Aquatic Insects as Indicators of
Heavy Metal Contamination
in Selected New Mexico Streams

A THESIS

Presented to the Graduate Division

School of Science and Engineering

New Mexico Highlands University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Lisa Franklyn Failing

1993

Lisa Carter

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ABSTRACT

The objectives of this study were to (1) document current conditions and establish baselines for future comparisons and trend analyses of metal contamination in selected streams; (2) discern patterns in metal concentrations in insects and streambed sediments collected at sites upstream and downstream from mining activities on the Pecos and Red Rivers; and (3) correlate metal concentrations in aquatic insects with metal concentrations in streambed sediment samples from the same site. Aquatic insects and streambed sediments were collected from three northeastern New Mexico streams and analyzed for aluminum, cadmium, copper, lead, manganese, molybdenum, nickel, and zinc. The Pecos and Red Rivers were selected because of varying effects of mining on each site. Comanche Creek was a control site.

Aquatic insects are useful indicators of the presence of metals in biota. Apparently, various insect taxa have different metal accumulation rates. Consequently, no single taxon consistently had the highest concentrations of metals. For instance, Ephemerellidae had the highest concentrations of Al, Cd, Cu, Mn, Ni, and Zn (1900, 26.2, 285, 1396, 114, and 2843 μg/g, respectively); whereas, Pteronarcella badia had the highest concentration of Mo (26.4 μg/g) and Claassenia sabulosa had the highest concentration of Pb (1.31 μg/g). The differences in metal

concentrations found in Ephemerellidae and other insect taxa could be a result of the combined effects of feeding behavior differences between Ephemerellidae and the other insect taxa, and the grouping of more than one genera into a composite Ephemerellidae sample.

A downstream increase of metal concentrations in aquatic insects and streambed sediments was apparent. In the Pecos River upstream and downstream from an abandoned copper mine, Cu concentrations in _C_. _sabulosa_ were 49 and 66 μg/g, respectively; Cu concentrations in streambed sediments were 97 and 550 μg/g, respectively. In the Red River upstream and downstream from a molybdenum mine, Cu concentrations in _P_. _badia_ were 36 and 159 μg/g, respectively; Cu concentrations in streambed sediments were 58 and 340 μg/g, respectively. However, a weak correlation in metal concentrations was found between aquatic insects and streambed sediments from the same site.

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ACKNOWLEDGEMENTS

My choice of advisors was a key to the success of this project. Gerald Jacobi was responsible for planting the original seed of thought and he then allowed me to develop it to the extent that I did. Larry Sveum provided the greatly needed technical support for the analytical procedures. He also accepted that I did not need to be a "chemist" to apply the principles of chemistry to natural systems. Finally, countless hours were spent discussing methodology, data analysis, and other aspects of this project with Kenneth Bentson. He helped culture both the idealistic and realistic approach to scientific research. Each was an inspiration in his own right, and I am greatly indebted to them.

Sample collection and preparation were extremely labor intensive. I would like to thank everyone that took the time to help me collect all of the necessary samples. In addition, I would like thank those who helped me prepare each sample for analysis.

Most of all I am thankful for my son, Adrian, because from start to finish he gave me the extra strength and courage to face each day. This might have started as a dream of one, but it ended as a reality because of the support, guidance, and inspiration of many.

INTRODUCTION AND LITERATURE REVIEW

New Mexico is known for its rich ore deposits. Exploitation of mineral resources has played a key role in the history of New Mexico (Beck and Haase 1969) and will continue to do so in the future. Current and historical mining practices have created a number of environmental problems. Steps to minimize environmental degradation are necessary, since mining will continue to be of economic importance in New Mexico.

Mining operations disturb large areas of land and concentrate many metals in certain locations. It has been projected that by the year 2000 mining activities will have directly disrupted 240,000 km^2 of the earth's surface (Salomons 1989). The release of metals into the environment results from impermeable, sulfide-containing rocks being crushed and subsequently weathered by contact with water and oxygen. Sulfuric acid production reduces pH during weathering and causes rapid dissolution of metals from the rock in tailings (Drever 1988). Certain metals such as cadmium, which may be found at relatively low levels in subsurface deposits, can become concentrated in tailings that remain after milling. The oxidation-reduction potential and pH of sediments and streamwaters determines the equilibrium of heavy metals between the solid and aqueous phases. In general, a moderately low redox potential and pH condition leads to metal mobilization (Gambrell et al. 1976). Consequently, metals in runoff and leachate from tailings have the potential of contaminating aquatic systems.

Several reasons for reducing environmental impacts associated with mining are (1) contamination of surface- and ground water reduces the already limited supply of high-quality freshwater; (2) demands for high-quality water will continue to increase; and (3) mining operations may pose ecological threats to aquatic organisms, ecosystems, and human health. According to Salomons (1989) and Hutchinson (1979), milling and smelting are presently releasing an estimated 7 to 70,000 metric tons of metals to aquatic environments. Ecosystem responses to metal exposures can be either structural, functional, or both (Luoma and Carter 1987). According to Luoma and Carter (1987), structural changes, shown by responses of species composition, species richness, and population sizes of the various taxa, are the most frequently used measures of community responses to metal contamination. Ecophysiological compensations frequently occur in response to metal exposures (Schindler 1987). Consequently, functional changes in a particular process, such as primary productivity, are difficult to interpret except in cases of severe impacts. Spehar et al. (1978) suggest that certain metals are taken up by aquatic organisms and concentrate in the food chain. Bioconcentration of metals can thus pose a threat to human health, if humans consume organisms from the ecosystem.

Biological monitors or indicator species are useful for rapid assessment of mining impacts and natural metal inputs to aquatic systems. In general, any species can be considered an indicator species if it is present in a particular environmental setting. According to Abel (1989),

> "the term indicator organism is ... sometimes reserved to those species which have narrow and specific environmental tolerances, so they will show a marked response to quite small changes in environmental quality."

For the purpose of this discussion, the term indicator species applies to organisms whose tissue levels of metal contaminants are measured in order to infer the possible extent of metal contamination in the environment.

Aquatic insects have been suggested as biological indicators because of their integration of metal contamination over time and space (Lynch et al. 1988). Aquatic insects spend a large portion of their life cycle in either lotic or lentic habitats and are integral components of specific ecosystems. Most benthic organisms are restricted to defined stream reaches, although some aquatic insects exhibit the phenomenon of drift (Cole 1983). Reduction of water quality by increased chemical contamination and sediment loads near mines can thus result in habitat loss and population reductions of sensitive aquatic organisms. Lynch et al. (1988) suggested that aquatic insects sorb metals from water and sediments and therefore integrate sporadic pulses of metals with background metal concentrations, whereas current water sampling techniques do not. Water sampling is often inadequate because metal concentrations are below the detection limits of current analytical techniques.

The objectives of this study were to (1) document current conditions and establish baselines for future comparisons and trend analyses of metal contamination in selected stream systems; (2) discern patterns in metal concentrations in insects and streambed sediments collected at sites above and below mining sites on the Pecos and Red Rivers; and (3) correlate metal concentrations in sediments with metal concentrations in insects from samples collected at the same sites. To achieve these objectives, aquatic insects and streambed sediments were collected from three surface water systems in northeastern New Mexico and analyzed for aluminum, cadmium, copper, lead, manganese, molybdenum, nickel, and zinc (Al, Cd, Cu, Pb, Mn, Mo, Ni, and Zn, respectively).

Three systems, the Pecos and Red Rivers and Comanche Creek, were selected because of the varying impacts of mining on each system. The Pecos and Red Rivers have been contaminated by metals from mining activities. Comanche Creek is a relatively pristine control site.

Aquatic insects and bed sediments from below mining activities should have higher concentrations of the selected metals than insects and bed sediments above mining activities. In addition, aquatic insects should indicate whether certain metals can enter the food chain. It was hypothesized that there should be relationship between the concentrations of metals found in aquatic insects and bed sediments from respective locations. The extent of temporal variability in metal concentrations detected in samples collected from the Pecos River during April and November, 1990 was uncertain.

Site Descriptions:

The following descriptions of each drainage system provide general background information on the geology, hydrology, and history of human activities in the study areas. It is difficult to separate the physical environment and human impact effects on water quality and ecosystems; therefore, the background information pertaining to each system is necessary to understand them.

The Pecos River is a tributary of the Rio Grande and its headwaters originate in Precambrian granite and quartzite mountain slopes (Jacobi and Smolka 1982) (Table 1). The river upstream of Pecos, New Mexico, is a high gradient coldwater stream with fast, turbulent flows (Sublette et. al 1990). Between 1880 and 1939, numerous mining operations within the upper Pecos River drainage removed high-grade ores containing zinc, lead, gold, silver, and copper. Tererro mine, which was a shaft mining operation located adjacent to Willow Creek and the Pecos River was a leading ore producer during its operation. The mine was abandoned in 1939 due to ore depletion and water intrusion (Harley 1940). As a result of mine tailing usage in the watershed and leaching of metals from mine tailings and wastes piles, the New Mexico Legislature appropriated $5.5 millon for cleanup of the abandoned mine site (Pederson 1993).

Table 1. Primary geological formations of selected basins (Dane and Bachman 1965).

Geological Formation	Pecos R.	Red R.	Comanche Cr.
Mississippian	+	-	-
Devonian	+	-	-
Devonian, undivided	+	-	-
Pennsylvanian, undivided	+	-	-
Intrusive rocks[a]	-	+	-
Extrusive rocks[b]	-	+	+
Landslides	-	+	-
Precambrian	+	+	+

[a] rocks of various ages

[b] rocks of various composition and age, including some sedimentary rocks and volcanic rock fragments

The Red River is another tributary of the Rio Grande and drains the north slope of Wheeler Peak. Undivided Precambrian rocks, consisting of metamorphic and granitic parent materials (New Mexico Geological Society 1981) with associated extrusive and intrusive volcanic material (Cordell et al. 1985), are the primary geological formation within the basin (Table 1). The reach selected for this study had a channel gradient of 1-3% and a substrate composition of cobble, boulder, and gravel (Smolka and Tague 1987). Currently, the Red River, upstream of the town of Red River, is classified as a high quality cold-water fishery (New Mexico Water Quality Control Commission 1988); and the lower Red River, near the Rio Grande confluence, is part of the Wild and Scenic Rivers Systems.

Beck and Haase (1969) stated that the richest Mo deposits in New Mexico are found in the Red River area. The Molybdenum Corporation of America (Molycorp) mine used an underground mining system from the time it acquired the property in the 1920's until the early 1960's (BLM 1978). According to a BLM Report (1978), an open pit mine was initiated in 1964. During its operation between 1966 and 1981 at least 72 breaks were reported in the tailings disposal pipeline adjacent to the river (Lynch et al. 1988).

Chemical, physical, and biological data were collected during previous intensive surveys to assess the water quality of the Red River (Smolka and Tague 1989, 1987). In general, the water quality of the Red River was shown to be good, but exceptions did exist. Al, Mn, and Zn concentrations tended to be higher in total (dissolved plus suspended) water samples than in dissolved water samples. Water samples from above the Molycorp boundary had mean total Al, Mn, and Zn concentrations of 2819, 243, and 75 μg/l, respectively, and mean dissolved Al, Mn, and Zn concentrations of 97, 187, and 50 μg/l, respectively. Likewise, water samples from below Molycorp at the USGS gage near the USFS Questa Ranger District office had mean total Al, Mn, and Zn concentrations of 5402, 904, and 182 μg/l, respectively, and mean dissolved Al, Mn, and Zn concentrations of 73, 690, and 97 μg/l, respectively (Smolka and Tague 1989). Smolka and Tague suggest this is largely a result of sediment transport during episodic runoff events from highly erodible areas between the town of Red River and the Questa USFS office.

Biological assessments of the Red River showed a reduction in diversity and abundance of invertebrates and diatoms between the towns of Red River and Questa (Smolka and Tague 1987, 1989). In addition, no fish were collected from the Red River near the Questa USFS office (Smolka and Tague 1989). Further investigations are needed to determine the direct cause of the reduction in diversity and abundance of biota in the Red River.

Comanche Creek is a tributary to Costilla Creek and is part of the Rio Grande watershed. It is similar to the other basins of this study because it is underlain by an undivided Precambrian geological formation (Table 1). Comanche Creek is a relatively pristine area with few anthropogenic impacts in the drainage basin. Few streams are completely unaffected by human activity; however, Comanche Creek represents the least impacted system in this study.

Metals Investigated:

Metals were chosen for study on the basis of association with commercial mineral deposits and presence in local geological formations. Metals are unevenly distributed in natural aquatic systems and tend to be associated with suspended particulate and colloidal materials (Namminga and Wilhm 1977). Suspended particle and colloidal materials eventually settle from the water column and become part of streambed and lake-bottom sediments. Changes in pH and redox potential at the sediment-water interface can result in the transformation of geochemical metal complexes to forms that have greater bioavailability (Gambrell et al. 1976). According to Gambrell et al. (1976), dissolved metals and metal ions weakly adsorbed to solid phases are available for uptake by aquatic and benthic organisms. Allen et al. (1980) suggest that decreasing strengths of metal-ligand bonds increases the availability of metals for uptake by aquatic biota. Since bioavailability is a function of ionic and complex adsorption strengths, the potential toxicity varies with parameters that govern metal speciation (Krantzberg and Stokes 1985). Therefore, variables such as pH and redox potential, that affect metal speciation invariably affect the severity of metal toxicity to organisms. Since metals are normally found in the solid phase, stream bed sediments were collected during this study to measure metal concentrations.

The following review of the metals selected for analysis during this study addresses their common sources, chemical forms in natural waters, toxicity, and other issues including their uptake by aquatic organisms. Factors which effect a metal's chemical form are discussed because the chemical form of a metal is related to its environmental distribution. The brief review of each metal is intended to provide an overview of their occurrence, distribution, and fate in aquatic ecosystems.

Aluminum is the second most abundant element in the crustal materials of the earth (Hem 1989). In natural water systems, Al is usually found in one of two dissolved forms. Al^{+3} cations predominate in solutions which have a pH less than 4. A polymerization process between Al and hydroxide ions occur at pH 4.5-6.5. $Al(OH)_4^{-1}$ anions predominate in solutions which have a pH greater than 7 (Hem 1989). In typical fresh waters the dissolved Al concentrations are usually very small (Drever 1988). Aluminum precipitates rapidly as a clay-mineral species when silica is present (Hem et al. 1973). Aluminum forms strong complexes with dissolved organic matter, sulfates, and fluoride ions. Aluminum speciation is important toxicologically because free or inorganically complexed Al is more toxic to fish than organically complexed Al (Baker and Schofield 1982). Baker and Schofield (1980) found fish population declines in Adirondack surface waters were the result of low pH and high dissolved Al concentrations.

