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AQUATIC INSECTS AS ENVIRONMENTAL MONITORS OF TRACE METAL CONTAMINATION: RED RIVER, NEW MEXICO

T. R. LYNCH¹ and C. J. POPP²

New Mexico Institute of Mining and Technology Socorro, NM 87801, U.S.A.

and

G. Z. JACOBI

New Mexico Highlands University. Division of Math and Science, Las Vegas, NM 87701, U.S.A.

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Abstract. Discontinuous sampling of water for toxic chemicals is unreliable in lotic ecosystems or in systems subjected to sporadic discharges. Such sampling either fails to detect the contaminants or seriously underestimates their concentrations. This study explored the use of resident aquatic insects as biomonitors of trace metal contamination in a river subjected to episodic spills of Mo mill tailings. Aquatic insects at sites downstream from the mill accumulated more Mo and Cu than upstream insects. Due to a prolonged shutdown at the mine, no tailings spills were recorded during this study and Mo and Cu levels in water and bottom sediments declined to near background levels. However, concentrations of these metals in insects declined only slightly. This study indicates that aquatic insects are useful biomonitors of trace metal contamination in an intermittently impacted system. Reduction of elevated trace metal concentrations from the insects occurred at a slower rate than from the non-living components of the river ecosystem thereby facilitating detection of the spills.

1. Introduction

The adverse impact of mining and milling of ore bodies on various types of aquatic ecosystems has been well documented (Starnes, 1983; Lewis, 1980; Jennett and Foil, 1979; Schrader and Furbish, 1978). In the western United States many mine/mill operations are located in relatively undisturbed mountain watersheds used for recreation or they support valuable fish and wildlife resources (Raleigh, 1977). Because streams are dynamic systems, inputs of toxicants may be swept away quickly with no apparent lasting effect. Alternatively, these materials may become trapped in bottom sediments where they can exert chronic, adverse effects. Aquatic insects are capable of concentrating metals such as Pb (Nehring et al., 1979), Cd (Colborn, 1981), Mo (Colborn, 1982), and a number of other trace metals (Namminga and Wilhm, 1977; Mathis and Cummings, 1973; Burrows and Whitton, 1983). Insects are near the bottom of the food chain and may be an important agent of trace metal entry into food chains (Nehring 1976; Spehar et al., 1978).

In this study, a potential source of heavy metal contamination was examined within

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¹ Department of Biology.

² Department of Chemistry.

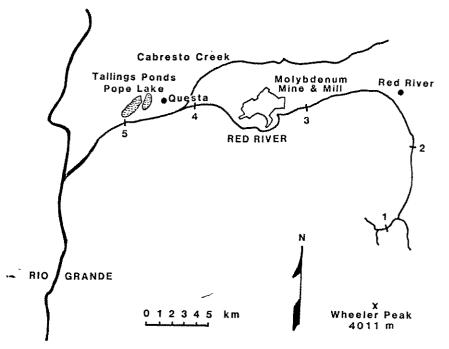


Fig. 1. Map of study area showing the location of sampling sites and possible sources of anthropogenic contaminants, Taos County, NM. The slurry pipeline parallels the Red River from the Molycorp mine to the tailings ponds.

the Red River drainage basin of Taos County, New Mexico (Figure 1). The Red River, a tributary of the Rio Grande, drains 490 km² of land, most of which is located in the Carson National Forest and in the Wheeler Peak Wilderness Area of northcentral New Mexico. Potentially significant anthropogenic impacts on water quality in the Red River watershed are the seasonal resort towns of Red River and Questa, a state-owned fish hatchery, and a large Mo mining operation. The mine/mill complex is connected by a pipeline to a tailings disposal pond (Pope Lake) located about 13.7 km downstream of the mine. The pipeline is located immediately adjacent to the Red River. At least 72 breaks occurred in the pipeline between 1966 and 1981 resulting in discharges of slurries of processed mill tailings directly into the river (BLM, 1978; United States of America vs Molycorp, Inc., 1981). Contamination of the river by trace metals may also occur as surface drainage from the mine/mill complex, discharge from the tailings disposal pond, and possibly by natural weathering of exposed rock formations in the watershed.

