Site (Fig. 1). Benthic invertebrates were collected from riffle habitats using a standard 0.1 m<sup>2</sup> Hess sampler (5 samples per site). Preliminary investigations at the Arkansas River indicated that five samples were adequate to characterize the benthic communities of this system (Clements, unpublished data). Samples were collected by disturbing the substrate to a depth of 200 cm and allowing currents to wash materials into a 500-<u>u</u>m mesh net. All samples were washed through a 500-<u>u</u>m mesh sieve in the field

and preserved in 10% formalin. In the laboratory, samples were sorted in white enamel pans. All organisms, except chironomids, were identified to the level of genus or species. Chironomids were identified to tribe.

# **Bioaccumulation of Metals**

To investigate the potential transfer of heavy metals through aquatic food chains, aufwuchs (e.g. includes both abiotic and biotic material) and dominant macroinvertebrate taxa collected from stations above and below California Gulch were analyzed for heavy metals. Aufwuchs samples were scraped from whole rocks collected within a riffle area at each sampling location. Rocks were scrubbed with a stiff brush and rinsed with distilled water into a plastic tub. Samples were then transferred into 25 ml polypropylene vials and placed on dry ice. Each rock was treated as one replicate and four replicates were collected from each station.

Macroinvertebrates were collected from within a riffle area at each station using a D-frame net. All organisms were sorted to genus in the field, except for chironomids which were sorted to tribe. Individual organisms were used for metals analysis when possible, except for chironomids and baetid mayflies, which were pooled because of their small biomass. Each vial was treated as a replicate sample. Certain macroinvertebrate species were not present at all stations as a result of either sensitivity to metals or habitat preference. Nevertheless, an effort was made to collect the same species from reference and contaminated sites. All organisms were placed in 25 ml polypropylene scintillation vials and immediately placed on dry ice.

Aufwuchs samples were filtered onto a 45  $\underline{u}$ m Gelman metricel filter and rinsed with 15 ml of glass distilled water. Metal concentrations were determined in whole-body samples of macroinvertebrates. Aufwuchs and macroinvertebrates samples were dried to a constant weight at 70 ° C, cooled in a dessicator, and weighed to the nearest 0.01 mg on a Sartorius microbalance. Samples were placed in 7 ml Falcon polystyrene tubes, and one ml of reagent grade nitric acid (HNO<sub>3</sub>) was added to each tube. The samples were allowed to digest at room temperature overnight. Samples were digested at 50 ° C for 4 h using a water bath placed on a Fisher hotplate. After 4 h 1.0 ml of H<sub>2</sub>O<sub>2</sub> was added to each tube and the samples were heated for 1 h to complete digestion. Tubes were diluted

to a final volume of 7 ml with glass-distilled water. All samples were analyzed for metals using a IL Video 22 Dual Channel Atomic Absorption Spectrophotometer. Levels of detection for zinc, copper, and cadmium, were determined to be 10, 15, and 8, <u>ug/L</u>, respectively. For quality control and to measure percent recovery of metals, National Bureau of Standards Bovine tissue, acid blanks, filter and acid blanks, and distilled water were digested utilizing the same protocol described above for each digestion.

# RESULTS

#### Water Quality

Water samples were collected from 10 stations (Fig. 1) at the Arkansas River during November 1989, May 1990, August 1990, October 1990, and May 1991. The primary contributors of metals to this system were the Leadville Tunnel and California Gulch. Stations EF1 and EF2 were located upstream of the Leadville Tunnel and served as reference stations on the East Fork of the Arkansas River. Stations AR1 and AR2 were located upstream of California Gulch and served as reference stations for the Arkansas River. Concentrations of Cd, Cu, and Zn (total recoverable) measured in water varied seasonally and among stations (Table 1). Although metal levels were elevated at stations EF5 and EF6, the greatest concentrations were measured at station AR3, immediately downstream from California Gulch. Ranges of Cd, Cu, and Zn at this station were 1-43 ug/L, 3-363 ug/L, and 353-8624 ug/L, respectively. The highest concentration of each metal at AR3 was measured in May, 1991, whereas the lowest levels were measured in October, 1990.