Cadmium is a relatively rare silver-white, lustrous metal that is often at low concentrations in zinc ores (Eisler 1985). Cadmium is usually divalent and is insoluble in water, although cadmium chloride and sulphate salts are freely soluble (Windholz et al. 1976). According to Gardiner (1974), adsorption and desorption processes are the most probable factors influencing Cd concentrations in natural waters. Bioavailability of sediment-bound Cd depends on ambient physicochemical conditions, especially redox potential and pH (Khalid et al. 1981). Cadmium is accumulated at highly differential rates and concentrations by various aquatic flora and fauna, and its behavior is strongly influenced by water hardness (Kinkade and Erdman 1975). Although Cd can be accumulated by living organisms, no evidence suggests that it is biologically essential or beneficial. Conversely, Cd is known to be injurious to humans, fish, and other wildlife (Eisler 1985).

Copper, which is an essential nutrient for plants and animals, has been introduced into the environment as a result of its widespread use. It is a component of agricultural pesticides and algal growth suppressors in water supplies. Both uses increase its potential availability for introduction into surface and groundwaters. According to a review by Hem (1989), mining is also a contributor to copper contamination throughout New Mexico. Urban runoff is another possible source of copper contamination.

Copper can be found in a number of forms in aquatic systems. In solution, it can be found in either the Cu^{+1} or Cu^{+2} oxidation state. In more oxygenated waters, however, redox potential promotes the Cu^{+2} valence state. Copper is predominately found as $Cu(OH)_3^{-1}$ in waters with a pH greater than 7 (Hem 1989). Complexation reactions of Cu with a variety of ligands such as humic materials, carbonates, cyanide, and amino acid complexes are also common (Roy et al. 1992). Regardless of the form Cu is found, it is not until Cu accumulates in biota that adverse effects are observed.

Irwin (1988) suggests that Cu can be accumulated by aquatic organisms through ingestion of either contaminated food, sediment bound copper, or suspended copper. These routes into the food chain may be possible, but ingestion of copper as a mode of entry is limited. In general, aquatic organisms do not drink water, and gut contents compete with the digestive tract for the adsorption of copper. Hodson et al. (1979) found that sensitive fish and aquatic insects had a high respiratory water flow that allowed large amounts of Cu to be rapidly absorbed by gills.

Lead has been detected in most biotic and abiotic systems, and it is considered to be the most ubiquitous toxic metal. Auto exhaust, industrial emissions, mining, and smelting are the primary sources of Pb in the environment (Roy et al. 1992). The principle dissolved inorganic forms of Pb in natural waters are Pb^{+2}, hydroxide complexes, and carbonates (Hem 1989). The free ion, Pb^{+2}, predominates when the pH < 7, $PbCO_3$ and $PbOH^{+1}$ predominate at pH 7-10, and $Pb(OH)_2$ and $Pb(CO_3)_2^{-2}$ when pH > 10 (Stumm and Morgan 1981). Lead tends to adsorb to organic and inorganic sediment surfaces and coprecipitate with manganese oxides (Hem 1989). Deposition of suspended Pb into stream sediments is a result of adsorption and coprecipitation processes (Snoeylink and Jenkins 1980). According to Eisler (1988) Pb is readily bioconcentrated by most life forms, although organic Pb complexes appear to be more toxic than inorganic Pb compounds.

Manganese, one of the more abundant metallic elements, is also an essential nutrient for plants and animals. Some terrestrial plant species are effective accumulators of Mn, and as plants dieback or loose foliage, Mn can become dissolved in runoff or soil moisture (Hem 1989). Aquatic plants are also known to accumulate Mn (Oborn 1964). Although certain plants have the potential to accumulate and release Mn within aquatic systems, weathering of basalts, olivines ((Mg, Fe)SiO_4), pyroxenes (Si_2O_6), and amphiboles (ferromagnesium silicate minerals) are major sources of Mn (Hem 1989).

Manganese can be found in three possible oxidation states in weathering environments (Mn^{+2}, Mn^{+3}, and Mn^{+4}) (Hem 1989). The types of possible chemical reactions are influenced by the Mn oxidation state. Manganese is one of the few elements that are predominant participants in aquatic redox reactions (Stumm and Morgan 1981). Discrete grains of Mn oxides and oxide coatings on silicates are usually widely distributed in stream sediments (Drever 1988). Under high pH conditions, Mn^{+2} dissolves during weathering processes and later precipates as Mn^{+4} or MnO_2 (most common, naturally occurring oxide). Other metals such as barium, cobalt, copper, lead, nickel, and zinc can be strongly adsorbed to the negatively charged surfaces of MnO_2, or coprecipitate with MnO_2, forming nodules when pH is high (Drever 1988, Hem 1989). In addition, Mn is known to form bicarbonate and sulfate complexes when these ions are present (Hem 1989).

Molybdenum is a relatively rare element that is an essential micronutrient for most life forms (Goyer 1986). MoS_2 mineral ores are found in several areas of the Rocky Mountains and Mo is used in steel alloys. Mo occurs in a number of oxidations states, ranging from Mo^{+3} to Mo^{+6}, although Mo^{+4} and Mo^{+6} are the dominant forms in sediments and water (Hem 1989). When pH >5, the most probable dissolved species of Mo in natural water under aerobic conditions is MoO_4^{-2} (Stumm and Morgan 1981). Molybdenum is found in solution as either $H_2Mo_4(aq)$ (when pH <2) or $HMoO_4^{-1}$ (when pH 2-5) (Hem 1989). These various solubilities indicate that Mo has a relatively high geochemical mobility.

Metallic Ni is a hard, silver-white metal (Coyle and Stiefel 1988) which has recently been introduced into aquatic environments in large quantities because of increased industrial growth (Richter and Theis 1980). The major anthropogenic sources of Ni are metal plating and finishing, combustion of fossil fuels, and Ni mining and refining (Coyle and Stiefel 1988). In natural waters, Ni is predominately found in the Ni^{+2} oxidation state (Hem 1989). The environmental fate of Ni is strongly influenced by its complexation with soluble species (e.g., OH^-, SO_4^{-2}, Cl^-, and NH_4^{+1}) and with fine grained particles (e.g., clays) (Snodegrass 1980). According to a review by

Jenkins (1980), Ni has been detected in most aquatic organisms, and many aquatic plants and animals are capable of accumulating nickel.

Zinc contamination of aquatic ecosystems can result from mine drainage, ore processing, smelting, and electroplating (Weatherley et al. 1980). Zinc is more soluble than Cu and Ni in most natural waters. Zn^{+2} is the only environmentally significant oxidation state (Hem 1989). The common dissolved species in natural waters under aerobic conditions are Zn^{+2}, $ZnOH^{+1}$, and $ZnCO_3$ (Stumm and Morgan 1981). Relatively low levels of Zn are found in natural waters because of adsorption, ion exchange, or coprecipitation processes with suspended or bed sediments (Hem 1989). According to Davis and Woodling (1980), Zn is the most common contaminant found in salmonids from streams containing metals from acid mine drainage. When Zn accumulation by crayfish was studied by Mirenda (1986), it was found that the gills are the main site of Zn uptake in crayfish. Therefore, it is possible that the gills of aquatic insect may be an important site of Zn uptake.

METHODS

Aquatic insects and stream bed sediments were collected from three northeastern New Mexico surface water systems (Fig. 1, 2, and 3). Samples were taken during periods of low flow in order to reduce the influence of high-runoff pulses of metals. Periods of high flow alter stream habitat characteristics and wash organisms downstream. Consequently, insects collected during high-flow episodes may not be representative of the community that normally inhabits an area. Insects and sediments were collected at random locations within a reach (approximately 100 m long) at each stream site. Sampling dates and additional information pertaining to these sites are shown in Table 2. Samples collected during April 1990 were intended to represent spatial variability with respect to mining operations. Pecos River samples were collected at various times to detect temporal changes in metal concentrations.

Metal concentrations found in aquatic insects and bed sediments are reported in $\mu g/g$ (dry weight). Wet weight (Appendix 1) concentrations can be calculated:

DRY WT. CONC. X (1-(% MOISTURE/100)) = WET WT. CONC.

Environmental parameters that influence the chemical speciation of metals are presented in Appendix 2.

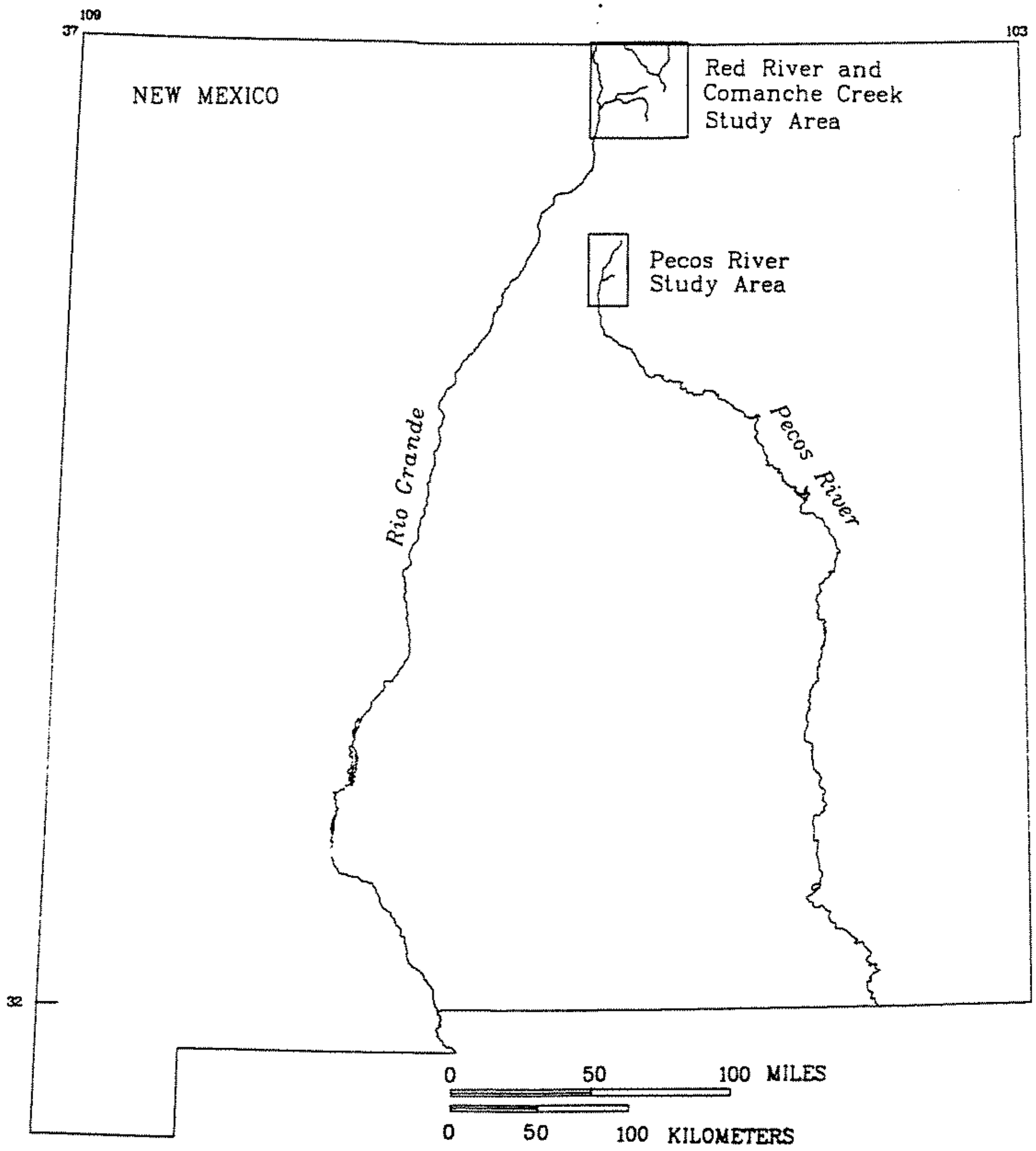

Figure 1. Map of New Mexico showing selected study areas.