Potential environmental impact was recognized by Bhappu et al. (1967) when cyanide, used in the milling of Mo, was implicated in a fish kill in the Red River. Data gathered by the U.S. Geological Survey (1979) indicated that Mn, Zn, and Mo concentrations in the Red River were higher (≥ one order of magnitude) below Molycorp's mine/mill complex compared to upstream values and compared to Cabresto Creek water samples. Cabresto Creek (Figure 1) enters the Red River between Questa and the mine, but drains

a largely undistudrainage. Faith (in water and secompared to samin Mo, specific calliver. Data pressed, Cu, Mo, and

The purpose of thirteen trace management to contain trations of Cd, C of metals (As, Cr used for comparidistance. The or milling operation a period which e

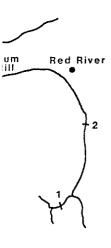
2.1. SAMPLE CO

Samples were col of the Red River the tailings pond sediment, and aq-1981 – a low flow and again during

Water was col 0.45 µm cellulose redistilled HNO₃

Bottom sedime washed glass jars a stainless steel s After freeze-dryin using HF, aqua r

Benthic macroi diameter mesh, M taxonomic group, identifications wer and Cummins (19 composite sample insects analyzed is the insects were



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ssible sources of anthropogenic ver from the Molycorp mine to

Figure 1). The Red River, of which is located in the ess Area of northcentral n water quality in the Red nd Questa, a state-owned nill complex is connected out 13.7 km downstream he Red River. At least 72 1g in discharges of slurries United States of America ce metals may also occur rom the tailings disposal mations in the watershed. at al. (1967) when cyanide, Red River. Data gathered , and Mo concentrations ow Molycorp's mine/mill esto Creek water samples. a and the mine, but drains

a largely undisturbed basin of 95 km² which is located just north of the Red River drainage. Faith (1974) reported that concentrations of Na, K, Ca, Mg, Ni, Sn, and Mo in water and sediments collected downstream from Molycorp's mine were elevated compared to samples taken upstream. Garn (1985) reported highly significant increases in Mo, specific conductance, and sulfate below the tailings pond discharge into the Red River. Data presented by Andreasen (1981) indicated that trout were bioaccumulating Cd, Cu, Mo, and Zn although apparently not at acute levels.

The purpose of this study was to determine the spatial and temporal distribution of thirteen trace metals in water, sediment, and aquatic insects in a mountain stream subject to contamination by a Mo mine/mill complex. In addition to examining concentrations of Cd, Cu, Mn, Mo, Ni, and Zn, the suite of metals studied includes a number of metals (As, Cr, Fe, Hg, Pb, Sc, and V) not associated with the Mo deposits that were used for comparison of mine-induced and naturally occurring changes with downstream distance. The opportunity to study residual contamination was present because the milling operation stopped in August 1981 and remained closed until September 1983, a period which encompassed the duration of this study.

7. Materials and Methods

2.1. SAMPLE COLLECTION AND TREATMENT

Samples were collected from the riffle sections of five different sites over a 27 km stretch of the Red River extending downstream from the Wheeler Peak Wilderness to below the tailings pond discharge. The sample sites are shown in Figure 1. Samples of water, sediment, and aquatic insects were collected on each of three dates: December 15–16, 1981 – a low flow period; May 26–27, 1982 – a period of high runoff due to snowmelt; and again during low flow on September 30, October 1, 1982.

Water was collected for trace metal analysis by grab sampling, filtered through $0.45 \mu m$ cellulose filters, placed in acid-washed polyethylene bottles, and stabilized with redistilled HNO₃. All acids were redistilled from Teflon containers.

Bottom sediments were collected as grab samples and frozen in widemouth, acid-washed glass jars. Prior to analysis, the samples were thawed and wet-sieved through a stainless steel sieve (0.063 mm diameter mesh) to collect the silt-clay size fraction. After freeze-drying (Labconco Model 5), the samples were digested in Teflon beakers using HF, aqua regia, and HClO₄ (Johnson and Maxwell, 1981).

Benthic macroinvertebrates were collected with hand-held kick screens (1.0 mm diameter mesh, Merritt and Cummins, 1984). The organisms were sorted in the field by taxonomic group, usually genus (Table I), placed in polyethylene bags, and frozen. Field identifications were verified by microscopic examination in the laboratory using Merritt and Cummins (1984). All insects belonging to the same taxon were analyzed as a composite sample for each sampling site and date. The total number and dry weight of insects analyzed is indicated by order, collection date, and site in Table II. For analysis, the insects were thawed, enumerated, weighed, freeze-dried, reweighed, and acid-

TABLE I

Insect taxa from the Red River that were analyzed for trace metals. Numbers following the name indicate the sampling sites where each was obtained.

Plecoptera Nemouridae Megarcys sp. Pteronarcella sp. Isogenoides sp. Isoperla sp.	1 1, 2 2, 3, 4, 5 3, 4, 5 5	Ephemeroptera Baetis sp. Rhithrogena sp. Ameletus sp. Ephemerella sp.	1, 2, 3, 4 1, 2 1 2, 3, 4
Chloroperlidae Trichoptera Rhyacophila sp. Arctopsyche sp. Hydropsyche sp.	1, 2 2, 3, 4, 5 3, 4, 5	Diptera Tipulidae Atherix sp.	1, 2, 3, 5 3, 4, 5

TABLE II

Composite number of taxa, individual insects, and their biomass for each sampling grouped by location relative to the mine/mill. Each taxon was analyzed separately for each site and sampling time.