# **Benthic Invertebrate Sampling**

Benthic invertebrate communities in the Arkansas River were severely affected by heavy metals. Stations located downstream from Leadville Tunnel (EF5, EF6) and California Gulch (AR3) showed the greatest signs of impact. The total number of taxa, number of individuals, number of taxa, and proportion of Ephemeroptera varied among stations and seasons (Fig. 2). Reference stations were characterized by high taxonomic richness and were generally dominated by several species of metal-sensitive mayflies

(Baetis bicaudatus, B. tricaudatus, B. hageni, Epeorus longimanus, Drunella doddsi). Stations located immediately downstream from Leadville Tunnel and California Gulch showed reduced taxonomic richness and were dominated by metal-tolerant groups such as caddisflies (Arctopsyche grandis, Brachycentrus americanus, B. occidentalis) and Orthocladiini chironomids. Macroinvertebrate density (e.g. number of individuals per sample) also varied among stations and was generally lower at stations EF5, EF6, and AR3 compared to upstream reference locations. Large increases in total abundance at station AR5 (August, 1990) and AR7 (November, 1989) resulted from increased numbers of Orthocladiini chironomids and Simuliidae, respectively.

During each season the number of taxa increased significantly at station AR5 compared to AR3, and then declined again at downstream stations AR7 and AR8. Although these results suggest that recovery occurred at station AR5, other evidence does not support this conclusion. For example, 6-9 species of mayflies were generally collected from upstream reference sites on the East Fork and the Arkansas River; however, significantly fewer (2-3 species) were collected from downstream station AR5 (Fig. 3). The increase in total number of taxa at this site was primarily due to more species of metal-tolerant groups, particularly Trichoptera. The reduced number of taxa observed at stations AR7 and AR8 resulted from fewer of these metal-tolerant species.

Percent community composition also varied among locations at the Arkansas River (Fig. 4). Upstream reference stations were generally dominated by several species of Ephemeroptera. Stations located downstream from Leadville Tunnel and California Gulch were dominated by Trichoptera, Orthocladiini, and other species of Diptera known to be highly tolerant of heavy metals.

# Multivariate Analysis of Community Composition

Canonical discriminant analysis was employed to examine spatial and temporal variation in benthic community composition. This multivariate statistical technique uses linear combinations of several variables to describe relative overlap and separation of locations. Important variables that contribute most to separation of locations along the canonical axes are identified by inspection of the within canonical structure. In the current

analysis, abundance of six dominant groups (Baetidae, Brachycentridae, Heptageniidae, Hydropsychidae, Orthocladiini, and Plecoptera) was employed to distinguish separation and overlap among stations in the Arkansas River. All analyses were conducted on logtransformed data. Stations from the East Fork of the Arkansas were not included in this analysis because other factors (e.g. water temperature, current velocity, substrate composition) confounded effects of heavy metals.

Canonical discriminant analysis of benthic invertebrate data collected from the Arkansas River revealed seasonal variation in the overlap and separation among stations (Table 2; Fig. 5). Multivariate analysis of variance (MANOVA) test statistics were highly significant on each sampling occasion. Canonical variables one (CAN1) and two (CAN 2) accounted for between 79-96% of the total variance. During November, 1989 reference stations AR 1 and AR 2 were clearly separated from downstream sites AR 3 and AR 5 (Fig. 5a). CAN1 was associated with abundance of the caddisflies Hydropsychidae and Orthocladiini chironomids whereas the CAN2 axis was associated with abundance of Hydropsychidae, and the mayflies Baetidae and Heptageniidae.

During May, 1990 CAN1 and CAN2 accounted for 92% of the total variance. Separation along CAN1 of stations AR1 and AR2 from stations AR3, AR5, and AR7 (Fig. 5b) resulted from decreased abundance of Heptageniidae at these downstream sites. CAN2 was associated with increased abundance of Hydropsychidae and Baetidae.