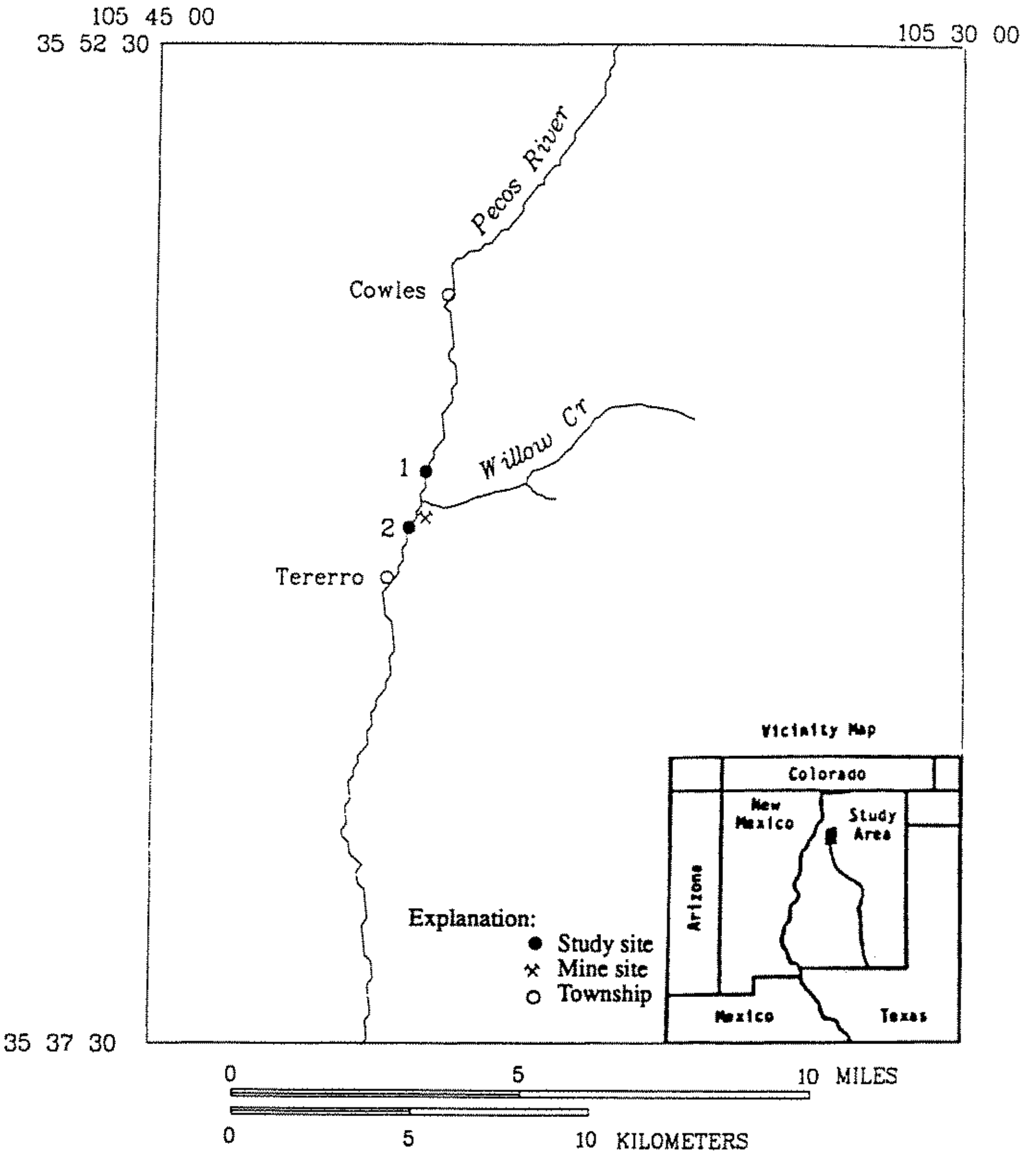

Figure 2. Location map of the Pecos River and study sites, San Miguel County, New Mexico.

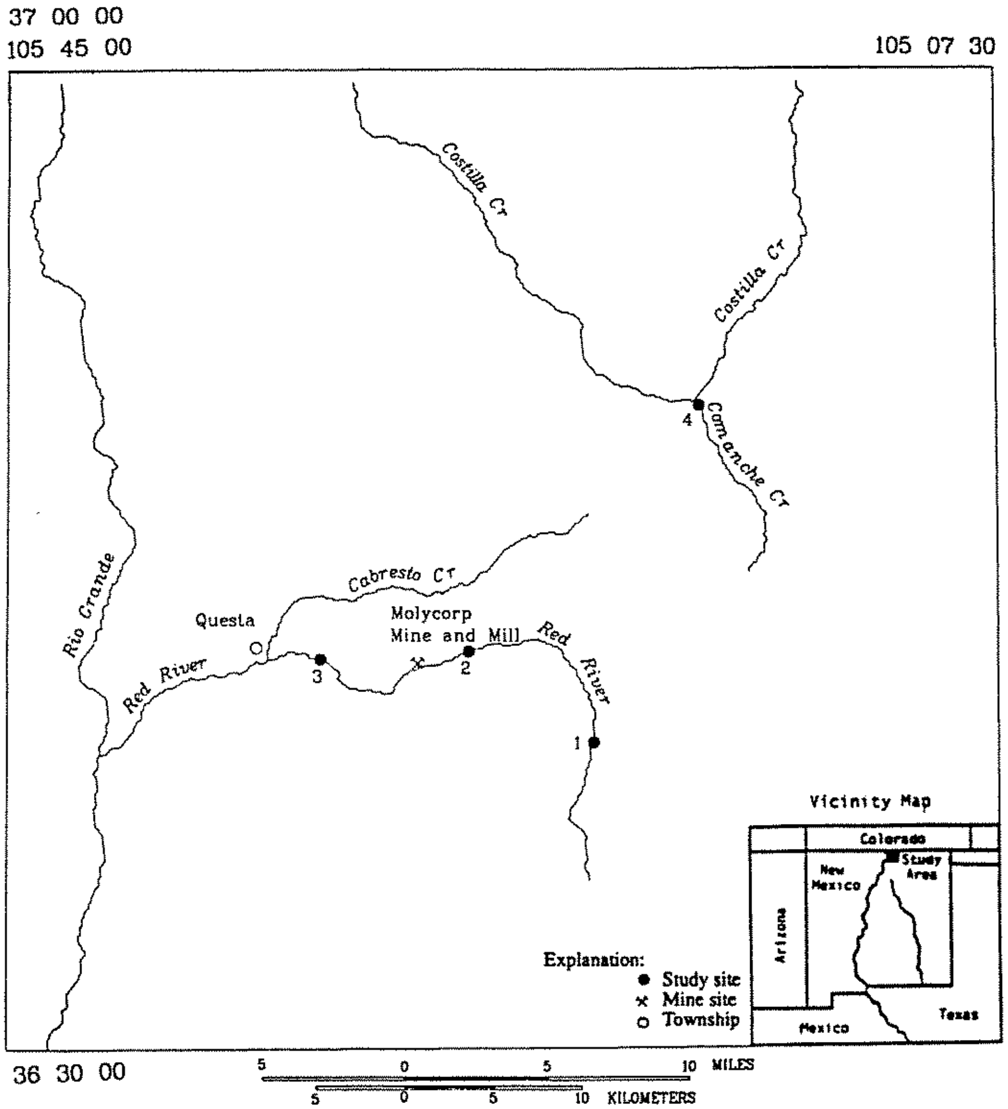

Figure 3. Location map of the Red River, Comanche Creek, and study sites, Taos County, New Mexico.

Table 2. Sampling dates and site summary.

Site	Date	Location (lat./long.[a])	Relative Location
COM[b]	April	36°49′53″/ 105°19′03″	100 m upstream of Costilla Creek confluence
R1[c]	April	36°42′07″/ 105°33′49″	100 m upstream of Zwergle Dam
R2[d]	April	36°42′01″/ 105°28′15″	above Molycorp property line
R3[e]	April	36°40′24″/ 105°22′45	below Molycorp
P1[f]	April and November	35°45′44″/ 105°40′14″	above Tererro mine
P2[g]	April and November	35°45′17″ 105°40′25″	below Tererro mine

[a] latitude/longitude
[b] Comanche Creek
[c] Red River #1
[d] Red River #2
[e] Red River #3
[f] Pecos River #1
[g] Pecos River #2

Site Selection:

Stream order was determined by the physiographic configuration of tributary streams above a site and by using a 1:100,000 scale topographic map. Selected sampling reaches of the Pecos River were designated as fourth order. P1 was located above the Terrero mine and was expected to represent background concentrations of metals upstream from mine drainage into the river (Fig. 2). P2 was located below the mine and downstream from mine drainage into the river (Fig. 2).

Three reaches were selected on the Red River between the USGS gage at Zwergle Dam and below the Molycorp mine complex. R1 was located at Zwergle Dam above the town of Red River, New Mexico (Fig. 3). Metals detected at R1 should represent background metal concentrations from the relatively undisturbed watershed. R2 was located above the Molycorp mine and mill (Fig. 3) and was selected to distinguish background metal concentrations associated with a highly erodible canyon above R2. R3 was located below the Molycorp mine (Fig. 3) and was selected to detect metal inputs from the mine. The selected reaches of R1 and R2 had a stream order of 3; R3 had a stream order of 4.

The selected reach on Comanche Creek (COM) was located approximately 100 m above its confluence with

Costilla Creek (Fig. 3). This stream reach was designated as third order.

Sample Collection, Preparation, and Analysis:

Benthic macroinvertebrates were collected using a hand-held kickscreen with a 1.0 mm diameter mesh (Merritt et al. 1984). Insects were sorted in the field according to taxonomic group and later verified in the lab. After taxonomic separation, the organisms were stored at 0°C in polyethylene bags. A revised procedure by Lynch et al. (1988) was followed for sample preparation. Insects were thawed, counted, weighed, lyophilized, reweighed, and acid-digested. Approximately 0.5 g of dried insects were used in the digestion process. If additional insects of the same taxon, site, and date were available, duplicate samples were digested. Prior to digestion, all glassware, beakers, and sample bottles were first rinsed with 10% nitric acid (HNO_3), then rinsed with deionized water. Weighed insect samples were placed in 50-ml teflon beakers. Ten ml of concentrated redistilled HNO_3 were added. The mixture was gently heated on a hot plate until the sample dissolved (approximately 1 hour). After the mixture cooled, 5 ml of 30% hydrogen peroxide were added, and the solution was heated until bubbling stopped (approximately 10 minutes). An additional 5 ml of concentrated redistilled HNO_3 were added. The solution volume was reduced to 10 ml by boiling. The remaining cooled solution was passed through a 0.2 micrometer (μm) membrane filter into polyethylene bottles, and diluted with deionized water. Filters were rinsed with 10% redistilled HNO_3 to remove any remaining metals from the filter. Solutions were diluted to various volumes to bring them within the linear range of the flame atomic absorption spectrophotometer. Samples were stored at 25°C until analysis.

Bottom sediments were randomly collected from depositional areas using an acid-washed watchglass. Sediment samples were stored at 0°C in acid-washed (10% v/v HCl) glass jars. Prior to analysis, samples were thawed and wet sieved through a 63 μm pore-size stainless steel mesh on a mechanical shaker to isolate the clay-size sediment fraction. Distilled water was used during sieving to aid in the separation. Water from sieving was decanted and later analyzed to determine whether metals were leached from sediments. Clay-fraction sediments were air dried and size homogenized by dry-sieving through a 63 μm pore-size mesh. The clay-sized sediment fraction (<63 μm) should contain the highest concentrations of metals due to the high surface area to volume ratios associated with clay materials.

A hot extraction technique was used to prepare sediment samples for flame atomic absorption spectrophotometry analysis (Husler and Connolly 1989). This method is a modification of a method for whole rocks. Two 0.5-g fractions of each sediment sample and a 0.2-g sample of National Bureau of Standards River Sediment #1645 (obtained from University of New Mexico, Department of Geology) were weighed and carefully transferred to 100-ml Teflon beakers containing 2 ml of 1% v/v HNO_3. Any adhering residues on the weighing boat were rinsed into the beaker with 1% HNO_3 from a polyethylene wash bottle. Ten ml of 1:1 redistilled HNO_3/H_20, 15 ml 48% (v/v) hydrofluoric acid (aq) in a plastic graduated cylinder, and 10 ml of 1:1 (v/v) perchloric acid (aq) were added to each sample. The mixture was evaporated to dryness on a hot plate. During evaporation, temperatures were sufficiently low to prevent the beaker from adhering to the hot plate. After evaporation, the residue was cooled and 20 ml of a cesium chloride-hydrochloric acid (CsCl-HCl) reagent (12 g scintillation grade CsCl dissolved in 2 l of 1:1 (v/v) HCl (aq)) were added and the solution was gently warmed to dissolve the salts. The solution was quantitatively transferred to acid-washed (10% HNO_3) polyethylene bottles, rinsing the beakers three times with deionized water, and then diluted with deionized water.

Samples were diluted to various volumes to bring them within the linear range of the flame atomic absorption spectophotometer. Samples were stored at 25°C until analysis.

A series of 11 sediment samples were digested for Comanche Creek. Comanche Creek sediment samples (COM) were fortified after digestion with various quantities of metals in an external fortification process. The amounts of metals added to various sediment samples were not known to the analyst. This series of sediment analyses was used to determine the validity of the analytical procedure, including metal species interferences, and spectrophotometer detection limits.

Two sediment samples were digested for the Pecos #1 site during April and November (P1A and P1N, respectively), the Pecos #2 site during April and November (P2A and P2N, respectively), and the Red River sites. One sample was internally fortified before analysis and the other was left unfortified. The analyst prepared standard solutions with concentrations between 50-100 $\mu g/g$ for each of the eight metals. Known volumes of the fortified standard solutions were used to fortify one sediment sample per sampling site.

An atomic absorption/atomic emission spectrophotometer (Instrumentation Laboratory model 457) was used for analysis. All metals, with the exception of Al and Mo, were analyzed using an oxidizing acetylene-air flame. A reducing nitrous oxide-acetylene flame was used in the analysis of Al and Mo to avoid the interference of oxides which commonly form under oxidizing conditions.

Quality Assurance and Quality Control:

Measures were taken to ensure quality assurance and quality control. When sufficient biomass of a particular insect species was available, the sample was split, allowing for a duplicate sample. Duplicate samples were digested and internally fortified before analysis. Internally and externally fortified sediments were also analyzed. Metal quantity differences between fortified and unfortified solutions should equal the quantity of metal added to fortified insect or sediment solutions.

National Bureau of Standards River Sediments (NBS 1645) were used as a quality control reference material for the analysis of sediment samples. Reference sediments were digested and analyzed along with each set of sediments. The reference sediment provided another measure of the validity of the analytical procedure. Reference tissues from the National Bureau of Standards were not available for quality control of insect analyses.

Finally, a blank, which consisted of all materials and procedures used in a particular digestion with the exception of the sample material, was analyzed to determine internal contamination associated with each set of digestions.

Results from the external fortification process of Comanche Creek sediment and NBS 1645 quality control measures are shown in Appendix 7. Insect and sediment solutions of the internally fortified process were fortified at levels that caused erroneous results. Elevated metal concentrations in these samples caused interferences in metal absorption during spectrophotometric analysis. Therefore, results from the internal fortification process were not appended.

RESULTS

Determining the biological consequences of a concentration of a particular element in an ecosystem is difficult. In this study, concentrations of metals found in aquatic insects and bed sediments were correlated to determine whether insects accumulate metals in response to metals in sediments. Metal concentrations reported in the literature are used to suggest whether an environmental risk might exist at the study sites. Metal concentrations in sediments will be considered first, followed by metal concentrations in aquatic insects. The purpose of this organization is to provide insight into the potential linkage between metal concentrations in sediments and insects.

Sediments:

Atomic absorption measurements and calculated concentrations for sediments from the different study sites are presented in Appendix 3. Confidence intervals could not be calculated for the sediments samples collected from each site due to the small sample size. Confidence intervals were calculated from analytical results of the metal. Reported confidence intervals represent instrumentational variability, not sample variability.