Insect order and sampling data		Upstream (sites 1-3)			Downstream (sites 4-5)		
	# taxa	# individuals	dry wt.	# taxa	# individuals	dry wi	
		Decen	nber 1981	7.41111		···	
Ephemeroptera	2	145	0.394	0	. 0		
Plecoptera	4	387	4.139	2	0	0.000	
Trichoptera	2	140	0.900	2	144	2.203	
Diptera	1	17	0.693	1	353	3.528	
		•.	0.075		35	0.479	
		Ma	y 1982	2. T	•		
Ephemeroptera	3	172:	2.034	1	58	0.000	
Plecoptera	3	265	9.095	3	250	0.979	
Trichoptera	2	237	1.754	2	228	3.935	
Diptera	2	23	0.637	2	4	1.459 0.311	
•		Octob	er 1982				
Ephemeroptera	3						
lecoptera	3	264	0.983	1	44	0.062	
richoptera	5	523	2.812	2	479	2.636	
пспораета Diptera	3	72	0.322	2	48	0.228	
whierg	2	77	2.119	1	14	0.205	

digested with redistilled HNO₃ and $\rm H_2O_2$. The digestion procedure used from 0.1 to 1.0 g of dried insects, depending on availability. If more than 1 g was available, a duplicate sample was prepared. The insects were placed in Teflon beakers with 10 mL of concentrated HNO₃ and heated gently for 1 hr. The mixture was cooled, 5 mL of 30% $\rm H_2O_2$ were added, and the solution was heated gradually to a boil followed by cooling and dilution to 25 mL for analysis.

2.2. ANALYSES

Trace metal anal spectrometer equigenerator system. Mo, Ni, Pb, V, ar was used for As Canadian Cert mission) and NBS quality control st digested samples run on 66 and 145 quality control sa water samples we

3.1. WATER

Trace metal concer of possible tailings concentrations of these changes are samples and the e

Mean co

Metal

As Cd Cr Cu Fe Hg

Mn Mo Ni

Pb Se V Zn

Numbers following the ained.

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ampling grouped by location site and sampling time.

wnstream (sites 4-5)

# individuals	dry wt.		
0	0.000		
144	2.203		
353	3.528		
35	0.479		
58	0.979		
250	3.935		
228	1.459		
4	0.311		
44	0.062		
479	2.636		
48 .	0.228		
14	0.205		

edure used from 0.1 to in 1 g was available, a lon beakers with 10 mL re was cooled, 5 mL of by to a boil followed by

2.2. ANALYSES

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Trace metal analyses were performed using a Perkin-Elmer 403 atomic absorption spectrometer equipped with a model HGA 400 graphite furnace and MHS-10 hydride generator system. Either flame or furnace techniques were used for Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, and Zn depending on the concentration. The hydride generator system was used for As and Se and a Coleman MAS-50 analyzer was used for Hg.

Canadian Certified Reference Material (SL-1, Canadian Atomic Energy Commission) and NBS 1645 (National Bureau of Standards River Sediment) were used as quality control standards for atomic absorption analysis of digested samples. All digested samples were run with blanks. Duplicate analysis for at least one metal were run on 66 and 14% of the sediment and insect samples respectively. Trace metal EPA quality control samples were also run to check the accuracy of the instrument when water samples were analyzed.

3. Results and Discussion

3.1. WATER

Trace metal concentrations in filtered water samples collected above and below the area of possible tailings contamination exhibited variable behavior (Table III). Increased concentrations of Mn, Mo, Ni, and Zn were observed at downstream sites. Whether these changes are significant could not be determined because of the small number of samples and the extensive variation in the data.

TABLE III $\begin{tabular}{ll} Mean concentrations and standard deviation ($\mu g \, L^{-1}$) of trace metals in filtered water samples from the Red River, NM. \end{tabular}$

Metal	Upstream $(n = 9)$ (sites 1-3)	Downstream $(n = 6)$ (sites 4, 5)
As	[4, (20)	14. (18)
Cd	5.1 (5.3)	4.1 (3.6)
Сг	2.5 (4.4)	1.2 (1.6)
Cu	14. (10)	17. (9)
Fe	67. (44)	93. (35)
Hg	< 0.1	< 0.1
Mn	77. (81)	490. (430)
Мо	22. (49)	120. (140)
Ni	4.1 (4.4)	22. (31)
Pb	1.1 (0.9)	1.3 (1.0)
Se	3.5 (3.5)	3.2 (3.2)
V	2.2 (1.2)	1.6 (0.8)
z Zn	36. (94)	110. (180)