In August, 1990 downstream station AR8 showed considerable overlap with stations reference AR1 and AR2 (Fig. 5c). Separation of these stations from stations AR5 and AR7 along CAN1 resulted from increased abundance of the caddisflies Brachycentridae and Hydropsychidae. There was considerable overlap between stations AR5 and AR7 in October, 1990 (Fig. 5d); however, each of the remaining stations was distinct. Separation of reference stations (AR1, AR2) and recovery station AR8 from downstream sites along CAN2 resulted from high numbers of mayflies (Heptageniidae, Baetidae) and low abundance of Orthocladiini and Brachycentridae.

During May, 1991 downstream stations AR5, AR7, and AR8 showed considerable overlap, whereas the remaining stations were relatively distinct (Fig. 5e). Separation of reference stations AR1 and AR2 along CAN1 was due to reduced abundance of

Heptageniidae and increased abundance of Orthocladiini at downstream stations.

# **Bioaccumulation of Heavy Metals By Benthic Invertebrates**

Concentrations of metals in periphyton were correlated with metal concentrations in the water, with large increases in metals observed at station AR1 and AR3 (Table 3). Metal concentrations in periphyton remained elevated at downstream stations AR5 and AR8.

Concentrations of metals in the benthic invertebrates increased between EF1 and AR1, and dramatically downstream from AR3. Despite decreased metal concentrations in the water at stations AR5 and AR8, concentrations in some invertebrates were higher than those observed at upstream reference stations. Concentrations were variable season to season, but the magnitude of the variation appears to be less than that of water concentrations. Some functional feeding groups, such as, grazers (Baetis spp.), collector-gatherers/filterers (Brachycentrus spp.), (Orthocladiinae) and detritivores (Pteronarcella spp.) bioaccumulated more metals than predators (Rhyacophila spp. and Skwala spp.).

Our research has demonstrated that several dominant invertebrate taxa collected from the Arkansas River are important in the diet of brown trout. In particular, mayflies (Baetis spp.), caddisflies (Arctopsyche grandis, Brachycentrus americanus), and Orhtocladiini chironomids comprise a significant portion of the diet of these fish (Clements, unpublished data). Because of the importance of these taxa in the diet of brown trout, these data suggest that benthic invertebrates are a potential source of metals to fish in the Arkansas River.

# <u>SUMMARY</u>

Results of this study indicate that aquatic communities in the Arkansas River are severely degraded by heavy metals. Both Leadville Tunnel and California Gulch contribute to reduced species richness, reduced abundance, and a shift in community composition from metal-sensitive to metal-tolerant taxa. Metal concentrations declined significantly at station 5, located approximately 5 Km downstream from California Gulch. Certain community-level parameters (e.g. number of taxa and number of individuals) also approached reference station values at this site.

Before concluding that recovery occurred at station AR5, it is important to note the inherent weaknesses in these two parameters. Increased macroinvertebrate abundance observed at station AR5 resulted from large numbers of Chironomidae (Orthocladiini) and Trichoptera (Brachycentrus spp.), two groups with high tolerance for heavy metals (Clements 1991). Similarly, the relatively large number of taxa at this station resulted from increased species richness of Trichoptera, with a concomitant decrease in the number of species of Ephemeroptera (Fig. 3).

Because of these limitations, changes in community composition are more useful indicators of the impact of heavy metals. Based on differences in community composition and abundance of metal-sensitive Ephemeroptera, I conclude that during most months recovery was not observed until station AR8, the furthest downstream site. In fact, during certain months (e.g. May, 1991), benthic community composition did not recover at this downstream site.

This study also found high concentrations of metals in several species of invertebrates known to be important in the diet of brown trout (<u>Salmo trutta</u>). In particular, concentrations of Cd, Cu, and Zn in the mayfly <u>Baetis</u> spp. were greatly elevated. Interestingly, metal concentrations in benthic organisms remained elevated at downstream stations, despite reduced water concentrations. On several occasions heavy metal levels in organisms were actually higher at stations AR5 and AR8 than station AR3, immediately downstream from California Gulch. These results suggest that other sources of heavy metals, in addition to water, were important at downstream sites. The elevated levels of metals measured in periphyton, an important food resource for many invertebrate taxa, supports this hypothesis.

