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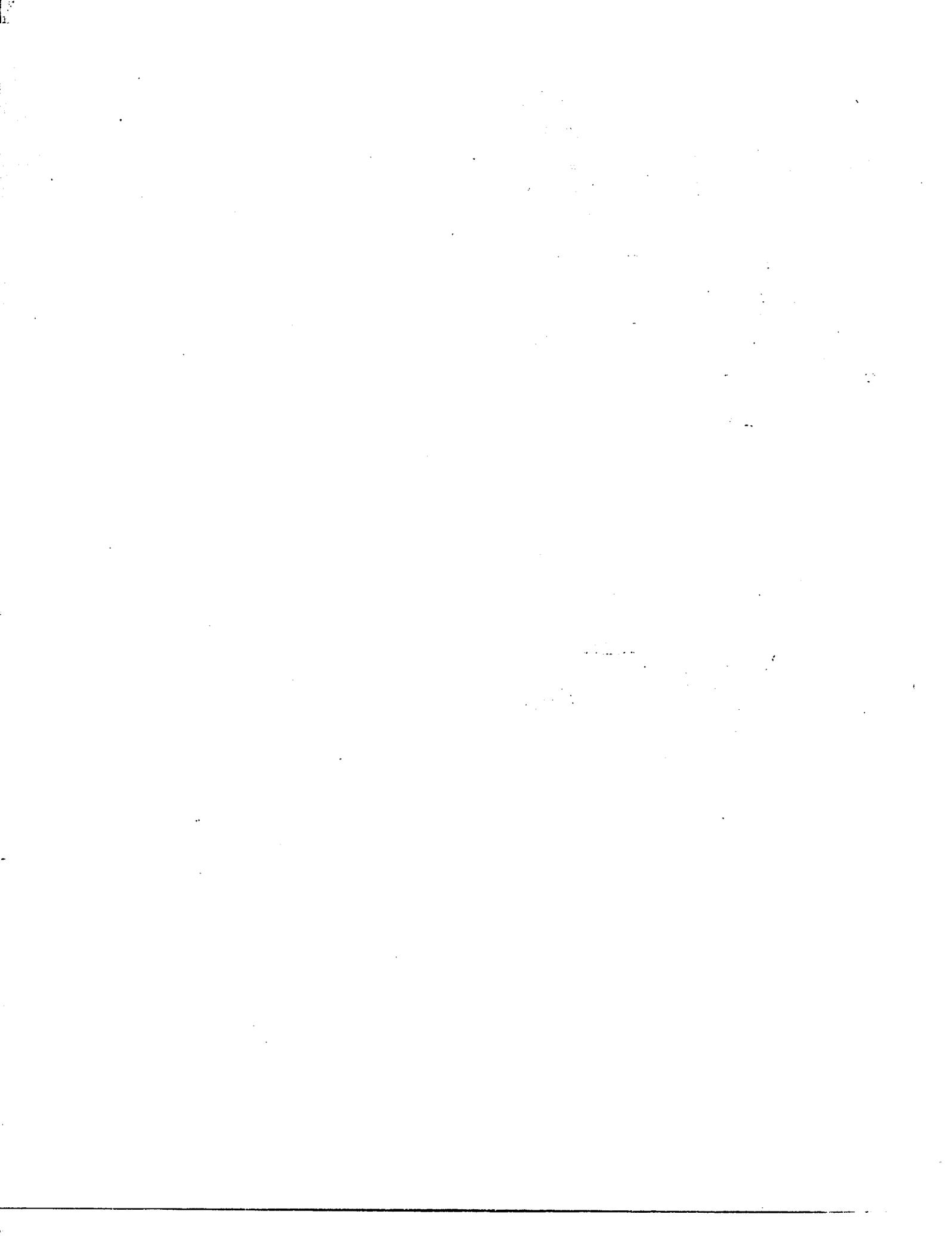
Copper, manganese, and zinc in Puerco River sediments

Henshel, Judy, M.S.

The University of Arizona, 1988

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COPPER, MANGANESE, AND ZINC
IN PUERCO RIVER SEDIMENTS

by

Judy Henshel

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A Thesis Submitted to the Faculty of the

SCHOOL OF RENEWABLE NATURAL RESOURCES

In Partial Fulfillment of the Requirements
For the Degree of

MASTER OF SCIENCE
WITH A MAJOR IN WATERSHED MANAGEMENT

In the Graduate College

THE UNIVERSITY OF ARIZONA

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ACKNOWLEDGEMENTS

Many people helped complete this study. Dr. James O. Klemmedson provided guidance regarding the design of the study, interpretation of results, and especially the writing of the manuscript. Dr. David M. Hendricks guided the laboratory analysis. Dr. Gordon S. Lehman and Dr. Wallace H. Fuller provided advice and encouragement.

Edwin K. Swanson of the Arizona Department of Health Services provided direction, inspiration, and contacts for the preliminary survey. Edwin Swanson also directed me to the highly competent staff of the Arizona State Laboratory, where my survey samples were exhaustively analyzed. Jerry Millard of the New Mexico Environmental Improvement Division, Chris Shuey of the Southwest Research and Information Center, and Robert Webb of the United States Geological Survey provided valuable background information and knowledge of the physical peculiarities of the Puerco River watershed.

Rick Axelson, David Blough, Mark Borgstrom, Pat Jones, James Klemmedson, and Robert Kuehl guided me through the complexities of statistical analysis and helped to develop interpretations that made order out of statistical chaos.

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ABSTRACT

A study was conducted to test for the presence of heavy metals (Cu, Mn, and Zn) in surface sediments of the Puerco River channel in the aftermath of a toxic spill in 1979 near Church Rock, New Mexico. Analysis of samples from five sites downstream from the spill showed that these substances were not present in unusually large amounts, though an increasing gradient of metal concentration with distance downstream was revealed. Statistical analysis revealed that Cu, Mn, and Zn were associated with clay and silt, soil organic matter, organic carbon, and carbonates, all of which existed as extraneous, uncontrolled variables. Adjusted metal concentrations, obtained with covariate analyses, confirmed the increasing gradient downstream. Clay and silt, used as a covariate, also increased downstream. Some toxic substances may have leached into the riverbed; possible mechanisms for this process are also discussed and further study to substantiate or disprove this hypothesis is recommended.

INTRODUCTION

In 1979, a uranium tailings pond dam broke at the United Nuclear Corporation (UNC) mine and mill northeast of Church Rock, New Mexico. Approximately 1,100 tons of mine tailings solids and 94 million gallons of acid tailings liquid were released into the Pipeline Arroyo and downstream into the north branch of the Puerco River. The spilled fluids carrying the tailings solids flowed down the channel through Gallup and into Arizona, approximately 60 to 70 miles from the spill site. As the spill flowed down the permeable stream beds, the solution infiltrated into the sediment of the streambed; eventually, the surface flow ceased near Chambers, Arizona (Aldis, 1979).

Scientists representing several institutions have monitored the Puerco River since the 1979 spill. Many samples of river surface water and well water taken from the alluvial aquifer had concentrations of radionuclides and trace metals that exceeded Arizona water quality standards when measured in 1985 and 1986 (Shuey, 1986).¹ The Arizona Department of Health Services (ADHS) suspects that those

¹. Arizona Department of Health Services. Water quality study: Puerco River, Arizona (Draft Report). Ambient Water Quality Unit, Water Assessment Section, Office of Emergency Respose and Environmental Analysis. Pheonix, Arizona. December, 1985.

violations were caused by activities on the New Mexico part of the Puerco River watershed.² The New Mexico Environmental Improvement Division (NMEID) found no violations of New Mexico's less stringent water quality standards.³ The NMEID implied that high trace metal and radionuclide concentrations found in Puerco River water were not significantly different from background levels in Puerco River tributaries.

In June, 1986, a preliminary study was conducted in Arizona that showed no toxic concentration of metals in plants or sediments in the Puerco River bankfull-channel (normally flowing channel) or the adjacent floodplain. A more detailed study, described in this thesis, was conducted in the Puerco River bankfull-channel in New Mexico in August, 1986, focusing on sediments in active-channel, upper-channel, and point-bar sites.

The objectives of this study were to analyze metal

2. Arizona Department of Health Services, New Mexico Environmental Improvement Division, U.S. Environmental Protection Agency, Region 6, and U.S. Environmental Protection Agency, Region 9. 1986. Report of the technical committee of the Puerco River working group. Draft.

3. Arizona Department of Health Services, New Mexico Environmental Improvement Division, U.S. Environmental Protection Agency, Region 6, and U.S. Environmental Protection Agency, Region 9. 1986. Report of the technical committee of the Puerco River working group. Draft.

concentrations from Puerco River sediments after the tailings spill of 1979 and to determine their distribution patterns, particularly any gradient distributions downstream from the spill. Tributary sediments provided control samples for comparison with Puerco River sediments.