3.2. SEDIMENTS

Stream bottom sediments were screened to collect the 230-size fraction (<0.063 mm) to provide a size-consistent set of samples. This small-sized material should contain the highest concentrations of metals because of the presence of clays in this fraction and the resulting high surface area to volume ratios of the sediments. Mean values for metal concentrations in these sediments are shown in Table IV. Concentrations of metals in sediments were usually three to four orders of magnitude higher than in the water column. Metals which showed large downstream increases were Mn, Mo, Ni, and Zn while the other metals exhibited little or no downstream change. The elements Mn and Zn show an approximate doubling of concentration from upstream to downstream sites. Molybdenum concentrations increased by a factor of six, while Ni increased by about one and one half. Data obtained from the USGS (1982) for a single set of sediment samples taken in September of 1982 at the same sites as in the present study also show substantial downstream increases in some trace metals (Cu, Mn, Mo, Zn, but not Cd, Fe, or Pb). This increase is especially evident for Cu, Mn, Mo, and Zn at site 5 which is located below the discharge point of the tailings settling pond (Pope Lake, Figure 1).

Concentrations of Cu, Mn, Mo, Ni, and Zn in the sediments were subjected to a statistical analysis using one-way ANOVA and a priori orthogonal contrasts (Nie et al., 1975). Molybdenum concentrations were significantly higher (p < 0.002) at the downstream sites than at the upstream sites (Table IV). No statistically significant differences were detected for Cu, Mn, or Ni. Zinc concentrations at stations 4 and 5 were signifi-

TABLE IV

Mean concentrations ($\mu g g^{-1}$) on a dry weight-basis and standard errors (S.E.) for trace metals in the bottom sediments (<0.063 mm) of the Red River. The data are grouped by sampling location relative to the area of disturbance.

Metal	Upstream $(n = 9)$ (sites 1-3)			ream $(n = 6)$ es 4, 5)	
	Mean	S.E.	Mean	S.E.	
As	16.	8.3	18.	11.	
Cd	3.8	2.9	5.8	2.9	
Cr	84.	7.2	71.	7.1	
Cu	220.	82.	240.	31.	
Fe	8600.	240.	8500.	200.	
Hg	0.7	0.3	0.5	0.3	
Mn	590.	56.	~1100. ³	610.	
Мо	9.0⊕	1.5	53.**	26.	
Ni	40.	5.1	62.	20. 24.	
Pb	41.	14.	30.	17.	
Se	1.4	0.3	1.0	0.2	
V	120.	44,	87,	29.	
Zn	230.	66.	650:	140.	

p < 0.002.

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Examples of downstream are behavior of Mn. stations 4 and 5 is typical of mos V; concentration downstream site as it appears to although concentration (Figure 2). Lead due to a single v the spring runoff is then little characteristics.

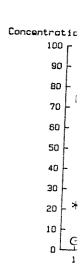


Fig. 2. Concentration size fraction of Red R

3.3. INSECTS

A variety of inse (Plecoptera, 6 gen 2 genera) were colpresent at all sam

Mean metal con different insect tax:

te fraction (< 0.063 mm) iterial should contain the lays in this fraction and s. Mean values for metal icentrations of metals in igher than in the water ere Mn, Mo, Ni, and Zn e. The elements Mn and am to downstream sites. e Ni increased by about a single set of sediment present study also show In, Mo, Zn, but not Cd, , and Zn at site 5 which 1 (Pope Lake, Figure 1). nts were subjected to a nal contrasts (Nie et al., p < 0.002) at the downly significant differences ns 4 and 5 were signifi-

rd errors (S.E.) Red River, The adisturbance.

ream (n = 6) es 4, 5)

es 4,	. 5)
	S.E.
	11. 2.9
	7.1
	31. 200.
	0.3
	610. 26.
	24.
	17. 0.2
	29.
	140.

cantly higher (p < 0.05) than stations 1 and 2 combined, but not when station 3 was included with the other upstream sites.

Examples of changes in trace metal concentrations in sediments as one proceeds downstream are shown in Figure 2. The behavior of Mo is also representative of the behavior of Mn, Ni, and Zn, all of which exhibit a notable increase in concentration at stations 4 and 5 (below the mine/mill complex and tailings pond). The behavior of Cr is typical of most of the other elements analyzed including As, Cd, Cu, Fe, Hg, Se, and V; concentrations of these elements did not change significantly between upstream and downstream sites during the sampling period. Lead behaves in an anomalous manner as it appears to decrease in concentration downstream of the mine/mill complex although concentrations at sites 4 and 5 were slightly higher than at sites 1 and 2 (Figure 2). Lead had a very high mean concentration at station 3 which is almost entirely due to a single value of $160 \mu g g^{-1}$ recorded for the sediment sample collected during the spring runoff. When this value is discarded, the mean becomes $48 \mu g g^{-1}$ and there is then little change from upstream to downstream locations.