Benthic organisms are known to be good monitors of heavy metals because they are relatively sedentary and readily bioaccumulate metals, even at low water concentrations. This research demonstrated that benthic invertebrates and periphyton are perhaps better indicators of water quality than abiotic samples. Because these organisms readily biocxoncentrate metals at levels much greater than those measured in water, they are useful for monitoring of water quality at stations where water levels approach limits

of analytical detection.

This study also showed that benthic invertebrates may represent an important link in the transfer of metals to higher trophic levels. These results have important implications for studying the uptake of heavy metals by <u>Salmo trutta</u> in the Arkansas River. At stations where water concentrations of metals are greatly elevated (e.g. AR3), uptake of metals across the gills will be the predominant route of exposure. At downstream sites where water concentrations have decreased, food chain transfer will contribute significantly to high body burdens of metals measured in these fish.

Bioaccumulation of metals through the diet by S. trutta will be greatly influenced by feeding habits and prey availability. In the Arkansas River I found that downstream sites were dominated by several species of metal-tolerant invertebrates (Orthocladiini chironomids, <u>Brachycentrus</u> spp., <u>Arctopsyche grandis</u>). Several mechanisms have been hypothesized to account for metal tolerance of benthic organisms. For example, some species have the ability to sequester and accumulate metals at high levels. Because brown trout are opportunistic predators that shift feeding habits based on prey availability, it is likely that these tolerant organisms will comprise a significant portion of the diet. As a result of reduced prey diversity and increased consumption of contaminated prey at impacted sites, dietary accumulation of metals may contribute significantly to total body burdens. This phenomenon, which has been termed the "food chain effect" has been reported by Dallinger et al. (1987). Preliminary studies conducted at the Arkansas River have found that brown trout consume highly contaminated prey at stations downstream from California Gulch (Rees, unpublished data). Documentation of differences in feeding habits of brown trout between stations at the Arkansas River is the focus of a current study funded by the Colorado Water Resources research Institute and will be presented in next year's annual report.

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· · · · · ·	Nov. 1989	May 1990	Aug. 1990	Oct. 1990	May 1991
Station					
EF1	0.4	1.2	0.2	0.4	1.7
EF2		0.1		0.2	0.4
EF5	0.9	3.6	0.6	0.7	1.1
EF6		3.8	0.6	0.7	0.7
AR1		2.1	0.5	0.5	1.0
AR2	1.3	1.8	0.3	0.3	2.2
AR3	8.4	4.8	8.0	0.9	43.0
AR5		2.0	2.1	0.6	5.6
AR7	0.9	1.0	0.7	0.8	2.2
AR8	0.4	0.9	0.5	0.4	5.6

Table 1a. Total dissolved cadmium concentrations (ug/L) at selected Arkansas River stations from November, 1989 to May, 1991.

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	Nov. 1989	May 1990	Aug. 1990	Oct. 1990	May 1991
Station					
EF1	1.9	5.7	3.6	2.1	9.1
EF2		1.6		1.0	2.2
EF5	1.0	2.2	3.3	1.0	2.1
EF6		2.0	3.0	1.0	1.7
AR1		3.1	8.3	1.0	2.5
AR2	2.1	2.6	3.1	1.0	4.1
AR3	13.0	9.6	33.4	3.4	363.0
AR5	2.8	6.8	7.8	2.9	20.7
AR7	2.0	5.1	6.3	2.5	8.2
AR8	1.7	4.2	0.5	1.8	23.7

Table 1b. Total dissolved copper concentrations (ug/L) at selected Arkansas River stations from November, 1989 to May, 1991.