DESCRIPTION OF PUERCO RIVER DRAINAGE

The north fork of the Puerco River begins west of the continental divide, east-northeast of Gallup, New Mexico (Figure 1). UNC's uranium mine and mill and Kerr-McGee Corporation's uranium mine are located on the Pipeline Arroyo, which flows into the north fork of the Puerco River approximately 1.5 miles downstream from the mill site. The Puerco River flows southwest from its confluence with the Pipeline Arroyo to Church Rock; the south fork of the river joins the north fork near this point. The river flows west-southwest through Gallup, which is approximately 20 river miles downstream from the UNC tailings pond. The Puerco River continues southwest to the Arizona/New Mexico border and joins the Little Colorado River near Holbrook, Arizona.

The geology of the Puerco River basin consists of Paleozoic and Mesozoic sedimentary rocks that dip slightly to the northeast. Steeply-dipping north-south-trending fault zones displace these rocks. The Defiance and Zuni Uplifts occur to the north and east, respectively (Cooley and others, 1969, as reported by Webb and others, 1987). Exposed rocks of Tertiary and Quaternary age in the area are relatively unaltered from their original horizontal plane. Major uranium and minor coal deposits are found in the Morrison Formation (Jurassic) to the east and northwest of Gallup. Uranium also occurs in the Petrified Forest member

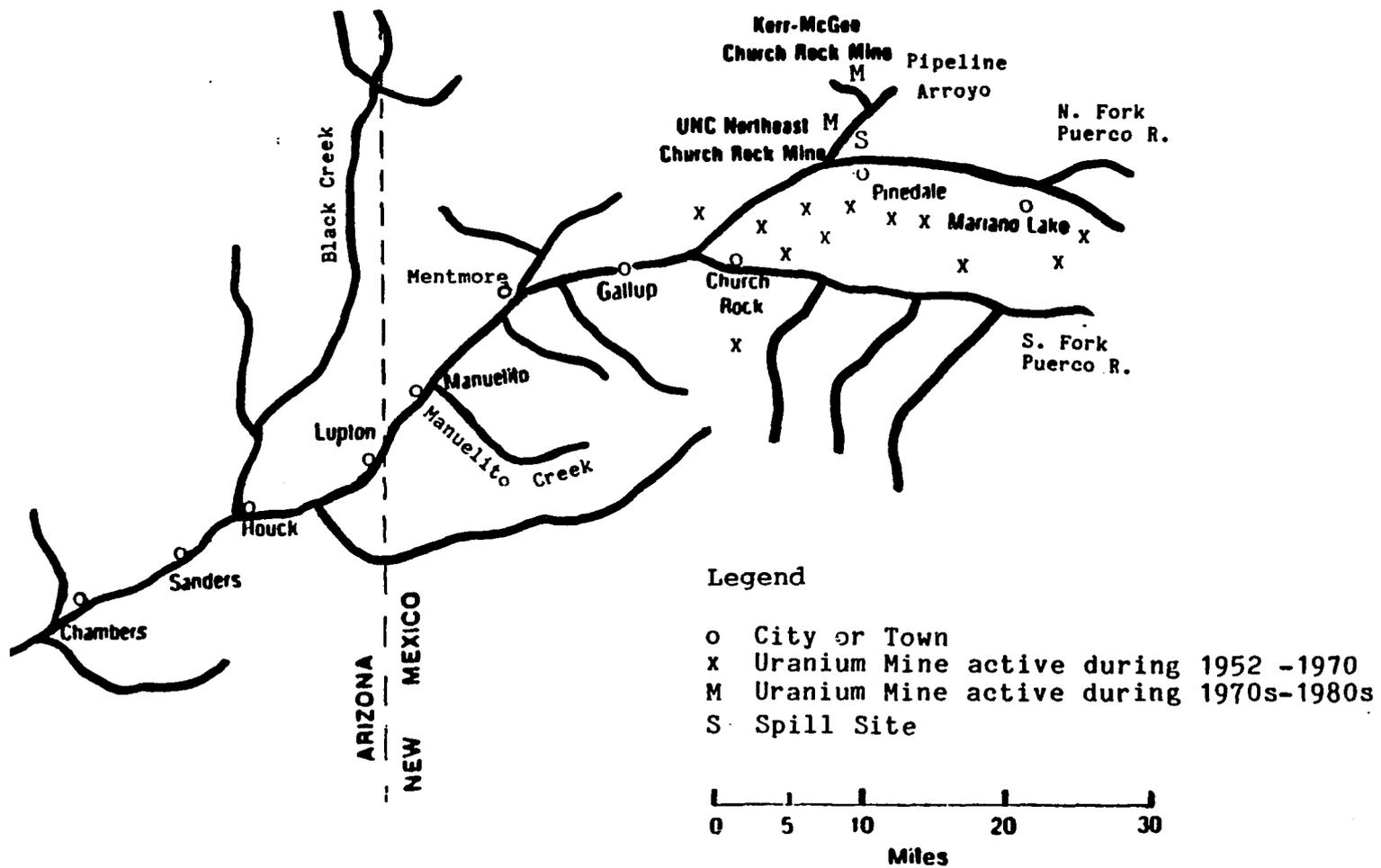


Figure 1. Uranium mines in Puerco River Basin

of the Chinle Formation (Triassic) in the western half of the basin. Natural erosion of exposed bedrock containing uranium and other radionuclides is the source of background radiation in regional water resources and sediments (Weimer and others, 1981, as reported by Webb and others, 1987).

The area bordering the Puerco River is high scrub desert dominated by sagebrush and some juniper. Soils are Entisols and Aridisols and are classified as Torriorthents, Haplargids, and Camborthids (Williams, 1986; Soil Conservation Survey, 1974). Gallup is at 6500 feet elevation; the study area ranges from 6000 to 7000 feet elevation. Mean annual precipitation for this region is about 8 to 12 inches, although the upper half of the North Fork of the Puerco River receives over 12 inches of annual precipitation. Approximately 50 to 60% of the precipitation for this area falls between October and May and 40 to 50% falls between June and September.⁴ Although flow of the Puerco River is historically intermittent, effluent water discharges from the uranium mines have made the arroyo perennial. Wastewater from Gallup also has increased flow in the channel (Shuey, 1986). Tertiary treatment in Gallup's wastewater treatment plant has been imperfect and may be a

4. LeViness, E.A. and P.R. Ogden. 1974. Range improvement potentials on Navajo land. Mimeograph report submitted to the Navajo Tribe.

continual source of metal pollution.⁵

The Puerco River varies from a wide and meandering stream in areas such as Sanders, to narrow and fast-flowing as in the vicinity of Mentmore, to a cement-lined channel in Gallup. A floodplain lies 1 to 4 feet above the level of the bankfull-channel on the inside of curves in the stream channel (Figure 2). The bankfull-channel and floodplain are sites of short-term sediment storage. Sediment is transported and deposited annually in the bankfull-channel, as indicated by grasses that sprout after regular flooding of the channel. On the floodplain, sediments may be shifted over longer time periods of 50 years or less, as indicated by the lack of older vegetation on the floodplain (Figure 3) (Miller, 1985). A higher terrace rises 5 to 10 feet above the riverbed in some sections of the river; these are sites of intermediate-term sediment storage (50 to 100 years) (Miller, 1985).