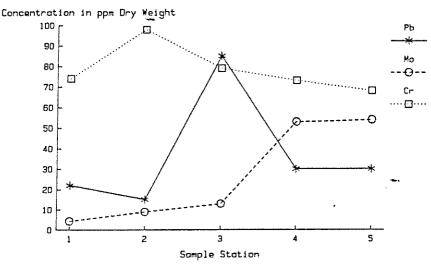


Fig. 2. Concentrations (µg g^{-t}) of selected trace metals on a dry weight basis in the 230-(<0.063 mm) size fraction of Red River sediments. Each point is an average of three analyses, one for each sampling date.

3.3. INSECTS

A variety of insects representing mayflies (Ephemeroptera, 4 genera), stoneflies (Plecoptera, 6 genera), caddisflies (Trichoptera, 3 genera), and true flies (Diptera, 2 genera) were collected and analyzed during the study (Table I). Not all genera were present at all sampling sites nor at all sampling times.

Mean metal concentrations for insects were calculated by pooling all data from the different insect taxa. This treatment of the data has the effect of smoothing out variation

due to differences in life history characteristics, size, physiology, and feeding habits. A more detailed analysis of the insect data by genus, trophic level, and functional role is

Levels of heavy metals accumulated by benthic insects often differed on the basis of in preparation. location relative to the mine/mill complex (Table V). When the data for all sampling times are pooled on an upstream or downstream basis, the concentrations for Cu, Mn, Mo, Ni, and Pb exhibited substantial increases below the mine/mill complex. Molybdenum concentrations increased by a factor of five while Cu, Mn, Ni, and Pb increased by a factor of two below the mine/mill complex. On the basis of this preliminary analysis, the data for Cu, Mn, Mo, Ni, and Zn were subjected to a more detailed inspection. Even though the Pb concentrations almost doubled, this element was not studied further because of its low concentration. The increase in Zn observed downstream from the complex was not large, but the data were included in the analysis primarily because of the corresponding downstream increases of Zn detected in water and sediment samples.

TABLE V

Mean concentrations (µg g $^{-1}$ dry weight) and standard errors (S.E.) of metals in pooled insect samples relative to the location of the mine/mill complex. The value n represents the number of pooled samples and is equivalent to the number of sites multiplied by the number of times

Metal		Upstream (sites 1-3)		Downstream (sites 4, 5)		
		Mean	S.E.	n	Mean	S.E.
As Cd Cr Cu Fe Mn Mo Ni Pb Se Sn Zn	3 6 9 9 9 9 3 2 3	0.9 1.9 4.9 43: 1040. 240. 2.8 7.1 0.5 0.9 4.9 320.		2 4 6 6 6 6 6 2 3 2 6	0.5 1.3 2.7 82.* 1300. 540. 17.* 13.* 0.9 0.2 5.5 350.	0.2 0.6 16. 190. 340. 3.4 2.7 - 0.

p < 0.05.

Concentrations of four of the five selected metals (Cu, Mn, Mo, Ni) in benthic insects tended to increase with downstream distance (Figure 3). This change was most striking for Mo which exhibited a major increase between site 3 (upstream) and sites 4 and 5 (downstream). Site 5 receives effluents from the Pope Lake tailings disposal site. Zinc concentrations were relatively constant from upstream to downstream. Orthogonal contrasts of the upstream and downstream locations averaged across time indicated Fig. 3. Co

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that downstrea upstream (p <

In addition t Manganese co than when site mean value (7 stantially, but 1 1982). Correst this study or it unknown, but

b p < 0.001.

y, and feeding habits. A l, and functional role is

differed on the basis of ne data for all sampling centrations for Cu, Mn, he mine/mill complex. ile Cu, Mn, Ni, and Pb basis of this preliminary ted to a more detailed d, this element was not in Zn observed downncluded in the analysis of Zn detected in water

S.E.) of metals in pooled insect value n represents the number tiplied by the number of times

Downstream (site	s 4, 5)
Mean	S.E.
0.5	
1.3	0.2
2.7	0.6
82.ª	16.
1300.	190.
540.	340.
17.b	3,4
13. ^a	2.1
0.9	
0.2	0.1
5.5	•••
350.	55.

10, Ni) in benthic insects thange was most striking ream) and sites 4 and 5 ilings disposal site. Zinc ownstream. Orthogonal ad across time indicated

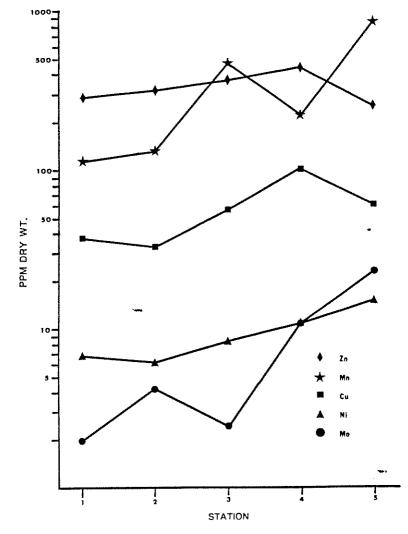


Fig. 3. Concentrations (µg g⁻¹ dry weight) of selected trace metals in insects by location.

that downstream Mo concentrations in insects were significantly higher than those upstream (p < 0.001, Table V).