	Nov. 1989	May 1990	Aug. 1990	Oct. 1990	May 1991
Station					
EF1	71.0	256.0	49.0	76.0	381.0
EF2		<10.0		<10.0	10.0
EF5	361.0	852.0	238.0	310.0	431.0
EF6		1004.0	205.0	341.0	341.0
AR1		425.0	158.0	208.0	188.0
AR2	356.0	426.0	118.0	117.0	382.0
AR3	2026.0	1459.0	2200.0	353.0	8624.0
AR5		453.0	611.0	143.0	1037.0
AR7	262.0	212.0	112.0	286.0	372.0
AR8	141.0	233.0	108.0	138.0	802.0

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Table 1c. Total dissolved zinc concentrations (ug/L) at selected Arkansas River stations from November, 1989 to May, 1991.

Table 2. Results of canonical discriminant analysis for the Arkansas River. Separation among stations was based on abundance of the six dominant groups (Baetidae, Brachycentridae, Heptageniidae, Hydropsychidae, Orthocladiini, Plecoptera). Dominant variables refer to those groups having within canonical values of greater than 0.30.

	November 1989	May 1990	August 1990	October 1990	May 1991
Hotelling's- Lawley trace	49.4	60.1	58.6	64.3	62.4
F-value	28.6	34.9	34.0	37.3	36.2
Eigenvalue Canonical 1 Canonical 2	38.0 8.1	46.8 8.3	27.8 18.5	38.8 22.9	47.5 8.8
Variance explained Canonical 1 Canonical 2 Total	77.0 16.5 93.5	77.7 13.8 91.5	47.5 31.6 79.1	60.4 35.7 96.1	76.1 14.2 90.3
Dominant varaibles Canonical 1	HYDROS ORTHOC	HEPTAG	BRACHY HYDROS	HYDROS ORTHOC	-HEPTAG ORTHOC
Canonical 2	HYDROS BAETID HEPTAG	HYDROS BAETID	HYDROS -ORTHOC	HEPTAG BAETID -ORTHOC -BRACHY	ORTHOC HEPTAG BAETID

Table 3a: Concentration of cadmium, copper, and zinc (ug/l), respectively, in <u>Arctopsyche spp.</u> collected from the Arkansas River, CO. Values equal mean concentrations  $\pm 1$  standard error.

Cadmium			<u>STATIONS</u>			
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990	1.95 <u>+</u> 0.93	6.13 <u>+</u> 0.78			16.00 <u>+</u> 2.50	5.37 <u>+</u> 0.02
November 1990	1.65 <u>+</u> 0.40	2.55 <u>+</u> 0.55	2.46 <u>+</u> 0.34	4.65 <u>+</u> 1.45	8.06 <u>+</u> 0.54	4.73 <u>+</u> 1.27
May 1991	5.55 <u>+</u> 2.67	4.23 <u>+</u> 1.26	2.51 <u>+</u> 0.17		20.30 <u>+</u> 3.90	
August 1991	1.95 <u>+</u> 0.50	3.32 <u>+</u> 0.60			5.26 <u>+</u> 0.27	
Copper						
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990	20.45 <u>+</u> 3.4	19.67 <u>+</u> 2.45			91.01 <u>+</u> 6.36	28.38 <u>+</u> 8.18
November 1990	15.85 <u>+</u> 1.95	9.30 <u>+</u> 1.10	8.30 <u>+</u> 1.90	55.60 <u>+</u> 1.70	68.23 <u>+</u> 4.16	27.66 <u>+</u> 9.24
May 1991	51.89 <u>+</u> 21.11	17.60 <u>+</u> 1.65	23.79 <u>+</u> 4.80		130.39 <u>+</u> 13.80	
August 1991	13.10 <u>+</u> 4.57	16.25 <u>+</u> 1.68			36.96 <u>+</u> 1.33	
Zinc						
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990	348.0 <u>+</u> 13.00	625.67 <u>+</u> 18.67			1871 <u>+</u> 296.6	609.5 <u>+</u> 60.90
November 1990	162.4 <u>+</u> 15.00	500.5 <u>+</u> 100.1	478.5 <u>+</u> 2.55	695.6 <u>+</u> 140.3	1226.2 <u>+</u> 257.2	652.9 <u>+</u> 163.2
May 1991	517.7 <u>+</u> 208.5	340.6 <u>+</u> 33.00	528.2 <u>+</u> 25.23		1526 <u>+</u> 216.9	
August 1991	265.5 <u>+</u> 100.5	447.5 <u>+</u> 20.50			634.5 <u>+</u> 22.50	