Aluminum

Bed sediments from R2 had the lowest mean concentration of Al (49,200 μg/g) of all sites (Table 3). Comanche Creek, which was considered to be the least impacted site, had the next lowest mean Al concentration (66,300 μg/g). Aluminum concentrations were variable in sediments from both the Red and Pecos Rivers. A downstream decrease in Al sediment concentrations was found at the R1 (upstream) and R2 (downstream) sites, although Al sediment concentrations from further downstream at R3 were greater than at R2. Temporal differences in Al concentrations existed in sediments collected at both Pecos River sites during April and November, 1990. A downstream increase was recorded in Al concentrations in sediments from the Pecos River in April, 1990, but a downstream decrease in Al concentrations was found in sediments from the Pecos River in November, 1990. Although the concentrations of Al reported in sediments collected during this study may seem high, the Al concentrations were less than or equal to the average composition of igneous rocks (79,500 μg/g) (Hem 1989). Also, the analytical procedure involved the total dissolution of the clay-size fraction of the sediment. Most clay material is largely composed of aluminosilicates containing large quantities of Al (Drever 1988).

Table 3. Aluminum concentrations (µg/g, dry wt.) in bed sediments.

SITE	CONC. (µg/g)	95% C.C.[a]
Comanche Cr.	66,300	590
Red R. #1	78,500	345
Red R. #2	49,200	163
Red R. #3	92,600	306
Pecos R. #1, Apr.	77,000	287
Pecos R. #1, Nov.	86,500	465
Pecos R. #2, Apr.	89,800	541
Pecos R. #2, Nov.	76,200	1600

[a] Confidence coefficient for instrumental variability

Cadmium

Bed sediment from Comanche Creek had the lowest concentration of Cd (5.15 μg/g) as compared to sediment samples from the other systems (Table 4). Cadmium concentrations were variable in sediments from both the Red and Pecos Rivers. Sediment samples from R1 and R2 sites had 7.37 and 8.14 μg/g of Cd, respectively. A Cd concentration of 6.85 μg/g was detected in sediments from R3. Cadmium concentrations in sediments from P1A and P1N were 7.59 and 6.71 μg/g, respectively. The Cd concentration in sediments from P2A (31.02 μg/g) was nearly twice the Cd concentration in P2N sediments (16.87 μg/g). This suggests an increased input of Cd into the Pecos River from mine tailing leachate during the spring snowmelt. In addition, in both April and November the downstream Pecos site had Cd concentrations two to four times larger than the upstream site, implying that the mine tailings are in fact leaching Cd into the river.

Table 4. Cadmium concentrations (µg/g, dry wt.) in bed sediments.

SITE	CONC. (µg/g)	95% C.C.[a]
Comanche Cr.	5.15	0.74
Red R. #1	7.37	0
Red R. #2	8.14	0
Red R. #3	6.85	0
Pecos R. #1, Apr.	7.59	0.59
Pecos R. #1, Nov.	6.71	0.55
Pecos R. #2, Apr.	31.00	0.46
Pecos R. #2, Nov.	16.90	0

[a] Confidence coefficient instrumentational variability

Copper

Bed sediments from Comanche Creek had the lowest observed concentration of Cu (Table 5). A downstream increase in Cu concentration was detected in sediments from the Red River. Sediment concentrations of Cu ranged from 58.6 µg/g at R1 to 339.2 µg/g at R3, which is an increase of more than five times. If Cu concentrations in sediments from R1 and R2 are pooled, the mean concentration of Cu would be 155 µg/g, which is slightly less than the mean Cu concentration of 220 µg/g reported for sediments upstream of mining disturbance on the Red River (Lynch et al. 1988). Pecos River sediment Cu concentrations also increased from above the Tererro mine to below the mine. P1A and P1N Cu concentrations were 97.3 and 90.4 µg/g, respectively. Copper concentrations in sediments from P2A and P2N were 547.5 and 292.4 μg/g, respectively, which is nearly a three to five fold increase from upstream to downstream of the mine tailings. Temporal differences of Cu concentrations in P2 sediments suggest an increased input of Cu into the river from the mine tailing leachate during spring snowmelt.

Table 5. Copper concentrations (μg/g, dry wt.) in bed sediments.

SITE	CONC. (μg/g)	95% C.C.[a]
Comanche Cr.	34.8	0.31
Red R. #1	58.7	2.06
Red R. #2	252.0	2.03
Red R. #3	339.0	1.12
Pecos R. #1, Apr.	97.3	0
Pecos R. #1, Nov.	90.4	0
Pecos R. #2, Apr.	548.0	5.47
Pecos R. #2, Nov.	292.0	2.53

[a] Confidence coefficient for instrumentational variability

Lead

Lead concentrations in sediment samples from COM and R1 were 76 and 78 $\mu g/g$, respectively. Lead concentrations found in sediments from the Red River were 78, 174, and 152 $\mu g/g$ at R1, R2, and R3, respectively. A progressive downstream increase in Pb concentrations of sediments from the Red River was not evident; this was in contrast to increased Pb concentrations in samples from the Pecos River (Table 6). Lead concentrations detected at P1A and P1N were 228 and 200 $\mu g/g$, respectively. Downstream Pb sediment concentrations were 372 $\mu g/g$ at P2A and 376 $\mu g/g$ at P2N, which is downstream increase of a factor of two. No temporal differences in Pb concentrations in sediments from either P1 or P2 were noted.

Table 6. Lead concentrations ($\mu g/g$, dry wt.) in bed sediments.

SITE	CONC. ($\mu g/g$)	95% C.C.[a]
Comanche Cr.	76.2	5.43
Red R. #1	78.3	0
Red R. #2	174.0	6.10
Red R. #3	152.0	0
Pecos R. #1, Apr.	228.0	0
Pecos R. #1, Nov.	200.0	0
Pecos R. #2, Apr.	372.0	9.33
Pecos R. #2, Nov.	376.0	0

[a] Confidence coefficient instrumentational variability

Manganese

The concentration of manganese in sediments from Comanche Creek was 1530 µg/g (Table 7). In the Red River, downstream sediments had approximately twice the Mn concentration of upstream sediments. Sediments from the Pecos River in April, 1990 showed a decrease in Mn concentration from upstream to downstream; however, in November, 1990 an approximate two-fold increase in Mn concentration was recorded from upstream to downstream. Concentrations of Mn in Pecos River sediments were significantly less than concentrations in sediments from either Comanche Creek or Red River. The maximum variation occurred the November samples from the Pecos River, where the upstream Mn concentration was about one-half the downstream Mn concentration.

Table 7. Manganese concentrations (µg/g, dry wt.) in bed sediments.

SITE	CONC. (µg/g)	95% C.C.[a]
Comanche Cr.	1530	25.2
Red R. #1	1550	3.27
Red R. #2	1610	11.6
Red R. #3	2590	0
Pecos R. #1, Apr.	1050	20.4
Pecos R. #1, Nov.	622	19.1
Pecos R. #2, Apr.	845	0
Pecos R. #2, Nov.	1230	12.7

[a] Confidence coefficient for instrumentational variability

Molybdenum

The only site with sediments that had detectable concentrations of Mo was R3, downstream of Molycorp. The mean concentration of Mo in sediments from R3 was 600 μg/g. This concentration is more than one magnitude greater than the average concentration of Mo in sediments below Molycorp (53 μg/g) reported by Lynch et al. (1988).

Nickel

Sediments from Comanche Creek had a Ni concentration of 41.7 μg/g, which was lower than concentrations in samples from the Red and Pecos Rivers (Table 8). A downstream increase of Ni was detected with concentrations ranging from 66.4 μg/g at R1 to 115 μg/g at R2; however, Ni concentrations decreased to 104 μg/g at R3. Sediments from the P1A had a Ni concentration of 86.7 μg/g, which was higher than Ni concentrations in sediments from P2A (74.7 μg/g). P1N had a sediment Ni concentration of 94.4 μg/g, which was lower than sediment Ni concentrations at P2N (186 μg/g).

Table 8. Nickel concentrations (μg/g, dry wt.) in bed sediments.

SITE	CONC. (μg/g)	95% C.C.[a]
Comanche Cr.	41.7	10.5
Red R. #1	66.4	0
Red R. #2	115.0	5.37
Red R. #3	104.0	0
Pecos R. #1, Apr.	86.7	0
Pecos R. #1, Nov.	94.4	5.55
Pecos R. #2, Apr.	74.7	4.74
Pecos R. #2, Nov.	186.0	7.10

[a] Confidence coefficient for instrumentational variability

Zinc

Concentrations of Zn in sediments from Comanche Creek were higher than Zn concentrations in any sediments sampled from the Red River and the upstream Pecos River site, and lower than Zn concentrations in sediments from the downstream Pecos River site (Table 9). A progressive increase in Zn concentrations in samples from the Red River was detected. The concentration of Zn at R3 (1060 μg/g) was approximately 10 times greater than the Zn concentrations at R1 (160 μg/g). A slight downstream increase was noted in Zn concentrations in sediments collected from P1A as compared to P1N. However, a dramatic decrease in Zn concentrations was record from P2A to P2N. Zinc sediment concentrations at P2A (7630 μg/g) were more than 13 times greater than the concentrations of

Zn at P1A (585 μg/g). Zinc concentrations in sediments from P2N (2750 μg/g) were more than four times greater than Zn concentrations in sediments from P1N (610 μg/g).

Table 9. Zinc concentrations (μg/g, dry wt.) in bed sediments.

SITE	CONC. (μg/g)	95% C.C.[a]
Comanche Cr.	1490	175
Red R. #1	160	1.14
Red R. #2	803	6.13
Red R. #3	1060	5.78
Pecos R. #1, Apr.	585	10.8
Pecos R. #1, Nov.	610	0
Pecos R. #2, Apr.	7630	7.71
Pecos R. #2, Nov.	2750	2.05

[a] Confidence coefficient for instrumentational variability

Aquatic Insects:

A total of 10 different taxa of insects was collected. Six taxa were common to at least two sampling reaches (Table 10). The highest diversity of insect taxa (five) was found in Comanche Creek and R1, the two least impacted reaches. Four different taxa were collected at R2, and two taxa were collected at both Pecos River sites. Only one species was found at the R3 site. The number of insect taxa collected does not represent the actual species richness of a particular reach because only taxa with biomass sufficient for analysis were collected.

Varying degrees of overlap in taxa present at the study sites were noted (Table 10). The stonefly, Pteronarcella badia, was collected at Comanche Creek and all Red River sites, and it was the most commonly found taxon. The stonefly, Hesperoperla pacifica, was the second most common taxon and was collected at Comanche Creek and both Pecos River sites. The mayfly Ephemerellidae, the caddisfly Arctopsyche grandis, the true fly Tipula sp., and the stonefly Claassenia sabulosa were found at two of the six sampling sites. Concentrations of metals in insects will be discussed by site because not all of the metals chosen for analysis were detected in each insect.

Table 10. List of taxa collected at each sampling site.

	Sampling Sites					
Taxa	COM[a]	R1[b]	R2[c]	R3[d]	P1[e]	P2[f]
Arctopsyche grandis		+	+			
Claassenia sabulosa					+	+
Ephemerellidae	+		+			
Hesperoperla pacifica	+				+	+
Isogeniodes sp.			+			
Megarcys sp.		+				
Anisoptera	+					
Pteronarcella badia	+	+	+	+		
Rhyacophila sp.		+				
Tipula sp.	+	+				

[a] Comanche Creek
[b] Red River #1
[c] Red River #2
[d] Red River #3
[e] Pecos River #1
[f] Pecos River #2

Comanche Creek

Metals detected in insects from Comanche Creek were Al, Cd, Cu, Mn, and Zn. The remaining metals (Mo, Ni, and Pb) were at or below the analytical detection limit. Atomic absorption measurements and calculated concentrations for each insect sample collected from Comanche Creek are presented in Appendix 4.

Aluminum, Cd, Mn, and Zn concentrations in Ephemerellidae were greater than metal concentrations in other insect taxa from Comanche Creek (Table 11). The highest concentration of Cu was found in *H. pacifica*, which contained Cu concentrations nearly two or more times that found in other insect taxa collected at Comanche Creek (Table 11). No difference in concentrations of Cd was detected in Ephemerellidae and *Tipula* sp. The Cd concentration in Ephemerellidae was higher than levels found in *Hesperoperla pacifica*, *Pteronarcella badia*, and Anisoptera (dragonfly). No difference in Cu concentrations between *Pteronarcella badia* and Anisoptera was found.

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Table 11. Mean metal concentrations (µg/g) in aquatic insects from Comanche Creek, and the Red and Pecos Rivers.

Site/Taxa	Al	Cd	Cu	Mn	Mo	Ni	Pb	Zn
Comanche Creek								
Ephemerellidae	1900	2.28	42.8	1396	--	--	--	489
<u>H</u>. <u>pacifica</u>	252	0.42	73.1	79.5	--	--	--	397
<u>P</u>. <u>badia</u>	607	0.82	28.4	264	--	--	--	239
Anisoptera	688	1.16	28.1	201	--	--	--	122
<u>Tipula</u> sp.	72.5	2.14	15.9	149	--	--	--	193
Red River #1								
<u>A</u>. <u>grandis</u>	227	0.72	22.5	494	--	--	--	272
<u>Megarcys</u> sp.	194	0.68	25.3	103	--	--	--	408
<u>P</u>. <u>badia</u>	663	1.10	34.6	146	--	--	--	124
<u>Rhyacophila</u> sp.	121	1.21	25.0	630	--	--	--	424
<u>Tipula</u> sp.	105	3.11	23.7	228	--	30.5	--	241
Red River #2								
<u>A</u>. <u>grandis</u>	98.2	1.45	59.7	1107	--	47.7	--	396
Ephemerellidae	108	26.2	285	711	14.7	114	0.99	2843
<u>Isogeniodes</u> sp.	120	2.98	119	132	10.5	46.9	0.71	459
<u>P</u>. <u>badia</u>	227	2.04	99.3	27.2	9.36	84.7	0.91	323
Red River #3								
<u>P</u>. <u>badia</u>	183	2.52	159	410	26.4	72.2	0.70	356
Pecos River #1, April								
<u>C</u>. <u>sabulosa</u>	189	2.09	48.7	53.5	--	22.7	0.72	521
<u>H</u>. <u>pacifica</u>	302	1.40	32.5	101	--	12.5	0.73	1114
Pecos River #1, November								
<u>C</u>. <u>sabulosa</u>	170	1.71	48.4	58.9	--	42.3	0.79	463
<u>H</u>. <u>pacifica</u>	389	1.31	38.4	96.8	--	17.8	0.91	966
Pecos River #2, April								
<u>C</u>. <u>sabulosa</u>	168	4.05	65.9	94.4	--	65.8	0.87	723
<u>H</u>. <u>pacifica</u>	141	2.24	52.7	79.1	--	76.3	0.92	2133
Pecos River #2, November								
<u>C</u>. <u>sabulosa</u>	187	2.67	49.5	72.9	--	48.1	1.31	351
<u>H</u>. <u>pacifica</u>	266	4.65	46.9	107	--	146	1.30	1785

* Cd, Co, Mo, Zn incr. below mine

* Co, Mo, Zn seds. also incr. below mine

Red River

All eight metals chosen for analysis were detected in aquatic insects collected at R2 and R3 (Table 11). Molybdenum, Ni, and Pb were not detected in aquatic insects at R1 (upstream).