5. Shuey, Chris. 1987. Personal communication. Southwest Research and Information Center. Albuquerque, New Mexico.

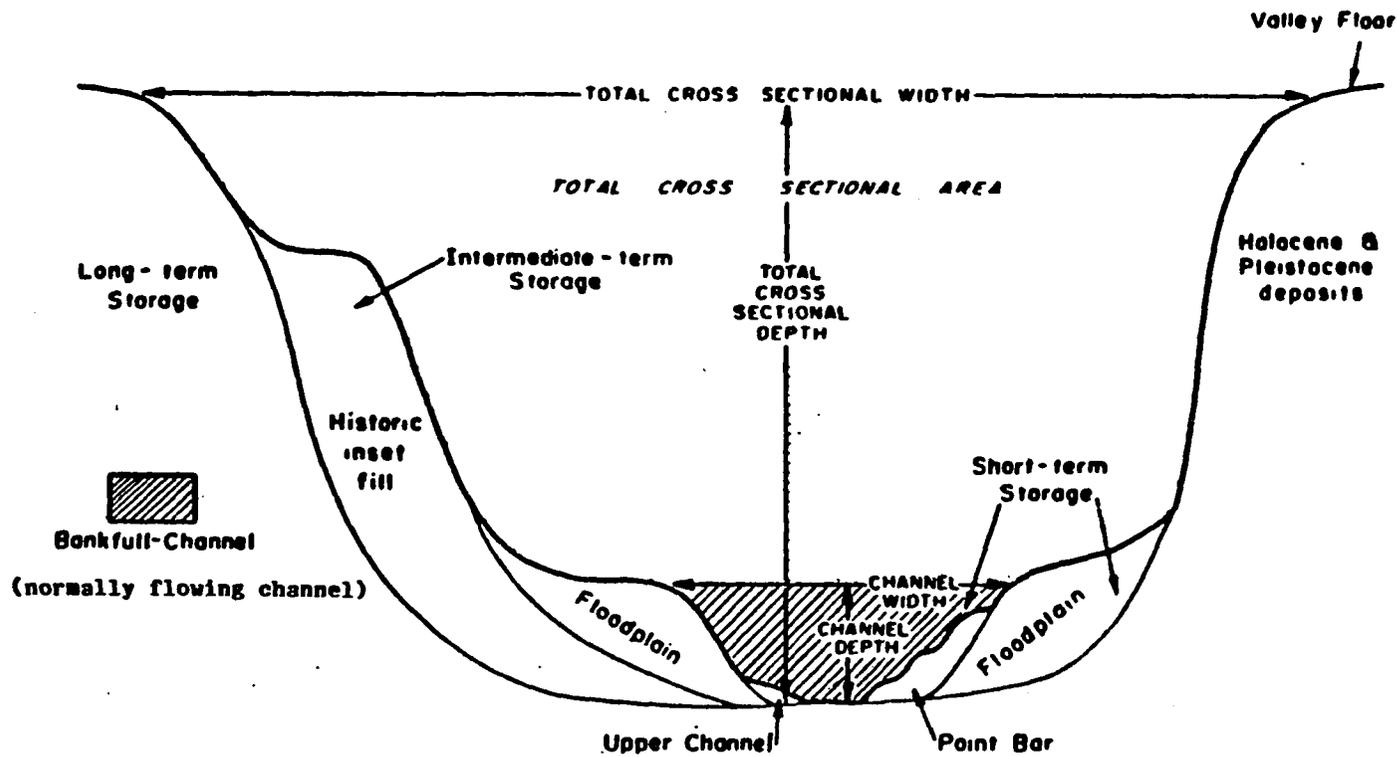


Figure 2. Diagrammatic representation of a cross-section characteristic of the Puerco River showing:
 (1) channel morphology,
 (2) differences between total and bankfull cross-sectional area and
 (3) long-term, intermediate-term, and short-term sediment storage sites
 (from Miller and Wells, 1986)

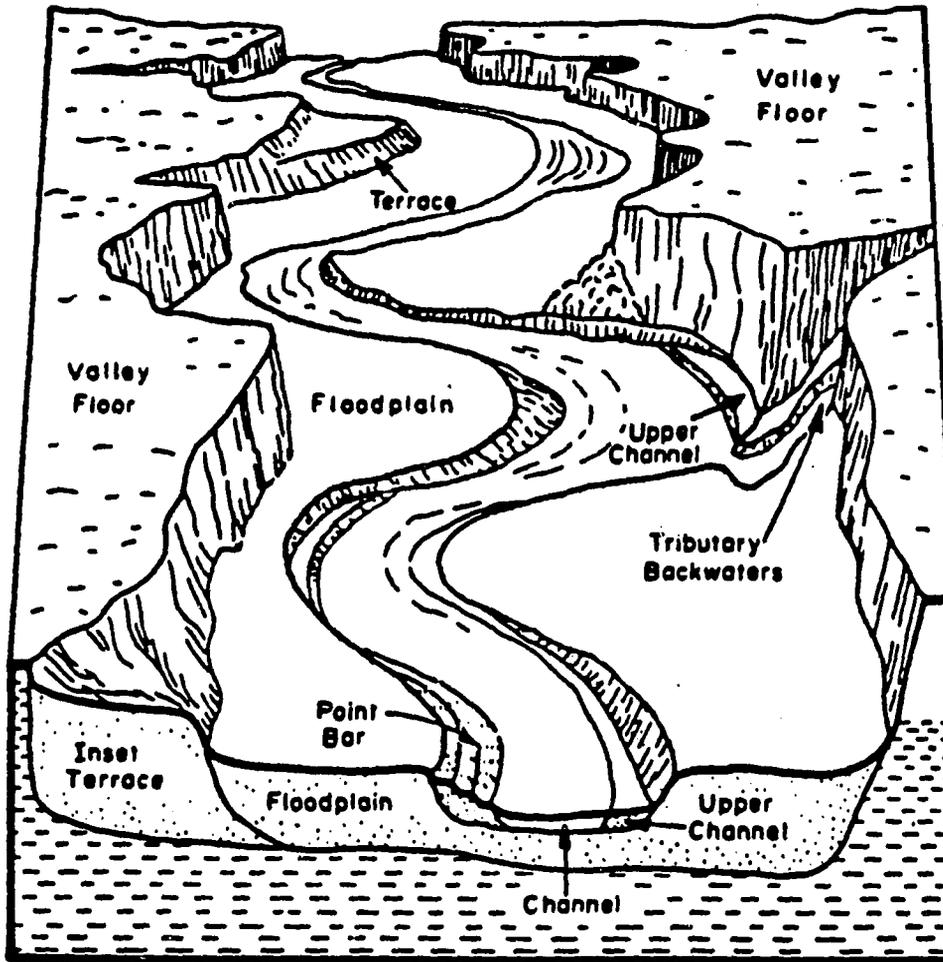


Figure 3. Diagrammatic sketch showing short-term sediment/contaminant storage locations along the Puerco River (from Miller and Wells, 1986)

BACKGROUND OF THE PROBLEM

The Puerco River watershed has been mined for uranium since the 1950's. The Old Church Rock uranium mine was operated by United Nuclear Corporation from 1960 through 1963 and from 1979 until early 1983 (Goad and others, 1980; Hilpert, 1969; as reported by Shuey, 1986). The ore body was 100 feet below the water table, so water in the ore zone had to be pumped out prior to mining (Shuey, 1986). The 1,400-foot-deep Northeast Church Rock mine was operated by UNC between 1969 and 1983. Water discharges, up to 1,300 gallons per minute (gpm) into the Pipeline Arroyo, resulted from dewatering the uranium mine. Kerr-McGee Corporation opened a mine a mile north of the Northeast Church Rock mine in 1972, and discharged mine water until early February 1986.

The Puerco River was receiving up to 5,000 gpm of mine water discharge from these mines between 1972 and 1983; about 3,500 gpm were released between 1983 and 1986. The Puerco River flowed as a perennial stream between 1969 and 1986 (Shuey, 1986). The discharged water was untreated until 1975. Federal discharge permit standards for treated effluent were not met until mid-1980 (Shuey, 1986). UNC also operated a uranium mill near the mines and had several tailings and wastewater ponds on the site. Table 1 lists the concentrations of some of the elements found in the tailings solution and dewatering effluent from the UNC mine.

Table 1. Quality of uranium mine dewatering effluents and United Nuclear Corporation mill tailings.
(from Weimer and others, 1981)

	Dewatering Effluent	Tailings Solution
pH	8 - 9	1.5
Spec. Cond. (umhos/cm)	500 - 1000	45000
Total Dissolved Solids (umhos/cm)	350 - 900	45000
Calcium (mg/l)	10 - 30	650
Potassium (mg/l)	1 - 2	100
Sodium (mg/l)	100 - 300	600
Magnesium (mg/l)	1 - 10	1000
Chloride (mg/l)	10 - 30	300
Sulfate (mg/l as SO ₄)	60 - 40	2000
Bicarbonate (mg/l as HCO ₃)	200 - 250	0
Nitrate and Nitrite (mg/l as N)	0.01 - 1.0	8
Ammonia (mg/l as N)	0.01 - 3.0	2000
Aluminum (mg/l)	< 0.250	1600
Arsenic (mg/l)	< 0.005 - 0.025	1.25
Barium (mg/l)	< 0.01 - 1.0	0.3
Cadmium (mg/l)	< 0.001	2
Molybdenum (mg/l)	< 0.01 - 1.0	0.1
Lead (mg/l)	< 0.005	1
Selenium (mg/l)	0.01 - 0.10	0.4
Uranium (mg/l)	0.1 - 10.0	11
Vanadium (mg/l)	< 0.01 - 1.0	50
Zinc (mg/l)	< 0.250	10
Gross alpha (pCi/l)	200 - 5000	80000
Radium 226 (pCi/l)	< 1 - 10	60

On July 16, 1979, the earthen dam of the south mill tailings pond at UNC broke, releasing approximately 1,100 tons of mine tailings "bottom" solids and 94 million gallons of acid tailings liquid downstream through the Pipeline arroyo into the Puerco River channel. The tailings solution was extremely acid (pH 1.5) and probably contained many of the elements listed in Table 1 as dissolved material. Uranium tailing slimes (<75um) were 35% by weight of total tailings produced; the dry solids contained 85% of the radioactivity (U. S. Environmental Protection Agency, 1980). The spilled fluids flowed through the city of Gallup to the state line, into Arizona and across the southeast corner of the Navajo Reservation for a total distance of 60 to 70 miles from the dam before they apparently infiltrated completely into the streambed alluvium (Aldis, 1979).