Cadmium		<u>S</u>	<u>TATIONS</u>			_
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1 <b>990</b>	3.39 <u>+</u> 1.08	5.14 <u>+</u> 0.51	2.82 <u>+</u> 0.21	14.20 <u>+</u> 1.59		
November 1990	1.90 <u>+</u> 0.27	2.76 <u>+</u> 0.43	4.83 <u>+</u> 0.89	11.70 <u>+</u> 0.45	6.30 <u>+</u> 1.70	
May 1991	3.34 <u>+</u> 0.58	2.71 <u>+</u> 0.39	6.24 <u>+</u> 0.45	11.20 <u>+</u> 0.94	3.74 <u>+</u> 0.41	
August 1991	2.44 <u>+</u> 0.15	1.72 <u>+</u> 0.30		5.34 <u>+</u> 0.09		
Copper						
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990	21.01 <u>+</u> 1.37	28.40 <u>+</u> 8.17		252.84 <u>+</u> 20.82		
November 1990	17.95 <u>+</u> 1.45	11.50 <u>+</u> 2.68	18.60 <u>+</u> 4.85	101.73 <u>+</u> 8.75	16.40 <u>+</u> 1.15	
May 1991	37.37 <u>+</u> 5.39	18.23 <u>+</u> 2.11	31.93 <u>+</u> 5.41	70.93 <u>+</u> 8.67	57.30 <u>+</u> 5.03	
August 1991	14.65 <u>+</u> 0.25	12.89 <u>+</u> 0.99	· · · · · · · · · · · ·	42.06 <u>+</u> 0.08		
Zinc						
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990	645.0 <u>+</u> 61.34	1015 <u>+</u> 95.5	804.0 <u>+</u> 64.35	2381.2 <u>+</u> 233.14		
November 1990	644.8 <u>+</u> 8.40	668.1 <u>+</u> 64.90	733.1 <u>+</u> 42.72	937.7 <u>+</u> 43.70	728.5 <u>+</u> 79.10	
May 1991	1201 <u>+</u> 316.80	1009 <u>+</u> 118.70	1293 <u>+</u> 103.20	4650 <u>+</u> 229.0	1526 <u>+</u> 216.85	
August 1991	553.50 <u>+</u> 100.50	448.0 <u>+</u> 95.00		796.5 <u>+</u> 96.5		

concentrations  $\pm 1$  standard error.

Table 3c: Concentration of cadmium, copper, and zinc (ug/l), respectively, in <u>Baetis spp.</u> collected from the Arkansas River, CO. Values equal mean concentrations  $\pm 1$  standard error.