Ephemerellidae from R2 had the highest concentrations of Cd, Cu, and Zn. The concentration of Cd in Ephemerellidae (26.1 μg/g) was approximately nine to 30 times greater than Cd concentrations in other insect taxa from the Red River. The concentration of Cu in Ephemerellidae (286 μg/g) was approximately two to 13 times greater than Cu concentrations in other insect species from the Red River. Nickel was not detected in all insect taxa from the Red River, although the Ni concentration in Ephemerellidae (114 μg/g) was approximately one to two times greater than concentrations in other insect taxa with detectable quantities of Ni. Zinc concentration in Ephemerellidae (2840 μg/g) ranged from six to 23 times greater than Zn concentrations in other insects from the Red River.

Certain metals in Ephemerellidae showed lower concentrations than those found in other insects from the Red River. In general, Ephemerellidae had higher concentrations of metals than other insects, although exceptions did occur. In one case, _P_. _badia_ from R1 exceeded Al concentrations found in Ephemerellidae collected at R2. The Al concentration in *P. badia* from R1 (663 μg/g) was approximately six times greater than in Ephemerellidae (108 μg/g). *P. badia* at R3, below the Molycorp mining complex, had a Mo concentration (26.4 μg/g) exceeding the Mo concentration in Ephemerellidae (14.7 μg/g) collected above the complex (R2). *A. grandis* from R2 had a Mn concentration (1110 μg/g) nearly twice that of Ephemerellidae at R2. The differences in metal concentrations found in Ephemerellidae and other insects from the Red River could be a result of the combined effects of feeding behavior differences between Ephemerellidae and the other insect taxa, and the grouping of more than one genera into a composite Ephemerellidae sample.

Metal accumulations were variable in different insect taxa collected from R1. *P. badia* from R1 contained greater Al and Cu concentrations compared to other insects at the site. Compared to other species from R1, *Rhyacophila* sp. had greater concentrations of Mn and Zn. The Cd concentration in *Tipula* sp. (3.11 μg/g) was greater than Cd concentrations found in other insects from R1. No single taxon consistently had the highest concentrations of metals at R1.

Variability in metal accumulation was also found in the various insect taxa collected at R2. In most cases Ephemerellidae had the highest concentrations of metals. Although Ephemerellidae contained the highest concentrations of metals (except Al and Mo), little similarity was seen in the accumulation of metals by the different taxa collected at R2.

Molybdenum was detected in four of the eight insect taxa from the Red River. Molybdenum was not found in any insect taxa from R1. _P_. _badia_ from R3 had a concentration of Mo greater than Mo concentrations in other insect taxa from upstream at R2.

Pecos River

_C_. _sabulosa_ and _H_. _pacifica_ from both Pecos River sites at both sampling times contained all metals, with the exception of Mo (Table 11). For ease of interpretation, each sampling site will be considered separately. This approach will emphasize species and temporal differences in metal accumulation.

Insects collected from P1A and P1N showed a species-dependent accumulation of each metal, except for Pb. _C_. _sabulosa_ from P1A and P1N, upstream of the Tererro mine, had Cd, Cu, and Ni concentrations higher than those found in _H_. _pacifica_ from the same site. However, _H_.

pacifica from P1A and P1N had Al, Mn, and Zn concentrations higher than those found in *C*. *sabulosa* from the same site. Lead concentrations in *C*. *sabulosa* and *H*. *pacifica* collected during April and November ranged from 0.72 to 0.91 μg/g. Therefore, with the exception of Pb concentrations in insects from P1, insects from P1 showed a species-dependent accumulation of metals.

Insects collected from P2A and P2N did not show the same species-dependent accumulation of metals as seen in insects collected from P1A and P1N (Table 11). *C*. *sabulosa* from P2A had higher concentrations of Al, Cd, Cu, and Mn (168, 4.05, 65.9, and 94.4 μg/g, respectively) than those found in *H*. *pacifica* from P2A (141, 2.24, 52.7, and 79.1 μg/g, respectively). However, *H*. *pacifica* from P2A had higher concentrations of Ni and Zn (76.3 and 2133 μg/g, respectively) than that in *C*. *sabulosa* from P2A (65.8 and 723 μg/g, respectively). Little difference in Pb concentrations was detected in *C*. *sabulosa* and *H*. *pacifica* from P2A.

H. *pacifica* from P2N had Al, Cd, Mn, Ni, and Zn concentrations (266, 4.65, 107, 146, and 1785 μg/g, respectively) higher than those found in *C*. *sabulosa* from P2N (187, 2.67, 72.9, 48.1 and 351 μg/g, respectively). Little differences were detected between Cu and Pb concentrations in *C*. *sabulosa* and *H*. *pacifica* from P2N.

The lack of consistent species-dependent metal accumulation in insects from P2A and P2N could be a consequence of higher metal concentrations in both sediments and insects at P2.

During both sampling periods at P1 and P2, _C. sabulosa_ had higher concentrations of Cu than did _H. pacifica_; however, _H. pacifica_ had higher concentrations of Zn than did _C. sabulosa_. The pattern of Cu and Zn accumulation by _C. sabulosa_ and _H. pacifica_ collected at P1 was very similar to accumulation of Cu and Zn in _C. sabulosa_ and _H. pacifica_ collected at P2. Copper and Zn concentrations in both insect taxa showed a decrease between April and November.

Nickel concentrations in _H. pacifica_ from P2 were greater than in _C. sabulosa_. The pattern of Ni accumulation by _C. sabulosa_ and _H. pacifica_ at P2 was opposite to the pattern at P1. Nickel concentrations in _C. sabulosa_ from P2 decreased over time. The average Ni concentration in _C. sabulosa_ from P2A was 65.8 μg/g as compared to 48.1 μg/g at P2N. Conversely, a significant increase was found in Ni concentrations over time in _H. pacifica_ (76.3 and 146 μg/g at P2A and P2N, respectively).

No differences in concentrations of Pb were detected in _C. sabulosa_ and _H. pacifica_ at P2 in the same sampling time. In addition, temporal variations in Pb concentrations in the two insect species were not apparent. C. sabulosa from P2A and P2N had Pb concentrations of 0.87 and 1.31 $\mu g/g$, respectively. H. pacifica from P2A and P2N had Pb concentrations of 0.92 and 1.30 $\mu g/g$, respectively.

In addition to looking at each site, metal concentrations in aquatic insects were evaluated according to stream system. When the insects were grouped according to sampling location, a downstream increase was noted in all metal concentrations except for Al. Although metal concentrations found in sediments fluctuated from upstream to downstream, aquatic insects downstream of impacted areas tended to have increased levels of metals.

Relationships Between Metal Concentrations in Aquatic Insect and Bed Sediments:

The relationship of Al, Cd, Cu, Mn, and Zn in aquatic insects and bed sediments from respective locations were examined. These five metals were selected for insect and bed sediment metal comparisons because each metal was detected in all aquatic insects samples.

Linear regressions were used to determine the relationships between concentrations of the selected metals in aquatic insects and bed sediments. Initially, regressions between Al, Cd, Cu, Mn, and Zn concentrations in all 23 insect samples and corresponding sediment samples were performed. These regressions were used to establish an overall relationship between each metal's concentration in sediments and those found in aquatic insects.

Specific relationships between Al, Cd, Cu, Mn, and Zn in *C. sabulosa*, *H. pacifica*, and *P. badia* and corresponding sediment samples were used to determine individual taxon metal accumulations. The three insect taxon were selected for further investigation because each taxa was found at either four or five different sites (Table 10).

Insect metal concentrations used in regressions were based on two different calculations of metal concentrations. Initially, insect metal concentrations were calculated on a sample dry weight basis (μg/g, dry weight). Insect metal concentrations were also calculated on a per organism basis (μg/g per organism, dry weight). Concentrations per organism were calculated using following formula:

Total wt. (g)/Total # organisms X Sample concentration (μg/g)/Sample wt. (g) = (μg/g)/organism.

Very little correlation existed between sediment and insect metal concentrations when all 23 insect taxa and corresponding sediment data were used (n = 23). Results from regressional analysis of sediments and insects on a dry weight basis are shown in Appendix 5. Results from regressional analysis of sediments and insects on a per organism basis are shown in Appendix 6. In most cases, relationships were constant between sediments and insects on a dry weight basis for the five selected metals. Although sediment metal concentrations increased, no corresponding increase in metal concentrations was noted in aquatic insects. The lack of correlation among all 23 insect taxa and corresponding sediment metal concentrations could be influenced by a number of factors related to the species involved in the analysis and to undetermined site specific variables.

In a limited number of cases, C. sabulosa, H. pacifica, and P. badia metal concentrations related to corresponding sediment metal concentrations on a dry weight basis (Appendix 5). Apparently, Al concentrations in selected taxa are not related to corresponding sediment concentrations. Concentrations of Cd in C. sabulosa increased linearly ($r^2 = 0.98$) with increases in sediment Cd concentrations (Fig. 4). A linear relationship for C. sabulosa and P. badia ($r^2 = 0.85$ and 0.97, respectively) exists with respect to Cu (Fig. 5). It appears that C. sabulosa has some mechanism to reduce Cu build up, because Cu concentrations in C. sabulosa do not increase as sediment Cu concentrations increase. In contrast, P. badia lacks a mechanism to remove a Cu, because concentrations of Cu in P. badia increased linearly with increases in sediment Cu concentrations. Concentrations of Mn in P. badia were only marginally related to corresponding sediment Mn concentrations (r^2 =0.66). Zinc concentrations in C. sabulosa and H. pacifica were only marginally related to corresponding sediment Zn concentrations (r^2 = 0.52 and 0.61, respectively).

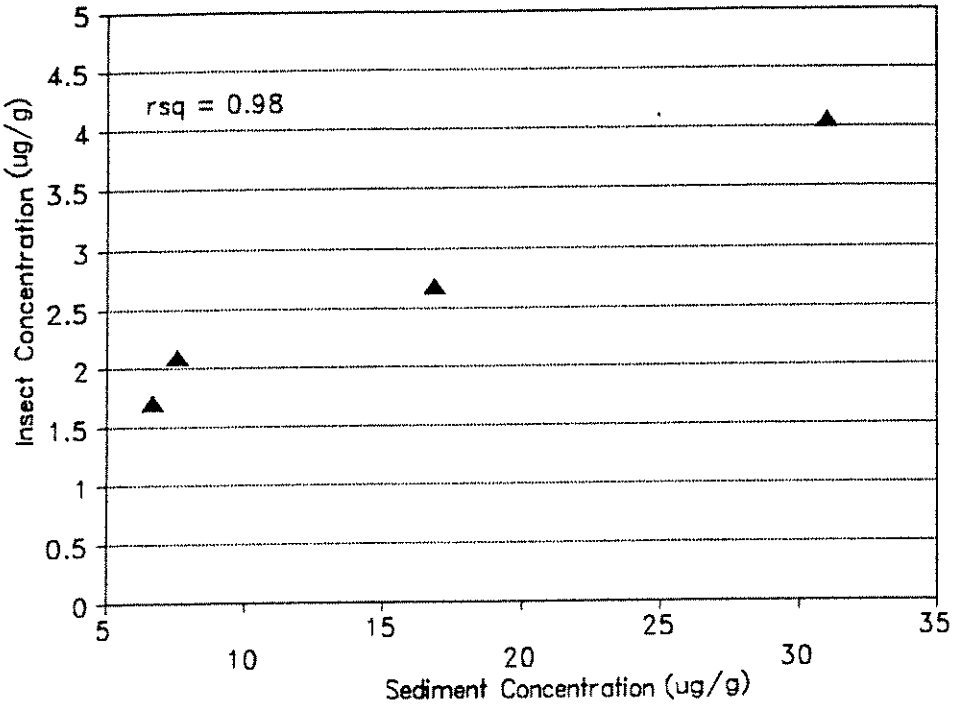

Figure 4. Comparison of cadmium concentrations in sediments versus C. *sabulosa*.