Numerous studies have been conducted in and around the Puerco River since 1979 to evaluate the health risk posed by failure of the tailings pond dam. After the 1979 spill, the U.S. Environmental Protection Agency, the NMEID, and personnel from the United Nuclear mine and mill at Church Rock began environmental sampling and monitoring programs of soil, water, and air on the Puerco River (Weimer and others, 1981). On-site sampling and analysis of sediments were conducted by Pacific Northwest Laboratory for the Nuclear Regulatory Commission in the fall of 1979 (Weimer and others, 1981). This survey of radionuclide distributions

along the riverbed from the spill site downstream into Arizona facilitated clean-up of the Puerco River by identifying "hot spots" of elevated concentrations of Thorium 230 (Weimer and others, 1981).

The ADHS and the NMEID monitored surface and well water at various times between 1980 and 1985. In 1985, the ADHS found 34 violations of state standards for radionuclides and heavy metals. The NMEID found only six violations of radionuclide standards. New Mexico's water standards in the Puerco River are based on the state's designation of the river only for protection of existing aquatic life and recreational uses. The NMEID considers natural background levels of radionuclides to be high enough around the Puerco River so that water from the river should not be used for livestock watering or irrigation. Arizona protects surface water quality based on "existing uses", which include agricultural irrigation, livestock watering, and domestic use of shallow alluvial well water for drinking (Aldis, 1979; Anders, 1983, as reported by Shuey, 1986). Arizona claimed that high levels of radionuclides in the water stemmed from uranium mining and milling in New Mexico.⁶ The Southwest Research

6. Arizona Department of Health Services, New Mexico Environmental Improvement Division, U.S. Environmental Protection Agency, Region 6, and U.S. Environmental Protection Agency, Region 9. 1986. Report of the technical committee of the Puerco River working group. Draft.

and Information Center (SRIC) also monitored the condition of the river from 1979 through 1986, sampling running water, standing water, and wells. SRIC found various violations of Arizona's water quality standards (Shuey and Morgan, 1986).

The ADHS developed a model to explain the differences between metal and radionuclide concentrations found in the river under high and low flow conditions. This "sediment loading model" assumes that radionuclides and metals are adsorbed onto sediments in the riverbed, since high sediment loads in flowing Puerco River water correlate well with high concentrations of metals and radionuclides and low sediment loads correlate with low concentrations of metals and radionuclides. In a flood event, the water may pick up large amounts of sediment, thereby transporting large amounts of adsorbed metals and radionuclides downstream.⁷

In 1979, the Nuclear Regulatory Commission surveyed radionuclide distributions from the spill site downstream into Arizona to facilitate cleanup of the riverbed (Weimer and others, 1981). Thorium 230 concentrations ranged "from background levels to levels elevated considerably greater than background" (Weimer and others, 1981).

7. Arizona Department of Health Services, New Mexico Environmental Improvement Division, U.S. Environmental Protection Agency, Region 6, and U.S. Environmental Protection Agency, Region 9. 1986. Report of the technical committee of the Puerco River working group. Draft.

In 1986, the United States Geological Survey (USGS) sampled wells near the Puerco River and found that all of the wells exceeded "one or more primary standards, secondary standards, or recommended levels of the EPA or the State of Arizona" (Webb and others, 1987). Concentrations of radionuclides and trace metals in sediments sampled from the Puerco River by the USGS in 1986 were "similar among channel, floodplain, and terrace." (Webb and others, 1987). Radionuclide concentrations in vegetation samples taken from the Puerco River by the USGS in 1986 generally were low. The USGS reported no significant difference between radionuclide concentrations in samples taken from "the potentially contaminated floodplain and the uncontaminated terrace" (Webb and others, 1987).

In a 1978 study sinuosity and meander length of the Puerco River bankfull channel were compared to 1945 air photographs; the channel form was found to be relatively stable and had not changed significantly after decades of uranium mine dewatering (Mills and Gardner, 1983). In the sand-rich perennial section of the river where floodplain widths were as wide as 90 m, average rates of migration of the arroyo floor laterally were estimated to be 1.1 m per year. In the clay-rich ephemeral reaches, lateral migration was estimated to be 0.7m per year. These rates are similar to that of other arroyos in northwestern New Mexico (Wells and Gardner, 1985).

In a 1985 study the relative storage capacity of short-term sediment storage sites in the Puerco River was measured and ranked (Miller, 1985). The following ranking of sites was suggested, from greatest to least potential sediment storage capacity in the arroyo: (1) floodplain deposits, (2) channel deposits, (3) upper-channel deposits, (4) point-bar deposits, and (5) tributary-backwater deposits (Figure 3) (Miller, 1985). Portions of the channel with high silt and clay content (>30%) tended to be relatively stable. Cross sections of these areas showed either degradation (loss of sediment) or stability. Channel cross-sections with <20% silt and clay content were largely aggradational; this was the case for most of the Puerco River below the confluence with the Pipeline Arroyo (Miller, 1986).

In another study Miller (1986) calculated how sediment from the 1979 tailings spill would have been deposited over the floodplain and in tributary backwater sites (Miller, 1986). Most of the contaminated sediments would have been deposited on arroyo floodplains. Scouring and filling during the event of the spill may have left tailings sediment within the bankfull-channel, especially in upper-channel deposits with high silt and clay contents (Miller, 1986). Increasing aggradation rates and decreasing flow rates downstream may have resulted in greater deposition of contaminated sediments downstream (Miller, 1986).

RELEVANT LITERATURE

The multivalent metals studied here, copper, zinc, and manganese, tend to be soluble in water at low pH (Bohn and others, 1985). As pH rises above 5, increasing proportions of these heavy metal ions are removed from aqueous solution by hydroxy complexation or by an excess of ligands in solution that form stable, uncharged or anionic, metal complexes (Farrah and Pickering, 1977). Specific solubility depends on what is available in solution that might affect metal precipitation and adsorption. Copper precipitates out of solution between pH 5.2 and 7.3, while precipitation of zinc occurs between pH 6.5 and 7.9 (Farrah and Pickering, 1977). Manganese precipitation occurs in approximately the same pH range, i.e. from 5.5 to 8 (Anderson, 1977). In one study, concentration of iron, manganese, nickel, cobalt, copper, and zinc was found to increase 1,000- to 10,000-fold in acid mine drainage as pH decreased (Forstner and Prosi, 1979).

Various laboratory and field studies have been conducted that show correlations between concentrations of metals in sediments and percentages of clay and silt and organic matter in those sediments. A good correlation was found between the concentration of heavy metals and percentage of clay and silt particle sizes in river sediments (Oliver, 1973). Collinson (1972) found metal concentration in lake

sediments was related to the amounts of organic carbon and certain size fractions of clay and silt in the sediments. Positive correlations have been found between percentage loss on ignition, or organic matter, and amount of clay and silt in sediments (Norton, 1968; Namminga and Wilhm, 1977). Similar relationships between heavy metals, amount of clay and silt in sediments, and organic matter have been discussed by other authors (Reimer and Toth, 1970; Gibbs, 1973; Shimp and others, 1970; Shimp and others, 1971).

Organic matter, iron and manganese oxides, carbonates, sulfides, and phosphates may all affect metal concentrations, depending upon the quantities and sorption characteristics of each of these sinks (Jenne, 1977). However, a positive correlation between metal and organic matter concentrations does not necessarily signify that the metal concentration is dependant upon the amount of organic matter in the sample. Organic matter and metal concentrations may both be dependant upon the percentage of clay and silt in the sediments (Jenne, 1977). Although clay minerals may contain trace metals as structural components, as exchangeable cations, and by specific sorption, the charged sites on layer silicates may not be as attractive to metal ions as are hydrous iron oxides, hydrous manganese oxides and other sinks with stronger attractive forces than clays (Jenne, 1977). Clay minerals may be important in metal transport processes primarily when coated with components

from these other sinks that strongly attract and react with metals (Davies-Colley, 1984). Sulfides, iron oxides, and possibly manganese oxides are nearly as important as organic matter as metal ion sinks (Jenne, 1977).

Each trace metal has different adsorption characteristics, and different studies reveal the complexity and variation of unique experimental conditions. Copper, in one model, was bound primarily with organic matter at pH 8, as long as high-energy binding sites were available. Copper is also bound in iron oxide complexes. Clay accounted for less than 10% of the adsorbed copper, while manganese oxide complexes were only slightly significant in binding with copper. Iron became slightly more significant as an adsorbant for copper as pH was decreased to 7 (Davies-Colley, 1984). In Lower Rhine River sediments, copper was mainly correlated with natural rock detritus, humates, and hydroxyoxides (Forstner and Prosi, 1979). Studies of copper mobility in polluted rivers showed ratios of the solid phase to the aqueous phase to be between 2:1 and 4:1 (Forstner and Prosi, 1979).

Studies of zinc mobility revealed that ratios of particulate species to dissolved species ranged from 1:1 to 1:2 (Forstner and Prosi, 1979). In Lower Rhine sediments, zinc was primarily found as carbonate precipitates, while a small percentage of the zinc was bound with humates (Forstner and Prosi, 1979). In another study, Kzenek and Ellis (1980) found that the cation exchange capacity of

clays and hydroxy oxides was directly related to zinc adsorption capacity in soils. In soil solution, 60% of the zinc has been reported to exist as an organic complex (Kzenek and Ellis, 1980).