Cadmium			<u>STATIONS</u>			
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990		15.10 <u>+</u> 3.45				36.34 <u>+</u> 1.06
November 1990		12.30 <u>+</u> 0.93	10.30 <u>+</u> 1.60	20.43 <u>+</u> 4.60	33.57 <u>+</u> 4.34	19.40 <u>+</u> 2.55
May 1991		9.64 <u>+</u> 0.85	9.91 <u>+</u> 0.75	24.76 <u>+</u> 0.34	33.08 <u>+</u> 2.75	24.09 <u>+</u> 1.76
August 1991		10.92 <u>+</u> 0.66		16.61 <u>+</u> 2.89	32.04 <u>+</u> 4.61	
Copper						
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990		44.29 <u>+</u> 8.70				92.56 <u>+</u> 8.25
November 1990		28.06 <u>+</u> 3.30	22.65 <u>+</u> 1.25	81.80 <u>+</u> 10.55	73.65 <u>+</u> 9.05	48.60 <u>+</u> 5.40
May 1991		52.49 <u>+</u> 12.01	56.03 <u>+</u> 8.06	158.84 <u>+</u> 22.10	106.9 <u>+</u> 6.24	80.95 <u>+</u> 3.82
August 1991		38.15 <u>+</u> 0.99		80.77 <u>+</u> 12.77	69.53 <u>+</u> 5.08	
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990		3133 <u>+</u> 31.50				6374 <u>+</u> 89.11
November 1990		4657 <u>+</u> 771.6	3048 <u>+</u> 53.50	4352 <u>+</u> 431.4	7657 <u>+</u> 873.5	3676 <u>+</u> 800.9
May 1991		8111 <u>+</u> 826.7	1485 <u>+</u> 15.70	8518 <u>+</u> 5.07	1342 <u>+</u> 51.70	926.6 <u>+</u> 33.81
August 1991		2800 <u>+</u> 100.0		3466 <u>+</u> 448.5	5300 <u>+</u> 781.0	

Table 3d. Concentration of cadmium, copper, and zinc (ug/l), respectively, in <u>Brachycentrus spp.</u> collected from the Arkansas River, CO. Values equal mean concentrations  $\pm 1$  standard error.

Cadmium			<u>STATIONS</u>			
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990		8.38 <u>+</u> 0.38			14.99 <u>+</u> 2.98	
November 1990		2.60 <u>+</u> 0.20			14.96 <u>+</u> 3.60	31.83 <u>+</u> 0.75
May 1991					14.90 <u>+</u> 1.57	
August 1991					17.88 <u>+</u> 0.89	
Copper						
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990		22.46 <u>+</u> 5.15			54.91 <u>+</u> 6.89	
November 1990		2.65 <u>+</u> 0.15			53.70 <u>+</u> 11.50	62.00 <u>+</u> 1.45
May 1991					88.62 <u>+</u> 7.29	
August 1991	1.0				53.51 <u>+</u> 1.02	
Zinc						
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990		2525 <u>+</u> 236.6			1476 <u>+</u> 229.1	
November 1990		111.5 <u>+</u> 12.50			1357 <u>+</u> 366.8	
May 1991					2153 <u>+</u> 381.8	
August 1991					1306 <u>+</u> 17.5	

Cadmium			<u>STATIONS</u>	2		
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990					20.23 <u>+</u> 3.10	
November 1990				5.30 <u>+</u> 0.20	7.85 <u>+</u> 1.15	
May 1991		5.47 <u>+</u> 1.35		7.35 <u>+</u> 2.51	5.30 <u>+</u> 0.76	6.22 <u>+</u> 0.62
August 1991				8.26 <u>+</u> 1.44		10.52 <u>+</u> 1.15
Copper	· · · · · · · · · · · · · · · · · · ·					
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990					60.59 <u>+</u> 11.08	
November 1990		11.80 <u>+</u> 1.80	58.30 <u>+</u> 27.60		31.75 <u>+</u> 5.85	62.00 <u>+</u> 1.45
May 1991		15.44 <u>+</u> 1.03		79.22 <u>+</u> 31.18	52.03 <u>+</u> 2.75	67.91 <u>+</u> 4.89
August 1991			•	100.31 <u>+</u> 17.39		53.37 <u>+</u> 8.85
Zinc						
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990					8448 <u>+</u> 552.0	
November 1990				777.5 <u>+</u> 202.5	1076 <u>+</u> 196.5	
May 1991		360.8 <u>+</u> 62.28		857 <u>+</u> 171.0	566.1 <u>+</u> 37.10	709.7 <u>+</u> 142.2
August 1991		·	·····	1712 <u>+</u> 275.5		1436 <u>+</u> 297.0

Table 3e: Concentration of cadmium, copper, and zinc (ug/l), respectively, in <u>Orthocladiinae spp.</u> collected from the Arkansas River, CO. Values equal mean

Table 3f: Concentration of cadmium, copper, and zinc (ug/l), respectively, in <u>Skwala spp.</u> collected from the Arkansas River, CO. Values equal mean concentrations  $\pm$  1 standard error.