In addition to Mo, high levels of Mn were also detected in insects at site 5 (Figure 3). Manganese concentrations at sites 4 and 5 (pooled) were significantly higher (p < 0.05) than when sites 1 and 2 were pooled, but not when site 3 was included in the upstream mean value (Table V). Manganese concentrations in sediments also increased substantially, but not significantly (p > 0.05), between sites 4 and 5 (this study and USGS, 1982). Corresponding Mn concentration increases in water samples were not found in this study or in the USGS data (1982). The source of the high Mn values at site 3 is unknown, but may result from a natural acid weathering zone produced by the oxidation

of sulfide minerals in exposed soils above sample site 3. High Mn levels at site 5 may result from chemical processes in the disposal site that mobilize Mn ions.

Concentrations of Cu, Ni, and Zn in insects did not exhibit consistent trends with respect to location (Figure 3). The nonparametric Mann-Whitney U test was used for the Cu and Ni concentrations for lack of homoscedasticity. Concentrations of both metals were significantly higher in downstream insect samples (p < 0.05) than in insects collected at the upstream sites (Table V). No significant differences existed between the upstream and downstream levels of Zn in insects.

The lower concentrations of Cu and Zn at site 5 compared to site 4 are not readily explained. Lower levels of Zn were observed in water and sediment samples, but the differences were not statistically significant (p > 0.05). Mean Cu concentrations in water and sediment samples increased between sites 4 and 5, but again the differences were not statistically significant (p > 0.05).

3.4. Temporal examination of water, sediment, and insect samples

The mine experienced a prolonged period of inactivity between August 1981 and September 1983 due to low market demand for Mo. The mine ceased to be a point source as no discharges to the river occurred during this interval. This presented an opportunity to study depuration of contaminant metals from the system and the role of the mine as a nonpoint source due to wind and water erosion of the tailings piles.

The Red River is normally exposed to high runoff during the late spring due to snowmelt and during the summer due to frequent thunderstorms. After this period of high runoff, the mean dissolved Fe, Mn, Mo, and Ni concentrations apparently

TABLE VI

Mean concentrations (µg L⁻¹) of dissolved trace metals in water samples from the Red River, NM, showing the effects of stream scouring during the high runoff period of spring and summer, 1982.

Metal	Upstream	m (n = 3)	Downstream $(n = 2)$		
	Dec. 1981	Oct. 1982	Dec. 1981	Oct. 1982	
As	0.3	0.4	0.3	2.0	
Cd	4.1	1.9	9.0	1.5	
Cr	6.5	0.5	3.0	0.4	
Cu	4,4	15.5	9.8	20.0	
Fe	91.0	59.0	130.0	58.0	
Hg	ND"	< 0.1	< 0.1	< 0.1	
Mn	170.0	36.0	880.0	470.0	
Мо	2.7	0.9	210.0	19.0	
Ni	5.7	3.5	57.0	7.0	
Pb	0.8	1.0	2.7	2.5	
Se	7.3	< 0.1	6.5	< 0.1	
v	1,0	2.1	1.8	0.6	
Zn	110.0	< 0.1	330.0	< 0.1	

[&]quot; Not determined.

decreas concent both the of these suggesti

substant sedimen from the was grea

Mean con-

Dec. 1981 May 1982

Oct. 1982

Dec. 1981 May 1982 Oct. 1982

Dec. 1981 May 1982 Oct. 1982

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levels at site 5 may Mn ions.

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SECT SAMPLES

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s. After this period of entrations apparently

amples from the Red River, moff period of spring and

Downstream $(n = 2)$					
c. 1981	Oct. 1982				
1.3	2.0				
),0	1.5				
1.0	0.4				
1.8	20.0				
),0	58.0				
).1	< 0.1				
),0	470.0				
1.0	19.0				
7.0	7.0				
2.7	2.5				
5.5	< 0.1				
1.8	0.6				
).0	< 0.1				

decreased at the downstream sites (Table VI). Other metals either did not change in concentration after flushing (As, Pb, V) or exhibited decreases of similar magnitude at both the upstream and downstream sites (Cd, Cr, Se, Zn). The statistical significance of these changes is unknown due to the small number of samples involved, but is suggestive of a scouring effect.