Manganese is known to form oxides, hydroxides, and mixed species (Kzenek and Ellis, 1980). Manganese, in rivers under normal Eh conditions, are transported largely as solid particles (Forstner and Prosi, 1979). Free-manganese oxides probably occur primarily as discrete particles rather than coatings, because a positive correlation is not usually found between these oxides and clay content in soils (Jenne, 1977). The silt (20-50um) size fraction of soils tends to have relatively high concentrations of oxidic manganese (Jenne, 1977).

Besides comprehending how these metals behave in sediments, the behavior of the sediments themselves must be understood. In ephemeral streams, silt and clay come primarily from eroding valley slopes. They move quickly through the channel, and are not stored in large quantities in the channel-fill between floods (Frostnik and others, 1983). Sand in the streambed comes mostly from scour of the channel itself (Frostnik and others, 1983). Although silt and clay are only a small percentage of the sediment particles carried in ephemeral streams, most of the suspended sediment in ephemeral streams consists of clay and silt (< 63 um) (Frostnik and others, 1983). During low

flows, metal concentrations in solution are highest, suggesting that metal concentrations are diluted in higher flows (Forstner and Prosi, 1979). Metal concentrations in solution also significantly increase in streams during the brief initial stages of storm runoff, possibly explained by silt and clay being swiftly flushed down the channel from above (Forstner and Prosi, 1979).

METHODS

EXPERIMENTAL DESIGN AND SAMPLING METHODS

In the preliminary survey conducted in June, 1986, selection of sample locations was based on the advise of several individuals familiar with the Puerco River pollution problem (Jerry Millard, Chris Shuey, and Edwin K. Swanson). Areas selected for sampling along the course of the stream were curves in the riverbed where the current slowed and sediment had been deposited (Figure 4 and Table 2). Sediments or water from some of these sites had been previously analyzed, and some sites revealed high metal concentrations in water (Shuey, 1986).⁸

Vegetation samples were selectively chosen at each site to obtain a cross-section of plants growing in sediment that may have contained residues of the spill (Table 3). In looking for areas of metal deposition, the top 1-2 cm of white salts and black deposits were selectively removed for preliminary samples. Results of this sampling showed no obvious pattern and no accumulation of metals in the

⁸. Arizona Department of Health Services. Water quality study: Puerco River, Arizona (Draft Report). Ambient Water Quality Unit, Water Assessment Section, Office of Emergency Respose and Environmental Analysis. Pheonix, Arizona. December, 1985.

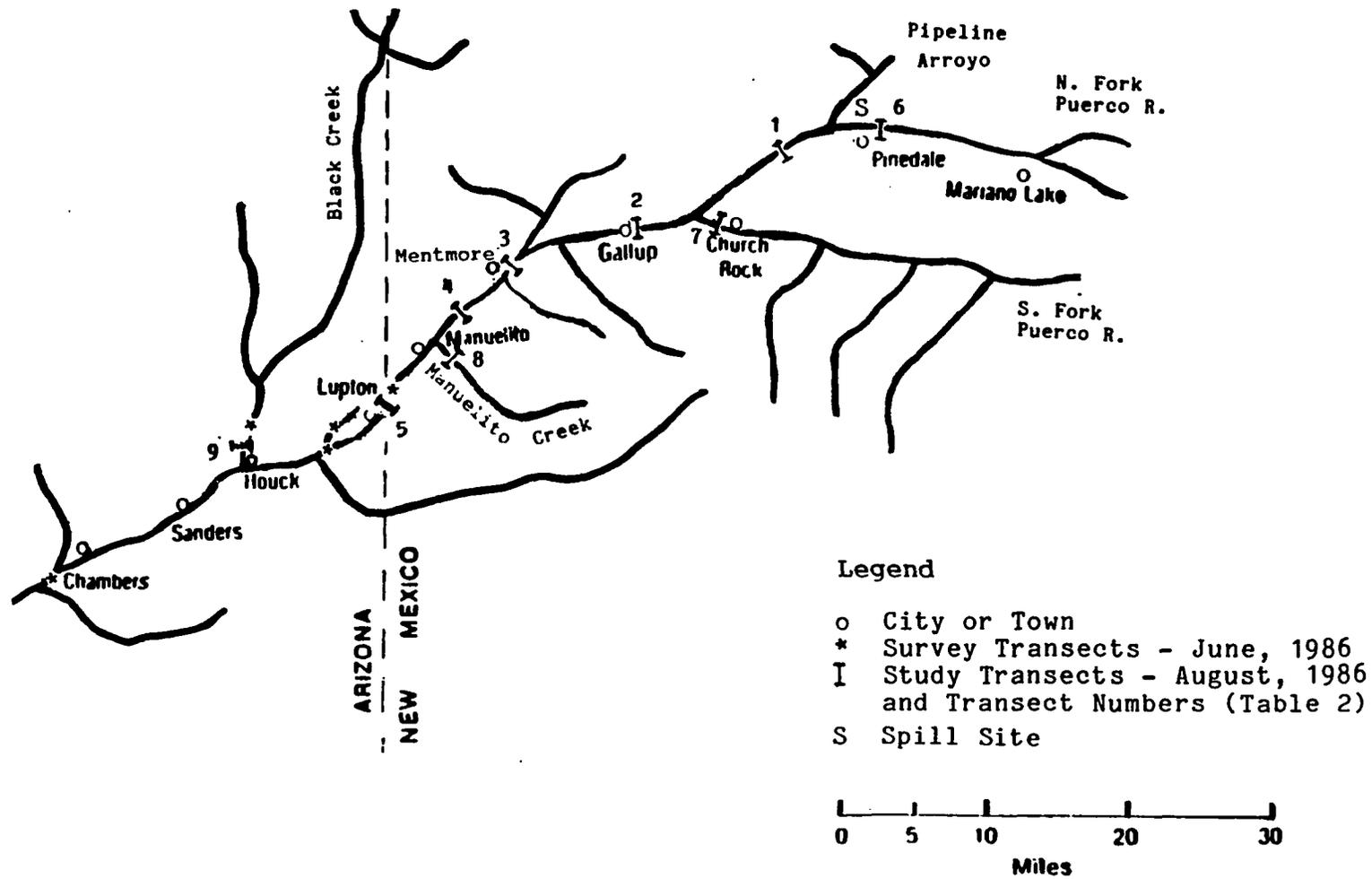


Figure 4. Survey and sample transects in Puerco River basin

Table 2. Location and description of transects on Puerco River and control tributaries

Transect Number	Transect Type	Location and Description
1	Treated	Downstream from confluence of Pipeline Arroyo and North Fork of Puerco River, below spill site
2		In Gallup, downstream from confluence of North and South Forks of Puerco River; cement channel walls
3		Near Mentmore, at bend in river, upstream from bridge; Gallup Wastewater Treatment Plant discharged upstream
4		Near Manualito Creek, at bend in river; just upstream from bridge
5		Downstream from bridge near Arizona/New Mexico border; wider floodplain and bend in river
6	Controlled	Narrow North Fork of Puerco River, upstream from confluence with Pipeline Arroyo; uranium mining occurred upstream in 1950's and 1960's
7		Downstream from Church Rock bridge on South Fork of Puerco River; mining occurred downstream of transect
8		Manualito Creek; no known mining activities
9		Black Creek; coal mining upstream

Table 3. Dominant plant species found in Puerco River bankfull-channel, floodplain, and terraces in Arizona, June, 1986

Location	Vertical distance above riverbed, feet	Vegetation
Bankfull-Channel	0	<u>Sitanion hystrix</u> <u>Polypogon monspeliensis</u> <u>Poa species</u>
Floodplain	1 to 4 feet	<u>Bromus tectorum</u> <u>Tamarix pentandra</u> <u>Chrysothamnus species</u>
Terrace	8 to 10 feet	<u>Baccharis species</u>

vegetation and associated sediment samples (Tables 4 and 5). This information was used to design the sampling plan for the study.

The sampling plan was simplified to sample only sediments from the Puerco River bankfull-channel. Sampling was designed to identify the distribution pattern of metals from the mine site downriver to Arizona and to detect any difference in concentration of metals between Puerco River sediments and those from tributaries (controls) that were unaffected by the 1979 spill.

Tributaries flowing through geological formations similar to the Puerco River provided control sampling points. These control sites had not been influenced by the 1979 spill, dewatering from the mines in question, or Gallup wastewater. However, some of these sites had been influenced by other mining activities. Uranium mining operations were conducted on the North Fork of the Puerco River in the 1950's and 1960's; these operations probably discharged water from the mines down the tributaries into the Puerco River (Shuey, 1986). Coal mining took place in the Black Creek watershed.⁹ Mine water was discharged into the South Fork of the Puerco River downstream from sampling site number 8.¹⁰ There have

⁹. Webb, Robert. 1987. Personal communication. United States Geological Survey. Tucson, Arizona.