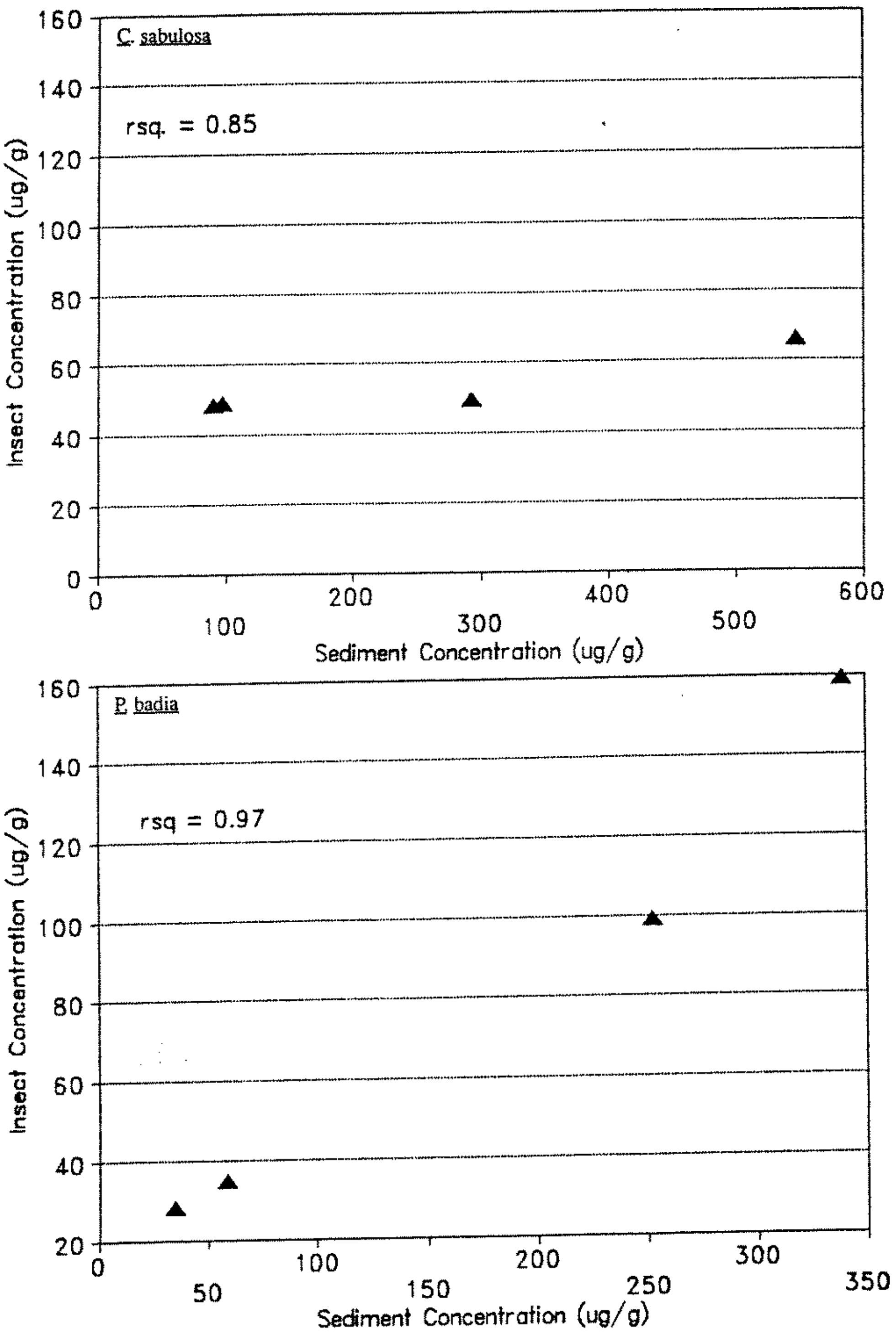

Figure 5. Comparison of copper concentrations in sediments versus C. sabulosa, and P. badia.

Only three cases were found in which a linear relationship between individual organism insect metal concentrations and corresponding sediment metal concentrations existed for specific insect taxa. Copper concentrations detected in H. pacifica increased linearly (r^2 = 0.91) as sediment Cu concentrations increased (Fig. 6). Zinc concentrations detected in C. sabulosa and H. pacifica had a linear relationship (r^2 = 0.79 and 0.77, respectively) that was marginal.

When relationships of metal in sediments and aquatic insects are analyzed according to either a dry weight sample or per organism basis, different correlations are noted. But in either situation, the number of linear relationships is limited. In most cases, metal concentrations in aquatic insects are not correlated to metal concentrations in the corresponding sediments.

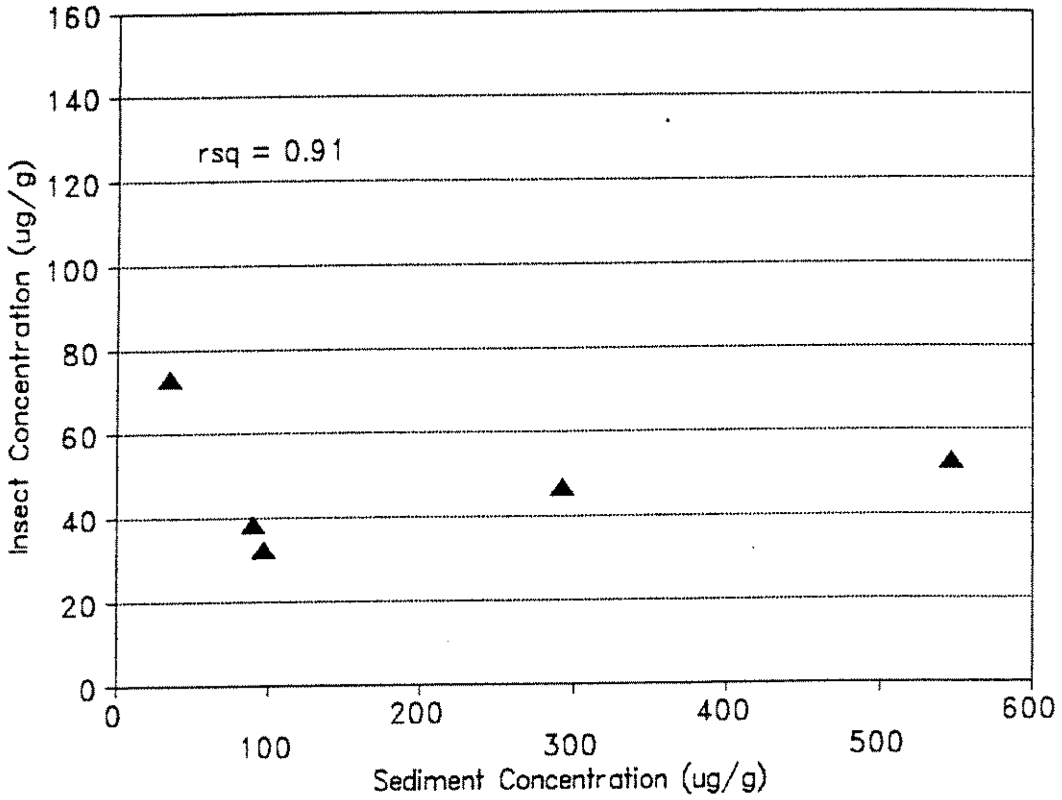

Figure 6. Comparison of copper concentrations in bed sediments versus H. pacifica, on a per organism basis.

Quality Assurance and Quality Control:

Eleven Comanche Creek sediment samples (QALC15-QALC25) were fortified with various metal concentrations after sample digestion. The concentrations of metals added to the samples ranged from 0 to several 1000 µg/g. Each metal was added to seven samples and a combination of metals was added to an additional four samples (Appendix 7).

The cadmium and Cu concentrations detected were similar to the fortified concentrations (Appendix 7). The difference between measured and fortified Cd and Cu concentrations ranged from -0.28 to +2.65, and -3.3 to +0.9 µg/g, respectively. The Mn concentrations detected varied from the fortified concentrations at low fortification levels. Little difference in Mn concentrations was found when samples were fortified with large quantities of Mn (QALC16). The detected and fortified Mn concentrations for QALC16 were 769 and 737 µg/g, respectively (Appendix 7). Variability in Mn recovery could be due to natural variablity of Mn presence in sediments because of nodule formation. In most cases, Ni concentrations measured were twice the fortified concentration when small quantities of Ni were added. When Pb concentrations were <70 µg/g, the measured values were 15-30 µg/g greater than fortified concentrations.

Little difference in Ni or Pb concentrations were detected when samples were fortified with large quantities of Ni or Pb (Appendix 7). Zinc concentrations were variable at low and high ranges of fortification (Appendix 7). Differences at low Zn concentrations could be due to low instrument sensitivity. Differences at the high Zn concentrations could be due to an undetermined matrix effect.

The concentrations of metals found in NBS-1645 sediment standards were all higher than the theoretical 95% confidence interval, with the exception of Cu (Appendix 7). Differences in analytical procedures and instrumentation could explain the differences between measured versus reported sediment standard concentrations.

The quality assurance and quality control results were used as a measure of variability. The metal concentrations in sediment and insect samples that were reported in this study are the actual concentrations detected.

DISCUSSION

Comparisons of previously reported sediment metal concentrations to those reported in this study are shown in Table 12. Whole-sediment samples were collected from the upper Rio Grande drainage in New Mexico by Roy et al. (1992). The <63 μm sediment fraction was analyzed for metals in both this study and by Lynch et al. (1988). However, Lynch and co-workers pooled their samples according to sampling location in order to reduce variability. This team had sampling locations upstream and downstream of the Molycorp mine along the Red River. Pooling of data according to upstream or downstream location had the effect of smoothing between-site variations.

Differences in sample collection and data analysis make it difficult to directly compare data from this study to those of Roy et al. (1992) and Lynch et al. (1988). Particle size differences between sediments analyzed in this study and Roy et al. (1992) resulted in higher metal concentrations for sediments collected during this study. Metals tend to adsorb more readily to clay particles (<63 μm) because of the higher surface-area to volume ratio found in clays.

Table 12. Comparison of mean metal concentrations (μg/g) detected in stream sediments from this and previous investigations.

Location	Al	Cd	Cu	Mn	Mo	Ni	Pb	Zn	Reference
COM[a]	66,300	5.15	34.8	1,540	--	41.7	76.2	1,490	Failing 1993
R1[b]	78,500	7.37	58.6	1,260	--	66.4	78.3	160	Failing 1993
R2[c]	49,200	8.14	252	1,610	--	115	174	803	Failing 1993
R3[d]	92,600	6.85	339	2,590	608	104	152	1,060	Failing 1993
P1A[e]	77,000	7.59	97.3	1,050	--	86.7	228	585	Failing 1993
P1N[f]	86,500	6.71	90.4	622	--	94.4	200	610	Failing 1993
P2A[g]	89,800	31.0	548	845	--	74.7	372	7,630	Failing 1993
P2N[h]	76,200	16.9	292	1,230	--	186	375	2,750	Failing 1993
pooled sample Red R., NM - upstream of mine	--	3.8	220	590	9.0	40	41	230	Lynch et al. 1988
pooled sample Red R., NM - downstream of mine	--	5.8	240	1,100	53	62	30	650	Lynch et al. 1988
Costilla Cr., NM	6,380	7.8	8.2	549	< 2.0	7.0	8.0	54.6	Roy et al. 1992
Red R. near Red River Pass, NM	--	9.85	--	--	--	--	--	--	Roy et al. 1992
Red R. upstream Red R. Hatchery, NM	--	--	--	--	--	--	183	--	Roy et al. 1992
Red R. @ Hwy. 3 Bridge, NM	--	--	96.5	--	--	--	--	494	Roy et al. 1992
Red R./Rio Grande confluence, NM	1,900	--	--	--	--	--	--	--	Roy et al. 1992

[a] Comanche Creek
[b] Red River #1
[c] Red River #2
[d] Red River #3
[e] Pecos River #1, April
[f] Pecos River #1, November
[g] Pecos River #2, April
[h] Pecos River#2, November

The distances that samples were collected from sources of contamination also influence the variability shown in the comparison of results from this and previous studies. Pooling data according to either upstream or downstream of a particular point source reduces the variability found in comparisons of individual point grab samples. When data sets are small such as in this study, it is difficult make comparisons to data which have been pooled.

Aquatic insect metal concentrations which were reported in previous investigations (Table 13) were compared to insect metal concentrations of this study. The effects of sex, life history characteristics, size, physiology, and feeding habits were not taken into consideration during this study because of the small number of samples collected. During a study by Lynch et al. (1988), however, all data from the different taxa were pooled according to sampling location. The pooling of data by Lynch and co-workers had the effect of smoothing out variations associated with sex, life history characterization, size, physiology, and feeding habits. Although data of this study did not lend itself to pooling, results of the two studies can be compared on a general upstream/downstream basis.

Table 13. Comparison of mean metal concentrations (µg/g, dry weight) detected in aquatic insects from this study and previous investigations.

Location/ Taxa	Al	Cd	Cu	Mn	Mo	Ni	Pb	Zn	Reference
Comanche Creek									Failing 1993
Ephemerellidae	1900	2.28	42.8	1396	--	--	--	489	
H. pacifica	252	0.42	73.1	79.5	--	--	--	397	
P. badia	607	0.82	28.4	264	--	--	--	239	
Anisoptera	688	1.16	28.1	201	--	--	--	122	
Tipula sp.	72.5	2.14	15.9	149	--	--	--	193	
Red River #1									Failing 1993
A. grandis	227	0.72	22.5	494	--	--	--	272	
Megarcys sp.	194	0.68	25.3	103	--	--	--	408	
P. badia	663	1.10	34.6	146	--	--	--	124	
Rhyacophila sp.	121	1.21	25.0	630	--	--	--	424	
Tipula sp.	105	3.11	23.7	228	--	30.5	--	241	
Red River #2									Failing 1993
A. grandis	98.2	1.45	59.7	1107	--	47.7	--	396	
Ephemerellidae	108	26.2	285	711	14.7	114	0.99	2843	
Isogeniodes sp.	120	2.98	119	132	10.5	46.9	0.71	459	
P. badia	227	2.04	99.3	27.2	9.36	84.7	0.91	323	
Red River #3									Failing 1993
P. badia	183	2.52	159	410	26.4	72.2	0.70	356	
Pecos River #1, April									Failing 1993
C. sabulosa	189	2.09	48.7	53.5	--	22.7	0.72	521	
H. pacifica	302	1.40	32.5	101	--	12.5	0.73	1114	
Pecos River #1, November									Failing 1993
C. sabulosa	170	1.71	48.4	58.9	--	42.3	0.79	463	
H. pacifica	389	1.31	38.4	96.8	--	17.8	0.91	966	
Pecos River #2, April									Failing 1993
C. sabulosa	168	4.05	65.9	94.4	--	65.8	0.87	723	
H. pacifica	141	2.24	52.7	79.1	--	76.3	0.92	2133	
Pecos River #2, November									Failing 1993
C. sabulosa	187	2.67	49.5	72.9	--	48.1	1.31	351	
H. pacifica	266	4.65	46.9	107	--	146	1.30	1785	
Red R., NM									Lynch et al. 1988
pooled sample upstream of mine	--	1.9	43.0	240	2.8	7.1	0.5	320	
Red R., NM									Lynch et al. 1988
pooled sample downstream of mine	--	1.3	82.0	540	17	13	0.9	350	
East R., CO									Colborn 1982
Pteronarcella badia downstream of mine	--	--	--	--	0.35	--	--	--	
Gunnison R., CO									Colborn 1982
Pteronarcella badia downstream of mine	--	--	--	--	0.14	--	--	--	
Chalus R., Iran									Nehring et al. 1979
Tipulidae	--	--	--	--	--	--	4038	--	
Hydropsychidae	--	--	--	--	--	--	1787	--	
Ephemerella grandis	--	--	94.7	--	--	--	--	1116	Nehring 1976
Pteronarcella californica	--	--	122.3	--	--	--	--	357	Nehring 1976

In most cases, Cd and Pb concentrations in all 23 insect samples of this study were comparable to values reported by Lynch et al. (1988). A relatively large range of Cd concentrations was recorded in insects of this study (0.42 - 26.1 μg/g), but most values ranged from 1 to 2 μg/g. Lead concentrations in aquatic insects of this study ranged from 0.71 to 1.23 μg/g, which is similar to values reported by Lynch et al. (1988). In another study by Nehring et al. (1979), Tipulidae and Hydropyschidae from the Chalus River, Iran had Pb concentrations of 4037.8 and 1787.4 μg/g, respectively when Pb concentrations in water were about 0.5 mg/l. This suggests that had water samples been collected during this study, Pb concentrations in the water would have been substantially lower than those reported by Nehring's team.