Concentrations of Cu, Mn, Mo, Ni, and Zn in stream sediments also dropped substantially between December 1981 and October 1982 (Table VII). Some changes in sediment metal concentrations were also observed at the site immediately upstream from the mine/mill complex, but the magnitude of the changes at the downstream sites was greater than at the upstream sites. Metal concentrations for Cu, Mn, Mo, Ni, and

TABLE VII

Mean concentrations (µg g⁻¹ dry weight) of selected trace metals in sediment and insect samples showing the effects of stream scouring during the high runoff period of spring and summer, 1982.

		Sediments			Insects	
	Station			Station		
	Upstream	Đ o wi	istream	Upstream	Downstream	
	1-3	4	5	1-3	4	$\frac{5}{n=2-4}$
	n = 3	n = 1	n = 1	n = 10-11	n=2-4	
			Мо			
	12	130.	83.	3.9	14.	29.
Dec. 1981	12.	14.	59.	2.2	12.	15.
May 1982	8.2	19.	20.	2.4	7.5	25.
Oct. 1982	6.4	17.	£ 0.			
			Cu			-
Dec. 1981	260.	420.	580.	38.	160.	64.
	330.	160.	150.	62.	93.	63.
May 1982 Oct. 1982	57.	78.	57.	28.	57.	56.
Uct. 1962	57.					
			Mn			
	660.	1200.	3400.	89.	240.	170.
Dec. 1981	640.	650.	790.	190.	100.	150.
May 1982	480.	210.	350.	450.	317.	2300.
Oct. 1982	400.	2.0	•			
			Ni			
5 . 1001	43.	120.	93,	5,0	\$3 .	10.
Dec. 1981	47.	48.	52.	9.1	13.	14.
May 1982 Oct. 1982	30.	27.	30.	7.3	6.1	22.
Oct. 1982	7407					
			Zn			
D 1091	270.	1000.	860.	160.	340.	250.
Dec. 1981	320.	440.	530.	360.	600.	240.
May 1982 Oct. 1982	100.	130.	170.	460.	400.	280.

Zn decreased by factors of 1.4 to 4.6 at the upstream stations, 4.6 to 7.5 at station 4 (below complex), and 3.1 to 10.2 at station 5 (below tailings disposal pond), respectively. This general decline in sediment metal concentrations is attributed to flushing of the contaminated sediments during the high flow period.

A more detailed analysis of the metal data in insects was undertaken in which the data were pooled for upstream or downstream location across all taxa, but separated on the basis of time of sampling (Table VII). Molybdenum concentrations in insects were significantly higher (p < 0.01) downstream from the mine/mill complex during each sampling. Copper concentrations in insects were significantly higher at downstream sites during the December 1981 (p < 0.001) and October 1982 (p < 0.001) samplings, but not during the May 1982 sampling. Manganese was significantly higher in downstream insects (p < 0.05) only during the December 1981 sampling which was prior to stream sediment purging by runoff. Nickel and Zn concentrations in downstream insects did not differ significantly from those found in upstream insects.

Despite the flushing and apparent removal of contaminated sediments during the high flow period, concentrations of Cu, Mo, and Ni in insects declined at station 4 only. Metal levels at other stations either increased or remained constant relative to December 1981 values. Thus, some mobilization and downstream transport of metals did occur during the study, but the insect metal concentrations were declining less rapidly than the sediments.

4. Conclusions and Summary

Reliance on stream water sampling is subject to considerable variation created by changing flow regimes, partitioning between suspended and dissolved forms, the formation and location of plumes, solubility differences, and the general inability to detect intermittent discharges. Unless water samples are taken continuously, detection of a spill hours or days after the event is unlikely because of rapid flushing from the system. Sampling of river sediments is readily accomplished; however, the significance of the detected concentrations in sediments is difficult to ascertain. Presumably the rationale for a toxic substance sampling program is to determine the potential impact of the contaminant on the biological community. The question of bioavailability is left unaddressed if only water or sediments are sampled. The use of resident stream organisms solve many of the aforementioned problems. Insects are numerous, easily sampled residents of the environment and permit the development of biologically relevant data. Insects may be particularly appropriate where the discharges into the system are irregular, unpredictable, and of short duration.

Aquatic insects may accumulate trace metals and are useful bioindicators of episodic discharges of trace metals to their environment. The insects below the mine/mill complex exhibited elevated levels of Mo, Mn, and occasionally Cu when compared to those from upstream locations. These metals are associated with the mineralization in the Mo deposit. Other heavy metals studied as controls did not exhibit this behavior. After nearly 15 mo of no recorded spills, metal concentrations were declining in water and

sediments, but a metals in the se complete depura associated with t significantly to t

We greatly appr Improvement Di grateful to Gian 1 Eileen Corbin, S Susan Britvec fo