¹⁰. Shuey, Chris. 1987. Personal communication. Southwest Research and Information Center. Albuquerque, New Mexico.

Table 4. Concentration of transition elements in vegetation and associated sediments from a survey of the Puerco River in Arizona, June, 1986

Sample Type	Location	Sublocation	Cu	Mn	Zn	As	Cr	Cd	Pb	Se
-----parts per million-----										
Sediment	Bankfull-Channel	River	9 ± 5 *	223 ± 68	32 ± 19	2.7 ± 0.8	6 ± 2	<1.0 ± 0	8 ± 3	<1 ± 0
		Control	9 ± 6	285 ± 98	40 ± 26	1.8 ± 0	9 ± 4	<1.0 ± 0	12 ± 9	<1 ± 0
Sitanion Hystrix	Bankfull-Channel	River	<50 ± 0	55 ± 6	16 ± 5	<1 ± 0	<50 ± 0	<10 ± 0	<50 ± 0	<1 ± 0
		Control	<50	<50	28	<1	<50	<10	<50	<1
Polypogon Monspeliensis	Bankfull-Channel	River	<50 ± 0	145 ± 42	27 ± 13	<1 ± 0	<50 ± 0	<10 ± 0	<50 ± 0	<1 ± 0
		Control	---	---	---	---	---	---	---	---
Poa Species	Bankfull-Channel	River	<50 ± 0	164 ± 23	39 ± 38	<1 ± 0	<50 ± 0	<10 ± 0	<50 ± 0	<1 ± 0
		Control	---	---	---	---	---	---	---	---
Combined Perennials	Terraces	River	<50 ± 0	51 ± 3	55 ± 30	<1 ± 0	<50 ± 0	<10 ± 0	<50 ± 0	1 ± 0
		Control	<50	<50	45	<1	<50	<10	<50	<1

* means plus or minus standard error

Table 5. Ranges in concentration of copper, zinc, and manganese in soil and plant samples (from Kzenek and Ellis, 1980)

Sample	Copper	Manganese	Zinc
	-----mg/kg-----		
Soil	10-80	20-3000	10-300
Plant	7-30	31-100	21-70

been no known mining operations on Manuelito Creek.¹¹

Transect locations were selected to cover the river channel between the uranium mines and the Arizona/New Mexico border, with a 5-10 mile interval between transect locations (Figure 4). Transects were established across the riverbed, perpendicular to the direction of flow, from one edge of the bankfull-channel to the other. The edge opposite the active-channel was an upper-channel or point-bar site (Figure 3).

Total transect length was determined by the boundaries of the bankfull-channel. For each transect location, four samples were systematically located $1/5$ of the transect length apart and from each bank. Sampling sites on control transects were located at distances $1/3$ of the total transect length apart when two samples were taken and $1/4$ of the total transect length when three samples were taken. Sediment deposition appeared to vary across bankfull-channel transects.

At each sampling point, surface and subsurface samples were collected. The surface sample was collected from the upper 1 to 2 centimeter layer of sediment within a one square meter area. A clean plastic dustpan was used to scoop approximately one liter of sediment into a labeled plastic bag.

The subsurface sample at each sampling point was

¹¹. Webb, Robert. 1987. Personal communication. United States Geological Survey. Tucson, Arizona.

collected whenever a layer of clay sediment was available within 1 to 2 feet of the surface. A pit was dug with a clean metal shovel. The pits were 1 to 2 feet wide and 1 to 2 feet deep. The side of the pit was cleanly scraped to reveal the profile of sediment. All of the sediment above the uppermost clay layer was removed to leave 1 to 2 square feet of exposed clay sediment. A clean dustpan was then used to remove up to a liter of the clay sediment into a second labeled plastic bag.

LABORATORY METHODS

Sediment samples were air dried, crushed on a marble slab, passed through a 2-mm plastic seive and stored in new plastic bags. Metals were extracted from the sediments sequentially with 1:1 nitric acid, 30% hydrogen peroxide, and 1:1 hydrochloric acid (U.S. Environmental Protection Agency, 1985). Acidic metal extracts were analyzed for Cu, Mn, and Zn by atomic adsorption spectroscopy (AAS) (Jones and Isaac, 1969). Samples were analyzed for particle size distribution by the hydrometer method (Day, 1956), organic matter by loss on ignition at 500 degrees Celcius (Ball, 1964), organic carbon by dry combustion using a LECO high frequency induction furnace (Allison, Bollen and Moodie, 1965), and pH with a glass electrode in 1:1 (soil:water) solutions.

RESULTS

ANALYSIS OF OBSERVED DATA

Metal concentrations of surface and subsurface samples were averaged separately for each transect. Mean metal concentrations of each transect were then regressed separately for surface and subsurface means with distance downstream from the spill site. Graphs of the regressions for Cu and Zn (Figure 5) show positive regression coefficients, indicating a possible increasing gradient of metal concentration downstream. Regression equations for Mn also showed an increase downstream. In a t-test, the regression coefficients of the three regression lines from surface sample means were significantly ($P < 0.10$) greater than zero, while those from the three subsurface sample means were not different from zero ($P < 0.10$). However, the large standard errors of the regression coefficients indicate that there was high variation about regression. This coupled with the small number of samples (a consequence of the sampling design) leads to low reliability in the results.

The methodology of the sampling plan used requires that samples collected systematically along each transect (i.e., across the stream) should be treated as subsamples. Thus, subsample values were pooled into one mean per transect. But

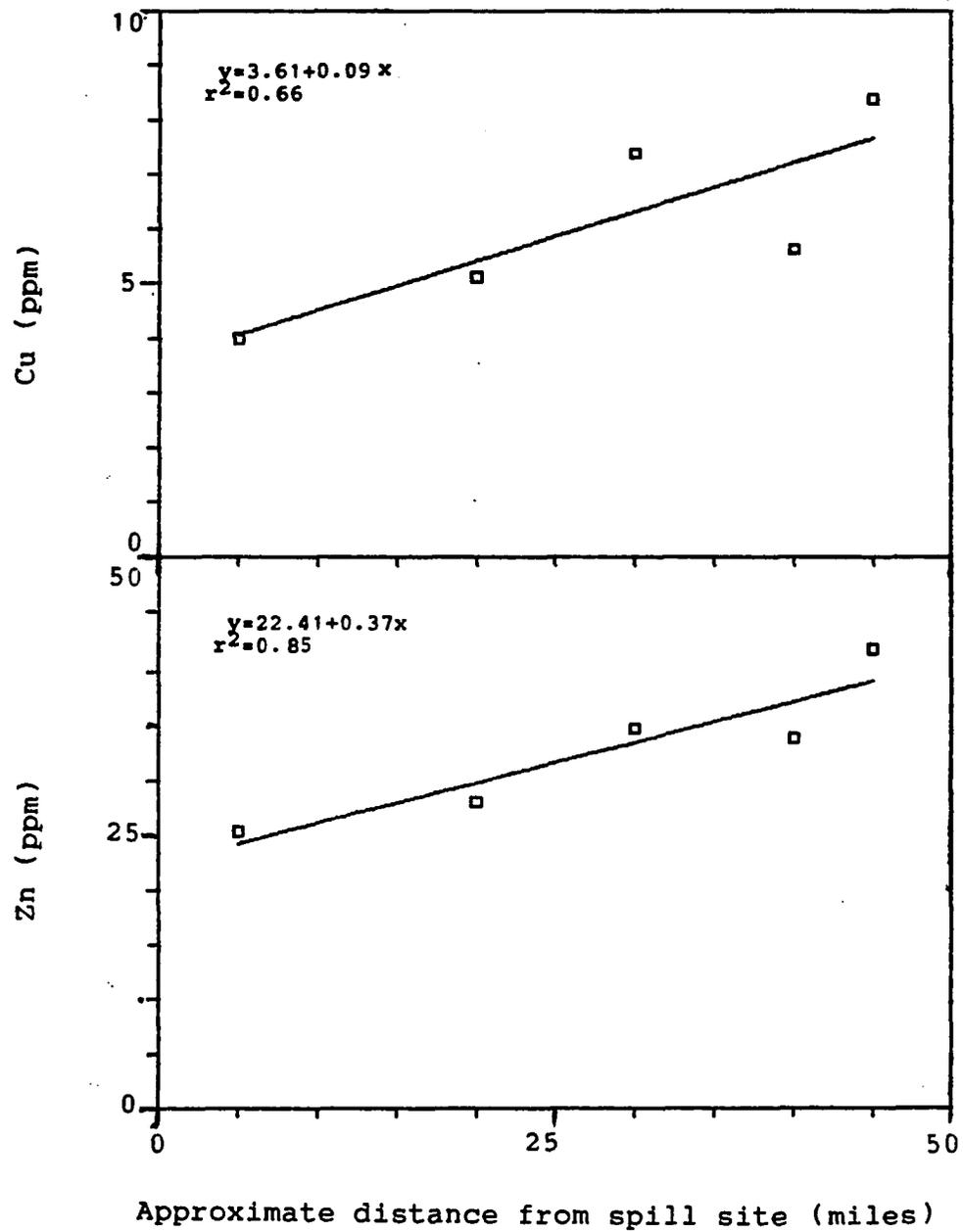


Figure 5. Relation between mean Cu and Zn concentration of sediments and approximate distance downstream for surface samples

the rationale for this procedure is based on the belief that sample points located equidistantly along a transect are non-independently related. However, the sample points considered here may, in fact, be independent of each other. Numerous hydrologic events have occurred in the basin since the spill and have produced complex sedimentation patterns in the riverbed, as noted previously. Under these circumstances, it seems more reasonable to believe that the sedimentation patterns approximate a random distribution rather than some definite relationship to distance, since hydrologic events are responsible for the basic distribution of sediments across the streambed. Testing this hypothesis by plotting sediment properties sequentially along transects verified sample independence, because no predictable or consistent trend emerged among ordered locations in the transects.