Zinc concentrations of P. badia from R3 were similar to results of the two previous investigations. P. badia from R3 had a Zn concentration of 355 μg/g. The pooled Zn value reported for the downstream sample of Lynch et al. (1988) was 350 μg/g, and 357 μg/g was reported for P. badia by Nehring (1976).

Molybdenum and Ni were not detected in insects from either Comanche Creek or R1. When Mo and Ni were measurable in aquatic insects of this study, concentrations were higher than values reported in earlier studies. The Mo concentration of P. badia from R3 was 26 μg/g, while 17 μg/g for the downstream pooled value was reported by Lynch et al. (1988). P. badia from R2 and R3 were up to 185 times greater than the values reported for P. badia from the East River - Upper Colorado River drainage, Colorado (Colborn 1982). During this study, P. badia appears to have been collected closer to a source of Mo contamination than the insects collected by Colborn (1982). Ephemerellidae from R2 had a Ni concentration of 110 μg/g, which was 16 times greater than the pooled upstream value (7.1 μg/g) reported by Lynch et al. (1988). P. badia from R2 had a Ni concentration six times greater than the pooled upstream value for insects collected by Lynch et al. (1988). P. badia from R3 had a Ni concentration six times greater than the pooled downstream value for insects collected by Lynch et al. (1988).

The differences of metal concentrations in aquatic insects from this study and those values reported in the literature can be explained. Metal accumulation can be species-dependent because of physiology, life history, and feeding habits. Differences in distances from sources of contamination can influence the amount of metals available for accumulation.

Comparisons of sediment and insect metal concentration of this study to previous investigations is further influenced by the natural distribution of metals in the environment. Previous work supports that metals tend to be bound to sediments (Gambrell et al. 1976). The chemical form of a metal and environmental parameters, such as pH and conductivity of water, regulate whether or not a metal is exchangeable. The exchangeable metal fraction in sediments is the most bioavailable. Without some measure of what fraction of metals in sediment is exchangeable, it is difficult to directly assess the risk to aquatic life.

CONCLUSION AND FUTURE WORK

Many metals tend to sorb to inorganic and organic particles and eventually are deposited in bottom sediments. The fates of metals once in sediments is diverse. Metals may (1) remain unavailable to the aquatic system, (2) transform into more or less toxic forms, or (3) migrate from bottom sediments into benthic organisms and water. With the exception of Mo, all metals were detected in all sediment samples. Molybdenum was only detected in R3 bed sediments. Although downstream increases in bed sediment and aquatic insect metal concentrations were apparent, a weak correlation in metal concentrations was found between bed sediments and aquatic insects from the same site.

Aquatic insects, as shown in this study, are capable of indicating the presence of metals in biota. Apparently, various insect taxa have different metal accumulation rates. Consequently, no single taxon consistently had the greatest concentrations of metals in this study.

Continued improvements of methodology for determining metal concentrations in aquatic insects are necessary to discriminate metals which are bioaccumulated in tissues, adsorbed to epicuticular or gill surfaces, or associated with gut contents. Methods used during this study were appropriate for indicating that metals were bioavailable. However, if the amount of metals being sequestered by an organism is of interest, a depuration step is necessary (Elwood et al. 1976). Depuration of aquatic insects in native water would probably remove most metals associated with extraneous gut material. However, how do factors such as depuration time effect results? More importantly, can these results be compared to other studies where depuration is not considered?

In trying to determine the relationship between the metal concentrations in aquatic insects and bed sediments, it was obvious that quantifiable methods for detecting bioavailable metals in sediments are necessary. It is well known that not all sediment-bound metals are bioavailable (Adams et al. 1992, Allen et al. 1980, and Gambrell et al. 1976). Quantification of bioavailable metals associated with sediments and other bed materials is needed before further relationships between aquatic insects and stream sediments can be developed.

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APPENDICES

Appendix 1. Wet and dry weight of aquatic insects (g), total number of insects per taxa collected (n), dry:wet weight ratio per insect taxa, and sample weight of insects (g) used during analysis.

Site	Taxa	Wet wt.	Dry wt.	n	Dry:Wet	Sample Wt.
COM[a]	Ephemerellidae	16.49	2.71	400	0.164	0.50
	H. pacifica	4.21	1.02	27	0.242	0.50
	Anisoptera	6.34	1.23	13	0.194	0.50
	P. badia	2.12	0.45	21	0.212	0.44
	Tipula sp.	10.59	1.83	49	0.172	0.50
R1[b]	Arctopsyche sp.	5.38	0.95	73	0.177	0.50
	Megarcys sp.	9.55	1.38	97	0.145	0.50
	P. badia	1.62	0.27	21	0.167	0.26
	Rhyacophila sp.	2.53	0.46	102	0.182	0.47
	Tipula sp.	12.60	1.88	79	0.149	0.50
R2[c]	Arctopsyche sp.	4.97	0.67	125	0.135	0.53
	Ephemerellidae	3.27	0.39	102	0.119	0.37
	Isogenoides sp.	3.13	0.56	23	0.179	0.56
	P. badia	21.85	4.40	334	0.201	0.50
R3[d]	P. badia	26.42	3.01	476	0.114	0.52
P1A[e]	C. sabulosa	5.71	1.45	49	0.254	0.54
	H. pacifica	4.05	0.94	66	0.232	0.51
P1N[f]	C. sabulosa	10.85	2.63	72	0.242	0.53
	H. pacifica	9.37	1.52	85	0.162	0.50
P2A[g]	C. sabulosa	3.25	0.50	18	0.154	0.46
	H. pacifica	5.90	1.27	48	0.215	0.48
P2N[h]	C. sabulosa	8.16	1.68	46	0.206	0.32
	H. pacifica	8.29	1.20	72	0.145	0.35

[a] Comanche Creek
[b] Red River #1
[c] Red River #2
[d] Red River #3
[e] Pecos River #1, April
[f] Pecos River #1, November
[g] Pecos River #2, April
[h] Pecos River#2, November

Appendix 2. Environmental field parameters.

	Environmental Parameter		
Site	H_20 Temp. (^oC)	pH	Conductivity (ohms)
COM[a]	6	7.1	80
R1[b]	7	8.3	122
R2[c]	6	7.5	179
R3[d]	5	7.0	195
P1A[e]	--	--	--
P1N[f]	3	7.6	109
P2A[g]	--	--	--
P2N[h]	2	7.7	121

[a] Comanche Creek
[b] Red River #1
[c] Red River #2
[d] Red River #3
[e] Pecos River #1, April
[f] Pecos River #1, November
[g] Pecos River #2, April
[h] Pecos River#2, November

Appendix 3. Atomic absorption (Abs.) and calculated metal concentrations ($\mu g/g$) in bed sediments from the Red and Pecos Rivers.

	Al		Cd		Cu		Mn	
Sample	Abs.	Conc.	Abs.	Conc.	Abs.	Conc.	Abs.	Conc.
R1[a]	0.121	78719	0.004	7.37	0.016	61.1	0.537	1259
	0.121	78719	0.004	7.37	0.015	57.3	0.535	1254
	0.120	78072	0.004	7.37	0.015	57.3	0.534	1252
R2[b]	0.160	48985	0.008	8.14	0.116	254	0.069	1626
	0.161	49290	0.008	8.14	0.114	250	0.068	1604
	0.161	49290	0.008	8.14	0.115	252	0.068	1604
R3[c]	0.323	92966	0.007	6.85	0.161	339	0.121	2594
	0.321	92392	0.007	6.85	0.162	341	0.121	2594
	0.321	92392	0.007	6.85	0.161	339	0.121	2594
P1A[d]	0.143	77311	0.007	7.96	0.040	97.3	0.021	1034
	0.142	76773	0.007	7.96	0.040	97.3	0.021	1034
	0.142	76773	0.006	6.86	0.040	97.3	0.022	1073
P1N[e]	0.172	86964	0.007	7.39	0.040	90.4	0.011	610
	0.171	86460	0.006	6.37	0.040	90.4	0.011	610
	0.170	85957	0.006	6.37	0.040	90.4	0.012	646
P2A[f]	0.232	89152	0.035	30.7	0.286	554	0.025	845
	0.235	90301	0.036	31.6	0.280	542	0.025	845
	0.234	89918	0.035	30.7	0.282	546	0.025	845
P2N[g]	0.271	77363	0.046	16.9	0.315	290	0.089	1219
	0.270	77077	0.046	16.9	0.318	292	0.088	1233
	0.260	74218	0.046	16.9	0.321	295	0.087	1246

	Mo		Ni		Pb		Zn	
Sample	Abs.	Conc.	Abs.	Conc.	Abs.	Conc.	Abs.	Conc.
R1	0	0	0.002	66.4	0.004	78.3	0.139	161
	0	0	0.002	66.4	0.004	78.3	0.138	160
	0	0	0.002	66.4	0.004	78.3	0.137	159
R2	0.005	45.6	0.010	118	0.015	170	0.078	807
	0.005	45.6	0.010	118	0.016	182	0.077	795
	0.004	45.6	0.009	108	0.015	170	0.078	807
R3	0.042	619	0.009	104	0.014	152	0.106	1063
	0.041	603	0.009	104	0.014	152	0.106	1063
	0.041	603	0.010	104	0.014	152	0.105	1052
P1A	0	0	0.006	86.7	0.018	228	0.037	591
	0	0	0.006	86.7	0.018	228	0.036	571
	0	0	0.006	86.7	0.018	228	0.037	591
P1N	0	0	0.007	91.0	0.017	200	0.040	610
	0	0	0.008	101	0.017	200	0.040	610
	0	0	0.007	91.0	0.017	200	0.040	610
P2A	0	0	0.007	77.6	0.038	382	0.536	7632
	0	0	0.007	77.6	0.036	362	0.535	7618
	0	0	0.006	68.7	0.037	372	0.536	7632
P2N	0	0	0.012	182	0.065	376	0.719	2751
	0	0	0.013	195	0.065	376	0.720	2747
	0	0	0.013	182	0.065	376	0.719	2747

[a] Red River #1
[b] Red River #2
[c] Red River #3
[d] Pecos River #1, April
[e] Pecos River #1, November
[f] Pecos River #2, April
[g] Pecos River#2, November

Appendix 4. Atomic absorption (Abs.) and calculated metal concentrations (μg/g) in aquatic insects.

	Al		Cd		Cu		Mn	
Site/Taxa	Abs.	Conc.	Abs.	Conc.	Abs.	Conc.	Abs.	Conc.
Comanche Creek								
Ephemerellidae	0.216	1897.8	0.014	2.271	0.107	43.789	0.075	1395.7
	0.222	1950.6	0.013	2.110	0.104	42.579	0.075	1395.7
	0.211	1853.7	0.014	2.271	0.103	42.176	0.075	1395.7
H. pacifica	0.027	251.95	0.002	0.360	0.167	73.216	0.172	79.180
	0.027	251.95	0.003	0.534	0.166	72.781	0.173	79.635
	0.027	251.95	0.002	0.360	0.167	73.216	0.173	79.635
P. badia	0.067	629.33	0.004	0.706	0.064	28.392	0.015	263.59
	0.067	629.33	0.005	0.879	0.064	28.392	0.015	263.59
	0.060	563.16	0.005	0.879	0.064	28.392	0.015	263.59
Anisoptera	0.075	700.40	0.006	1.046	0.064	28.210	0.030	201.27
	0.071	662.84	0.007	1.218	0.064	28.210	0.030	201.27
	0.075	700.40	0.007	1.218	0.063	27.779	0.030	201.27
Tipula sp.	0.009	78.645	0.012	2.029	0.036	15.771	0.336	148.87
	0.008	69.479	0.013	2.197	0.036	15.771	0.338	149.75
	0.008	69.479	0.013	2.197	0.037	16.191	0.336	148.87
Red River #1								
A. grandis	0.029	235.40	0.005	0.766	0.058	22.476	0.049	501.05
	0.029	235.40	0.005	0.766	0.058	22.476	0.048	491.16
	0.026	210.69	0.004	0.615	0.058	22.476	0.048	491.16
Megarcys sp.	0.024	199.83	0.003	0.478	0.064	25.455	0.247	101.36
	0.022	182.88	0.005	0.788	0.064	25.455	0.252	103.40
	0.024	199.83	0.005	0.788	0.063	25.070	0.251	102.99
P. badia	0.045	657.84	0.005	1.373	0.050	34.857	0.203	145.26
	0.047	687.35	0.004	1.102	0.050	34.857	0.204	145.97
	0.044	643.08	0.003	0.832	0.049	34.181	0.206	147.39
Rhyacophila sp.	0.015	118.73	0.007	1.056	0.066	25.206	0.070	627.42
	0.015	118.73	0.009	1.355	0.066	25.206	0.071	636.17
	0.016	126.87	0.008	1.205	0.064	24.460	0.070	627.42
Tipula sp.	0.012	99.583	0.020	3.165	0.059	23.861	0.044	229.22
	0.013	108.18	0.020	3.165	0.059	23.861	0.043	224.20
	0.013	108.18	0.019	3.007	0.058	23.861	0.044	229.22
Red River #2								
A. grandis	0.096	98.170	0.007	1.329	0.125	59.427	0.095	1099.6
	0.010	98.170	0.008	1.517	0.125	59.427	0.096	1111.0
	0.010	98.170	0.008	1.517	0.127	60.366	0.096	1111.0
Ephemerellidae	0.011	115.44	0.128	25.62	0.007	310.17	0.017	711.33
	0.010	104.52	0.131	26.22	0.006	273.87	0.017	711.33
	0.010	104.52	0.133	26.62	0.006	278.87	0.017	711.33
Isogeniodes sp.	0.015	114.39	0.020	2.888	0.329	118.85	0.351	133.09
	0.016	122.24	0.021	3.031	0.329	118.85	0.347	131.58
	0.016	122.24	0.021	3.031	0.331	119.57	0.349	132.33
P. badia	0.023	226.90	0.011	2.040	0.214	99.258	0.055	27.390
	0.023	226.90	0.011	2.040	0.214	99.258	0.054	26.907
	0.023	226.90	0.011	2.040	0.214	99.258	0.055	27.390
Red River #3								
P. badia	0.024	182.78	0.018	2.569	0.010	159.02	0.027	414.48
	0.023	175.02	0.017	2.426	0.010	159.02	0.026	400.03
	0.025	190.53	0.018	2.569	0.010	159.02	0.027	414.48

Appendix 4 (cont.). Atomic absorption (Abs.) and calculated metal concentrations (μg/g) in aquatic insects.