Andreasen, J. K.: 198 Wildlife Service, C. Bhappu, R. B., Fair, Molybdenum', in P. BLM: 1978, Water Ou. of Land Manageme Burrows, I. G. and W. Colborn, T. E.: 1981. M.S. Thesis, Weste Colborn, T. E.: 1982, Faith, S. E.: 1974, 'An Thesis, New Mexico Garn, H. S.: 1985, J. Jennett, J. C. and Foil Johnson, W. M. and M. Lewis, M. A.: 1980, 'Se Drainage (Arizona)'. pp. 191-204, Mathis, B. J. and Cum

Merritt, R. W. and Cum Company, Dubuque, Namminga, H. and Wi Nehring, R. B.: 1976, E Nehring, R. B., Nisson. Nie, N. H., Hull, C. H., Social Sciences, McG Raleigh, R. F.: 1977, Fi. Schrader, E. L. and Fu-Spehar, R. L., Anderso: Starnes, L. B.: 1983, Fi. United States of Americ: for the District of Ne United States Geologic Geological Survey, W United States Geologic Geological Survey, W

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ators of episodic ine/mill complex ed to those from ition in the Mo behavior. After ng in water and sediments, but concentrations in insects remained relatively unchanged. Either the metals in the sediments were slowly moving downstream and the time required for complete depuration was longer than the sampling program or non-point sources associated with the mine/mill complex or natural geochemical sources were contributing significantly to the elevated levels seen in downstream insects.

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References

Andreasen, J. K.: 1981, The Accumulation of Metal Contaminants in Red River, New Mexico, U.S. Fish and Wildlife Service, Columbia, MO.

Bhappu, R. B., Fair, J. H., and Wright, J. R.: 1967, 'Waste Problems Relative to Mining and Milling of Molybdenum', in Proceedings of the 22nd Industrial Waste Conference, Purdue University, Lafayette, IN. BLM: 1978, Water Quality Monitoring Plan for the Rio Grande and Red River, Taos County, New Mexico, Bureau of Land Management, Santa Fc, NM.

Burrows, I. G. and Whitton, B. A.: 1983, Hydrobiologia 106, 263.

Colborn, T. E.: 1981, 'Aquatic Insects as Measures of Trace Element Presence: Cadmium and Molybdenum', M.S. Thesis, Western State College, Gunnison, CO. 81230.

Colborn, T. E.: 1982, Bull. Environm. Contam. Toxicol. 29, 422.

Faith, S. E.: 1974, 'An Equilibrium Distribution of Trace Elements in a Natural Stream Environment', M.S. Thesis, New Mexico Institute of Mining and Technology, Socorro, NM 87801.

Garn, H. S.: 1985, J. Soil and Water Conserv. 40, 458.

激素使用的多种激素的多种。 "我们还是我们还是我们还有一个人。"

Jennett, J. C. and Foil, J. L.: 1979, J. Water Poll. Control Fed. 51, 378.

Johnson, W. M. and Maxwell, J. A.: 1981, Rock and Mineral Analysis, 2nd ed., John Wiley & Sons, New York. Lewis, M. A.: 1980, 'Selected Heavy Metals in Sediments and Biota from Desert Streams of the Gila River Drainage (Arizona)', in Aquatic Toxicology, ASTM STP 707, American Society for Testing and Materials, pp. 191-204.

Mathis, B. J. and Cummings, T. F.: 1973, J. Water Poll. Control Fed. 45, 1573.

Merritt, R. W. and Cummins, K. W.: 1984, Aquatic Insects of North America, 2nd Ed., Kendal/Hunt Publishing Company, Dubuque, IA.

Namminga, H. and Wilhm, J.: 1977, J. Water Poll. Control Fed. 49, 1725.

Nehring, R. B.: 1976, Bull. Environm. Contam. Toxicol. 15, 147.

Nehring, R. B., Nisson, R., and Minasian, G.: 1979, Bull. Environm. Contam. Toxicol. 22, 103.

Nie, N. H., Hull, C. H., Jenkins, J. G., Steinbrenner, K., and Bent, D. H.: 1975, Statistical Package for the Social Sciences, McGraw-Hill Inc., New York, NY.

Raleigh, R. F.: 1977, Fisheries 2, 2-5 and 13.

Schrader, E. L. and Furbish, W. J.: 1978, Bull. Environm. Contam. Toxicol. 20, 159.

Spehar, R. L., Anderson, R. L., and Fiandt, J. T.: 1978, Environ. Pollut. 15, 195.

Starnes, L. B.: 1983, Fisheries 8, 2.

United States of America vs Molycorp, Inc.: 1981, Judgement by Consent, District Court of the United States for the District of New Mexico, Albuquerque, NM.

United States Geological Survey: 1979, Water Resources Data for New Mexico, Water Year 1978, U.S. Geological Survey, Water Data Report, New Mexico 79-1.

United States Geological Survey: 1982, Water Resources Data for New Mexico, Water Year 1981, U.S. Geological Survey, Water Data Report, New Mexico 82-1.