In another test for independence of samples, observed metal concentrations for all sample locations were regressed on distance downstream. Residual Y-values (observed metal concentration minus predicted metal concentration from the regression line) were then plotted as a function of their sequential order of collection (Pedhazur, 1982). The standardized residuals (i.e. residuals divided by their standard deviation) for Cu concentration of surface samples displayed in Figure 6 appear to be randomly distributed. Comparable graphs of standardized residuals for Mn and Zn

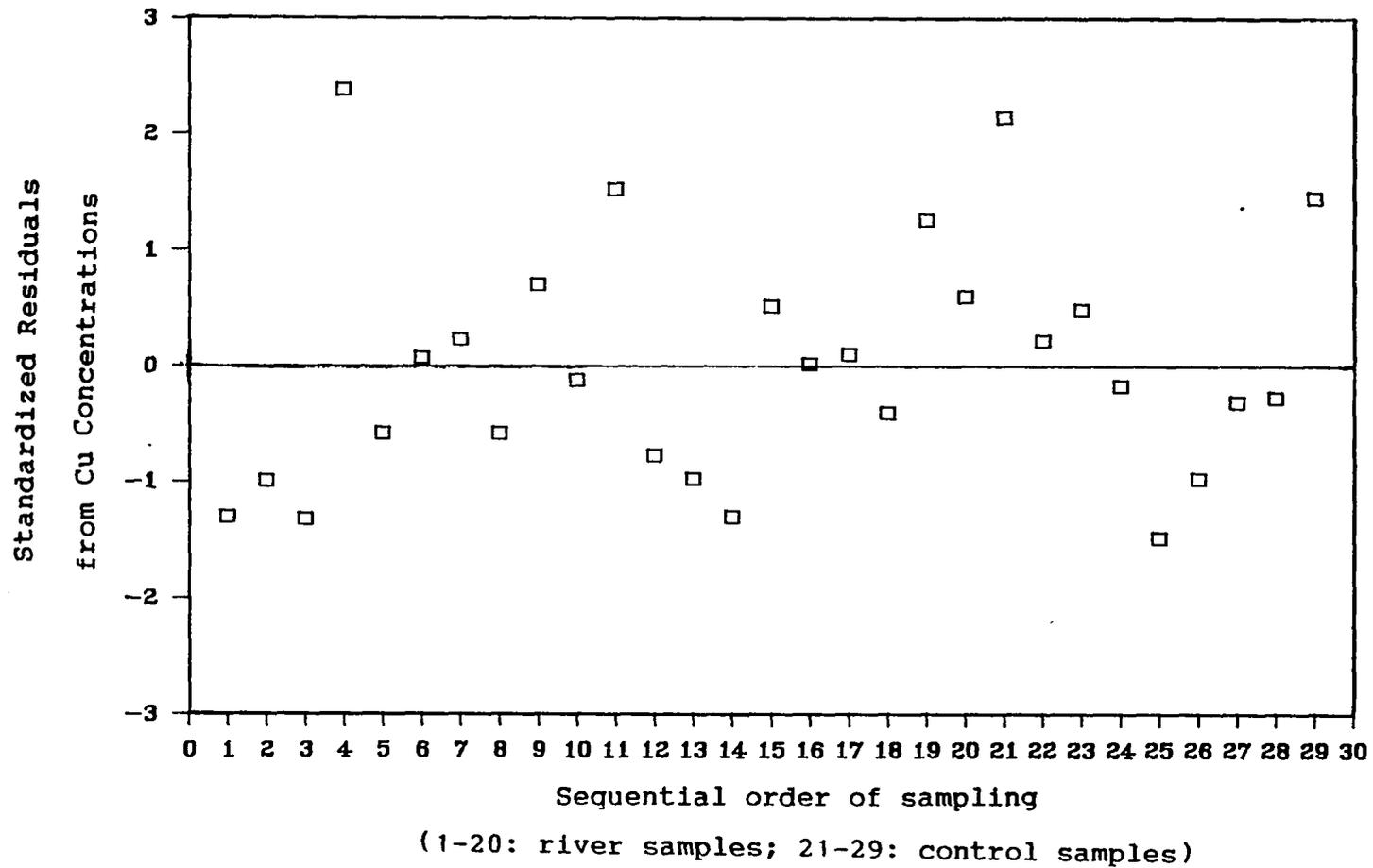


Figure 6. Standardized residuals of copper concentration from surface samples plotted sequentially in downstream order of collection

concentration of surface and subsurface samples as well as for Cu concentration of subsurface samples displayed similar patterns of random distribution.

Graphs of sediment properties across transects and graphs of standardized residuals indicated that sediment properties in one sample location could not be predicted from sediment properties in any other location. Therefore, sample sites were considered to be independent of one another. From this point forward, individual samples along each transect rather than transect means will be used in analysis of these data. Values of n for the remainder of the analyses are 20 for river surface samples, 13 for river subsurface samples, 9 for control surface samples, and 2 for control subsurface samples.

Surface and subsurface Cu, Mn, and Zn concentrations were pooled separately for all Puerco River samples and for all control samples, for comparison of their differences. Table 6 shows mean metal concentrations for each data set. Standard errors within each grouping also are given in the table. T-tests were then used to determine if average metal concentrations were different in river sediments than in tributary (control) sediments. These tests revealed no significant difference between mean metal concentrations from river sediments and mean metal concentrations from control sites, either for surface or subsurface samples. Similarity of mean values for metal concentration of river

Table 6. Mean metal concentrations of sediments from Puerco River and tributary (control) locations

Layer	Metal	Location		Probability of significant difference
		River	Control	
Surface	Cu	6 ± 1 *	6 ± 1	0.83
	Mn	194 ± 14	209 ± 28	0.59
	Zn	33 ± 3	37 ± 3	0.45
Subsurface	Cu	8 ± 1	9 ± 4	0.93
	Mn	228 ± 22	245 ± 17	0.79
	Zn	40 ± 4	48 ± 12	0.52

* means plus or minus standard error

and control samples and the high standard errors associated with these means both contributed to insignificant differences between the means.

Metal concentration of surface and subsurface river sediments were then regressed on distance downstream from the spill site (Figure 7). Significance of the relationship was determined by a test of the hypothesis that regression coefficients differed from zero. Probability values for the t-tests:

	<u>Cu</u>	<u>Mn</u>	<u>Zn</u>
Surface	0.08	0.03	0.07
Subsurface	0.12	0.18	0.44

indicate that slopes of regression lines differed significantly from zero ($P < 0.10$) for surface but not for subsurface sediments. Regression equations, the significance of their regression coefficients, and the r^2 values for these equations were similar to those obtained from mean metal concentrations shown in Figure 5. In both Figures 5 and 7, metal concentration appears to increase as distance downstream from the spill site increases, despite high variation about regression. If sources of variation caused by confounding sediment properties could be identified, those properties may be used in a covariate analysis to reduce variation in analyses of adjusted metal