Cadmium	- <u></u>		<u>STATIO</u>	<u>ONS</u>		
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990			4.20 <u>+</u> 0.82		6.94 <u>+</u> 0.54	2.05 <u>+</u> 0.19
November 1990			3.50 <u>+</u> 0	•	7.46 <u>+</u> 0.84	
May 1991			2.13 <u>+</u> 0.23	4.99 <u>+</u> 0.66	4.03 <u>+</u> 0.54	
August 1991						
Copper						
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990					59.36 <u>+</u> 4.18	62.41 <u>+</u> 4.70
November 1990			27.30 <u>+</u> 4.00			46.10 <u>+</u> 3.07
May 1991			66.00 <u>+</u> 7.80	113.73 <u>+</u> 10.22	67.26 <u>+</u> 6.08	
August 1991						
Zinc						
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990			603.7 <u>+</u> 21.30		1089 <u>+</u> 43.67	
November 1990			293.5 <u>+</u> 52.50		1152 <u>+</u> 88.33	
May 1991			345.0 <u>+</u> 24.20	713.2 <u>+</u> 33.34	553.7 <u>+</u> 7. 90	
August 1991						

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Table 3g. Concentration of cadmium, copper, and zinc (ug/l), respectively, in periphyton collected from the Arkansas River, CO. Values equal mean concentrations  $\pm$  1 standard error.

Cadmium		<u>ST</u>	ATIONS			
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990						
November 1990	7.13 <u>+</u> 0.61	32.90 <u>+</u> 7.30	32.70 <u>+</u> 6.81	62.10 <u>+</u> 17.5	81.93 <u>+</u> 11.93	23.00 <u>+</u> 4.72
May 1991	47.00 <u>+</u> 11.80	41.00 <u>+</u> 10.80	10.80 <u>+</u> 3.30	90.00 <u>+</u> 30.40	130.60 <u>+</u> 21.30	54.00 <u>+</u> 11.50
August 1991						
Copper						
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990						
November 1990	96.90 <u>+</u> 23.14	69.50 <u>+</u> 15.30	330.5 <u>+</u> 125.0	613.6 <u>+</u> 56.40	375.3 <u>+</u> 32.50	143.0 <u>+</u> 56.50
May 1991	447.2 <u>+</u> 114.0	66.10 <u>+</u> 25.80	32.00 <u>+</u> 4.00	348.0 <u>+</u> 87.60	183.0 <u>+</u> 15.80	293.0 <u>+</u> 59.00
August 1991						
Zinc						
MONTH	EF 1	AR 1	AR 2	AR 3	AR 5A	AR 8
August 1990						
November 1990	1744 <u>+</u> 237.00	6992 <u>+</u> 1332	6397 <u>+</u> 2254	15647 <u>+</u> 2617	16714 <u>+</u> 2617	4696 <u>+</u> 1212
May 1991	2136 <u>+</u> 551.0	4023 <u>+</u> 1088	1823 <u>+</u> 446.0	2999 <u>+</u> 974.0	4022 <u>+</u> 790	7722 <u>+</u> 1751
August 1991				•••••		

# FIGURE LEGENDS

- Fig. 1. Map of sampling locations at the Arkansas River.
- Fig. 2. Responses of benthic communities to heavy metals in the Arkansas River. Each point represents the mean (n=5) per sample. Arrows indicate the location of Leadville Tunnel (above EF5) and California Gulch (above AR3).
- Fig. 3. Mean number of Ephemeroptera and Trichoptera collected from reference station AR2 and impacted station AR5 at the Arkansas River.
- Fig. 4. Percent composition of dominant groups collected from the Arkansas River.
- Fig. 5. Canonical discriminant analysis of benthic communities collected from the Arkansas River.



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