	Al		Cd		Cu		Mn	
Site/Taxa	Abs.	Conc.	Abs.	Conc.	Abs.	Conc.	Abs.	Conc.
Pecos River #1, Apr								
C. sabulosa	0.025	194.30	0.014	2.040	0.133	48.739	0.140	53.863
	0.024	186.39	0.015	2.185	0.133	48.739	0.139	53.483
	0.024	186.39	0.014	2.040	0.133	48.739	0.138	53.102
H. pacifica	0.038	304.27	0.010	1.495	0.086	32.483	0.258	101.12
	0.038	304.27	0.009	1.347	0.086	32.483	0.257	100.73
	0.037	296.17	0.009	1.347	0.086	32.483	0.257	100.73
Pecos River #1, Nov								
C. sabulosa	0.140	170.06	0.011	1.763	0.120	48.380	0.140	59.184
	0.020	170.06	0.010	1.604	0.120	48.380	0.140	59.184
	0.020	170.06	0.011	1.763	0.120	48.380	0.138	58.349
H. pacifica	0.039	388.88	0.007	1.307	0.081	38.130	0.197	96.319
	0.039	388.88	0.007	1.307	0.082	38.592	0.199	97.288
	0.039	388.88	0.007	1.307	0.082	38.592	0.198	96.804
Pecos River #2, Apr								
C. sabulosa	0.018	168.33	0.023	4.051	0.148	65.622	0.203	94.261
	0.019	177.91	0.023	4.051	0.149	66.061	0.203	94.261
	0.017	158.76	0.023	4.051	0.149	66.061	0.204	94.722
H. pacifica	0.014	137.50	0.012	2.241	0.112	52.685	0.160	78.732
	0.014	137.50	0.012	2.241	0.114	53.613	0.161	79.219
	0.015	147.62	0.012	2.241	0.110	51.757	0.161	79.219
Pecos River #2, Nov								
C. sabulosa	0.014	196.62	0.010	2.674	0.073	49.461	0.101	71.498
	0.013	182.14	0.010	2.674	0.073	49.461	0.104	73.588
	0.013	182.14	0.010	2.674	0.073	49.461	0.104	73.588
H. pacifica	0.019	265.64	0.017	4.475	0.070	46.876	0.152	105.67
	0.019	265.64	0.018	4.737	0.070	46.876	0.154	107.05
	0.019	265.64	0.018	4.737	0.070	46.876	0.154	107.05

Appendix 4 (cont.). Atomic absorption (Abs.) and calculated metal concentrations (μg/g) in aquatic insects.

	Mo		Ni		Pb		Zn	
Site/Taxa	Abs.	Conc.	Abs.	Conc.	Abs.	Conc.	Abs.	Conc.
Comanche Creek								
Ephemerellidae	0	0	0	0	0	0	0.098	483.46
	0	0	0	0	0	0	0.099	488.54
	0	0	0	0	0	0	0.100	493.62
H. pacifica	0	0	0	0	0	0	0.190	395.19
	0	0	0	0	0	0	0.190	395.19
	0	0	0	0	0	0	0.192	399.41
P. badia	0	0	0	0	0	0	0.059	247.90
	0	0	0	0	0	0	0.056	243.67
	0	0	0	0	0	0	0.056	243.67
Anisoptera	0	0	0	0	0	0	0.072	122.69
	0	0	0	0	0	0	0.072	122.68
	0	0	0	0	0	0	0.070	119.14
Tipula sp.	0	0	0	0	0	0	0.077	193.16
	0	0	0	0	0	0	0.077	193.16
	0	0	0	0	0	0	0.077	193.16
Red River #1								
A. grandis	0	0	0	0	0	0	0.102	273.65
	0	0	0	0	0	0	0.101	270.89
	0	0	0	0	0	0	0.101	270.89
Megarcys sp.	0	0	0	0	0	0	0.255	409.05
	0	0	0	0	0	0	0.254	407.43
	0	0	0	0	0	0	0.254	407.43
P. badia	0	0	0	0	0	0	0.050	144.41
	0	0	0	0	0	0	0.040	113.82
	0	0	0	0	0	0	0.040	113.82
Rhyacophila sp.	0	0	0	0	0	0	0.176	422.97
	0	0	0	0	0	0	0.177	425.41
	0	0	0	0	0	0	0.176	422.97
Tipula sp.	0	0	0.004	32.36	0	0	0.174	239.69
	0	0	0.003	26.63	0	0	0.176	242.49
	0	0	0.004	32.36	0	0	0.175	241.09
Red River #2								
A. grandis	0	0	0.005	45.39	0	0	0.127	394.13
	0	0	0.006	52.22	0	0	0.128	397.30
	0	0	0.005	45.39	0	0	0.128	397.30
Ephemerellidae	0.001	10.16	0.014	113.7	0.015	0.995	0.272	2860.7
	0.002	23.65	0.013	106.5	0.015	0.995	0.269	2828.8
	0.001	10.16	0.015	121.0	0.015	0.995	0.270	2839.4
Isogeniodes sp.	0.001	7.307	0.007	45.21	0.006	0.712	0.173	460.27
	0.002	17.01	0.007	45.21	0.006	0.712	0.173	460.27
	0.001	7.307	0.008	50.43	0.006	0.712	0.172	457.56
P. badia	0.001	9.359	0.011	84.67	0.002	0.910	0.259	318.36
	0.001	9.359	0.011	84.67	0.002	0.910	0.266	327.06
	0.001	9.359	0.011	84.67	0.005	0.912	0.263	323.33
Red River #3								
P. badia	0.003	26.39	0.012	70.48	0.004	0.703	0.092	359.74
	0.003	26.39	0.013	75.64	0.004	0.703	0.091	355.71
	0.003	26.39	0.012	70.48	0.004	0.703	0.090	351.67

Appendix 4 (cont.). Atomic absorption (Abs.) and calculated metal concentrations (μg/g) in aquatic insects.

	Mo		Ni		Pb		Zn	
Site/Taxa	Abs.	Conc.	Abs.	Conc.	Abs.	Conc.	Abs.	Conc.
Pecos River #1, Apr								
C. sabulosa	0	0	0.003	24.48	0.003	0.717	0.148	520.91
	0	0	0.002	19.22	0.003	0.717	0.149	524.51
	0	0	0.003	24.48	0.003	0.717	0.147	517.33
H. pacifica	0	0	0.002	19.68	0.005	0.735	0.332	1107.5
	0	0	0	8.89	0.004	0.734	0.332	1107.5
	0	0	0	8.89	0.004	0.734	0.388	1127.7
Pecos River #1, Nov								
C. sabulosa	0	0	0.006	44.26	0.003	0.787	0.198	461.02
	0	0	0.005	38.47	0.003	0.787	0.199	463.38
	0	0	0.006	44.26	0.003	0.787	0.200	465.74
H. pacifica	0	0	0.001	17.79	0.002	0.913	0.456	967.32
	0	0	0.001	17.79	0.003	0.914	0.454	963.05
	0	0	0.001	17.79	0.003	0.914	0.456	967.32
Pecos River #2, Apr								
C. sabulosa	0	0	0.008	61.55	0.003	0.868	0.262	726.79
	0	0	0.009	67.93	0.002	0.867	0.259	718.38
	0	0	0.009	67.93	0.002	0.867	0.261	723.98
H. pacifica	0	0	0.009	71.83	0.002	0.917	0.078	2123.9
	0	0	0.010	78.57	0.002	0.917	0.079	2152.1
	0	0	0.010	78.57	0.002	0.917	0.078	2123.9
Pecos River #2, Nov								
C. sabulosa	0	0	0.004	54.48	0.001	1.311	0.081	349.94
	0	0	0.003	44.84	0.001	1.311	0.082	354.42
	0	0	0.003	44.84	0.001	1.311	0.081	349.94
H. pacifica	0	0	0.015	158.6	0.002	1.295	0.440	1783.5
	0	0	0.013	139.5	0.002	1.295	0.440	1783.5
	0	0	0.013	139.5	0.002	1.295	0.441	1787.6

Appendix 5. Regressional outputs for aquatic insects and sediment metal concentrations, on a dry weight basis.

Metal:Insect	r^2	n[a]	d.f.[b]	S.E.[c]
Al:All[d]	0.012	23	21	0.0076
Al:Claa[e]	0.010	4	2	0.0004
Al:Hesp[f]	0.180	5	3	0.0029
Al:Pter[g]	0.393	4	2	0.0184
Cd:All	0.004	23	21	0.1529
Cd:Claa	0.984	4	2	0.0083
Cd:Hesp	0.245	5	3	0.0747
Cd:Pter	0.157	4	2	0.3548
Cu:All	0.148	23	21	0.0760
Cu:Claa	0.848	4	2	0.0109
Cu:Hesp	0.000	5	3	0.0428
Cu:Pter	0.972	4	2	0.0487
Mn:All	0.126	23	21	0.1755
Mn:Claa	0.000	4	2	0.0491
Mn:Hesp	0.026	5	3	0.0204
Mn:Pter	0.657	4	2	0.1132
Zn:All	0.141	23	21	0.0681
Zn:Claa	0.516	4	2	0.0231
Zn:Hesp	0.609	5	3	0.0844
Zn:Pter	0.015	4	2	0.1587

[a] number of observations
[b] degrees of freedom
[c] standard error of coefficient
[d] all 23 insect samples grouped together
[e] C. sabulosa
[f] H. pacifica
[g] P. badia

Appendix 6. Regressional outputs for aquatic insects and sediment metal concentrations, on a per organinsm basis.

Metal:Insect	r^2	n[a]	d.f.[b]	S.E.[c]
Al:All[d]	0.001	23	21	0.0004
Al:Claa[e]	0.573	4	2	0.0001
Al:Hesp[f]	0.060	5	3	0.0002
Al:Pter[g]	0.424	4	2	0.0011
Cd:All	0.245	23	21	0.0022
Cd:Claa	0.483	4	2	0.0043
Cd:Hesp	0.381	5	3	0.0036
Cd:Pter	0.007	4	2	0.0068
Cu:All	0.099	23	21	0.0023
Cu:Claa	0.208	4	2	0.0037
Cu:Hesp	0.906	5	3	0.0008
Cu:Pter	0.451	4	2	0.0019
Mn:All	0.039	23	21	0.0051
Mn:Claa	0.286	4	2	0.0053
Mn:Hesp	0.317	5	3	0.0026
Mn:Pter	0.053	4	2	0.0045
Zn:All	0.521	23	21	0.0002
Zn:Claa	0.794	4	2	0.0007
Zn:Hesp	0.773	5	3	0.0041
Zn:Pter	0.049	4	2	0.0021

[a] number of observations
[b] degrees of freedom
[c] standard error of coefficient
[d] all 23 insect samples grouped together
[e] C. sabulosa
[f] H. pacifica
[g] P. badia

Appendix 7. Quality assurance and quality control for external forifications of sediments and NBS sediments.

	Concentration in µg/g											
	[Cd]		[Cu]		[Mn]		[Ni]		[Pb]		[Zn]	
Sample	M.[a]	T.[b]	M.	T.	M.	T.	M.	T.	M.	T.	M.	T.
QALC15	8.61	6.70	927	961	-49.6	9.81	60.1	29.0	42.4	50.9	-165	3.85
QALC16	6.92	4.56	11.6	14.9	769	737	61.1	28.1	63.2	45.1	494	3.89
QALC17	7.57	4.92	14.2	16.2	-18.0	10.2	67.0	30.2	57.1	48.7	122	4
QALC18	5.15	4.92	13.8	16.0	1.59	10.2	1360	1330	62.9	48.9	-478	4
QALC19	4.55	4.83	13.7	15.7	-7.26	10.0	60.1	29.6	3710	3980	-535	4.02
QALC20	5.11	4.56	15.7	14.8	-86.7	9.44	48.9	28.0	74.0	45.1	-350	926
QALC21	6.55	4.47	15.0	14.5	23.1	9.27	47.3	27.4	58.9	44.3	322	3.63
QALC22	10.8	9.32	26.6	27.3	29.4	18.5	10.6	0	-1.06	0	200	0
QALC23	0.06	0	0.35	0	-28.0	0	93.8	60.5	123	102	-196	8
QALC24	8.92	8.99	-0.35	0	16.7	17.8	72.2	52.9	1.06	0	-396	7.02
QALC25	-0.06	0	44.0	30.0	28.0	0	-10.6	0	165	162	-200	0
1645-B	20.01	10.2[c]	126	109[d]	896	785[e]	67.88	45.8[f]	--	--	--	--
1645-C	26.88	10.2	154	109	996	785	83.33	45.8	--	--	--	--
1645-D	22.61	10.2	126	109	884	785	76.70	45.8	--	--	--	--
1645-E	19.79	10.2	131	109	961	785	74.21	45.8	--	--	--	--

[a] measured metal concentration

[b] fortified or theoretical metal concentration, theoretical metal concentrations for NBS sediment standards were obtained using isotope dilution mass spectroscopy, neutron activation, and polarography ($p < 0.5$)

[c] 95% confidence interval +/- 1.5 µg/g

[d] 95% confidence interval +/- 19 µg/g

[e] 95% confidence interval +/- 97 µg/g

[f] 95% confidence interval +/- 2.9 µg/g