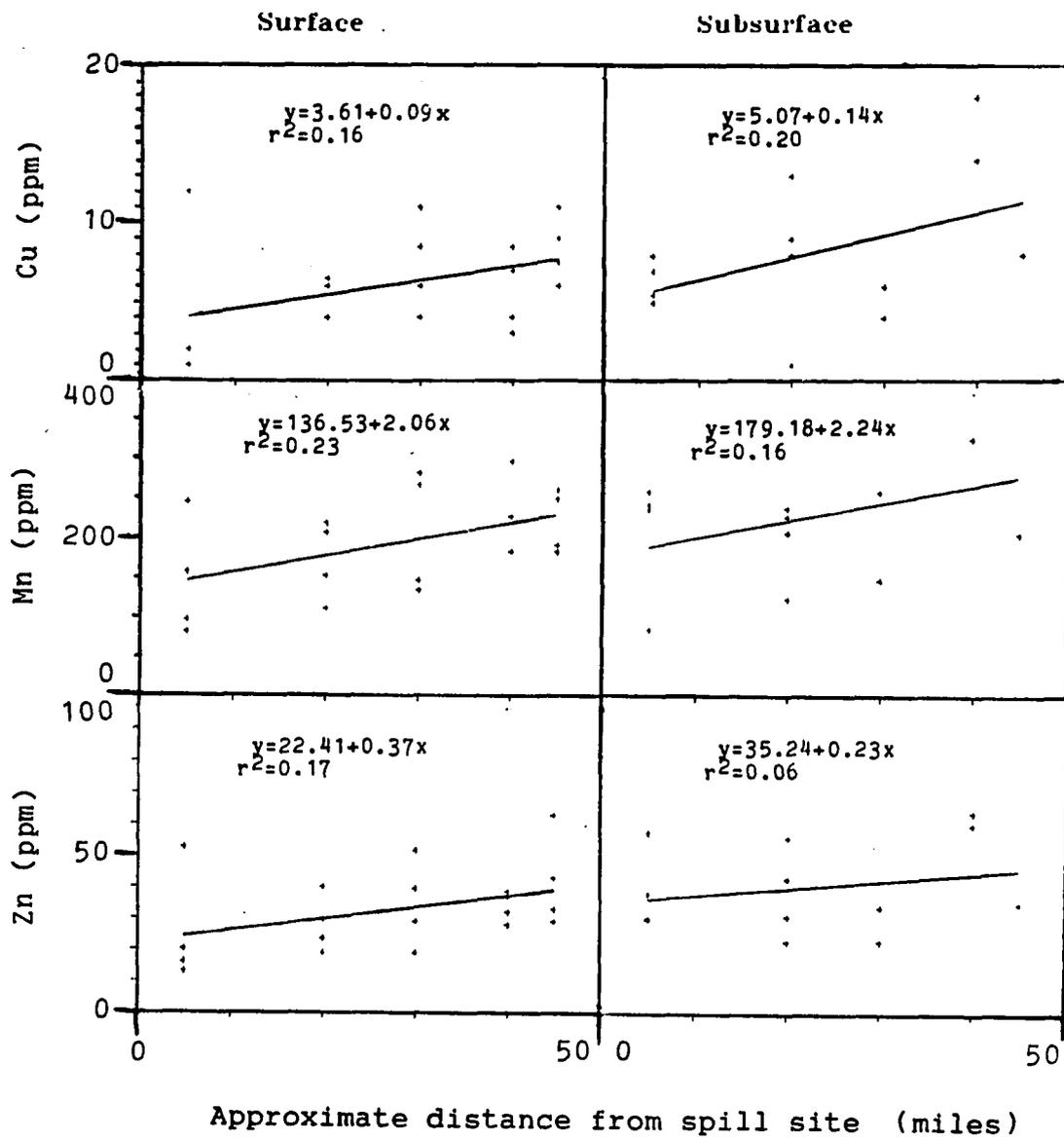


Figure 7. Relation between metal concentration of sediments and approximate distance downstream from spill

concentrations and possibly increase reliability of the resulting relations.

IDENTIFICATION OF CONFOUNDING VARIABLES

In an attempt to find those extraneous sediment properties upon which metal concentrations might be dependent, a search for sources of variation was pursued. Such confounding sediment properties might be used to adjust observed metal concentrations with a covariate analysis. Sediment properties that correlated highly with Cu, Mn, and Zn were identified as possible confounding variables. As discussed in the literature section, clay minerals, soil organic matter (SOM), total organic carbon (TOC), carbonates and other soil components have been correlated with metals.

The relation between amounts of various particle size fractions of the sediments and the concentration of Cu, Mn, and Zn was determined. Correlation of metal concentrations with amount in each size fraction declined as size fraction declined, as shown in the text table below:

<u>Size Fraction</u>	<u>Coefficient of Determination (r^2)</u>		
	<u>Cu</u>	<u>Mn</u>	<u>Zn</u>
<50um	.77	.51	.82
<15um	.50	.33	.61
<5um	.26	.17	.34
<2um	.18	.13	.21

Thus, Cu, Mn, and Zn were correlated best with the amount of <50um size fraction and most poorly with the amount of <2um clay fraction. These data indicate that the <50um size fraction of clay and silt may be a suitable covariate for adjusting observed values of Cu, Mn, and Zn, in an analysis of covariance.

Regression analysis was then used to reveal specifically how metals were related to the clay plus silt fraction (<50um) and to other properties of the sediment samples: % TOC, % SOM, and % carbonates. The regression of Cu, Mn, and Zn on these sediment properties (Figures 8 and 9) was linear and their slopes were significantly different from zero at $P < 0.05$. Manganese had lower correlation coefficients with these properties than Cu and Zn and the lowest correlation with TOC. Clay and silt showed the strongest relationship with all three metals tested, as indicated by high correlation coefficients. This set of analyses has shown that of TOC, SOM, carbonates, and clay and silt, none of which were controlled in sampling or in the regressions of Figure 7, all may be variables that contribute variation to observed values of Cu, Mn, and Zn.

Additionally, TOC, SOM, carbonates, and particle size were correlated with each other to determine which of these sediment properties would be most useful as covariates. Values of r^2 for the covariates with each other are presented in Table 7. Two sediment properties (e.g. SOM and

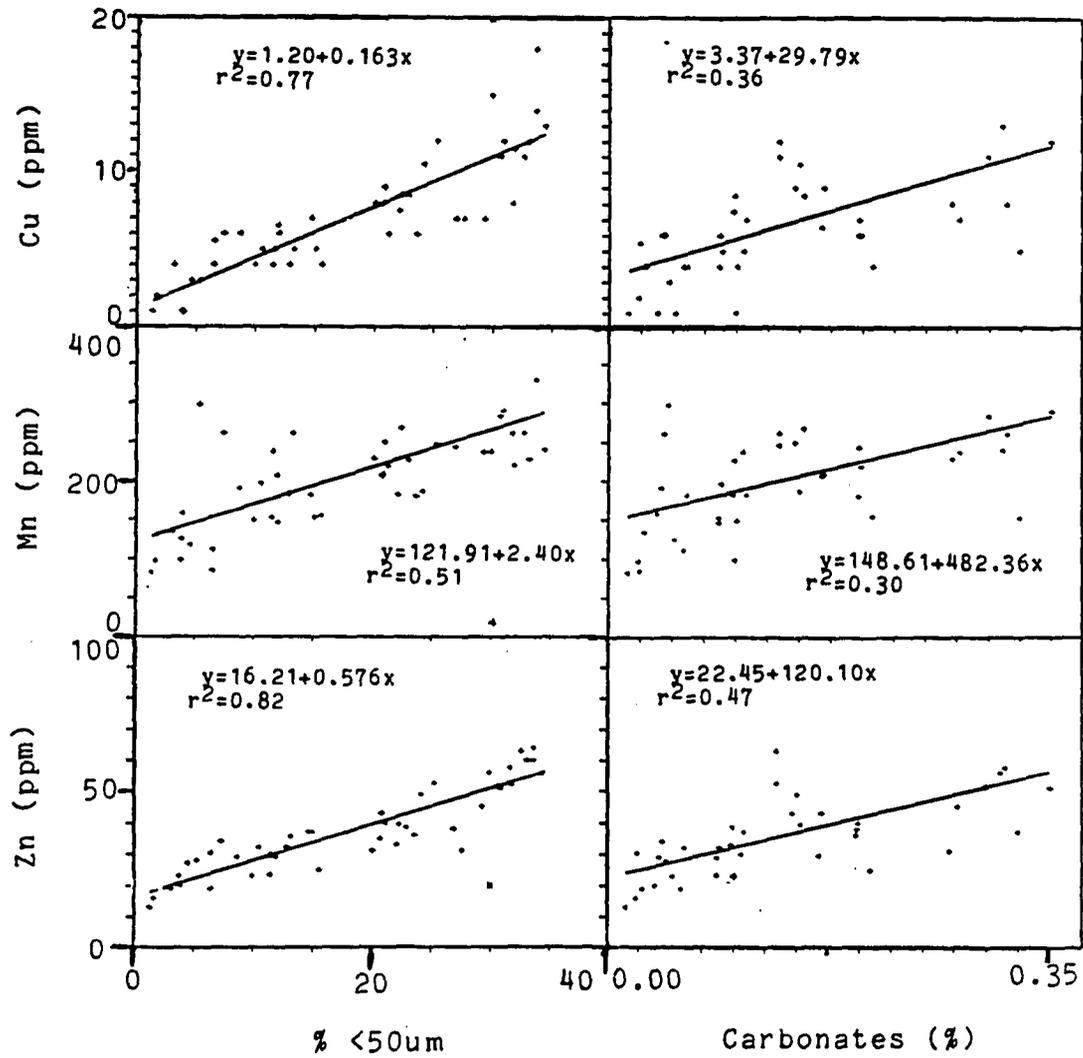


Figure 8. Relation between metal concentration of sediments and clay and silt particle size and carbonates

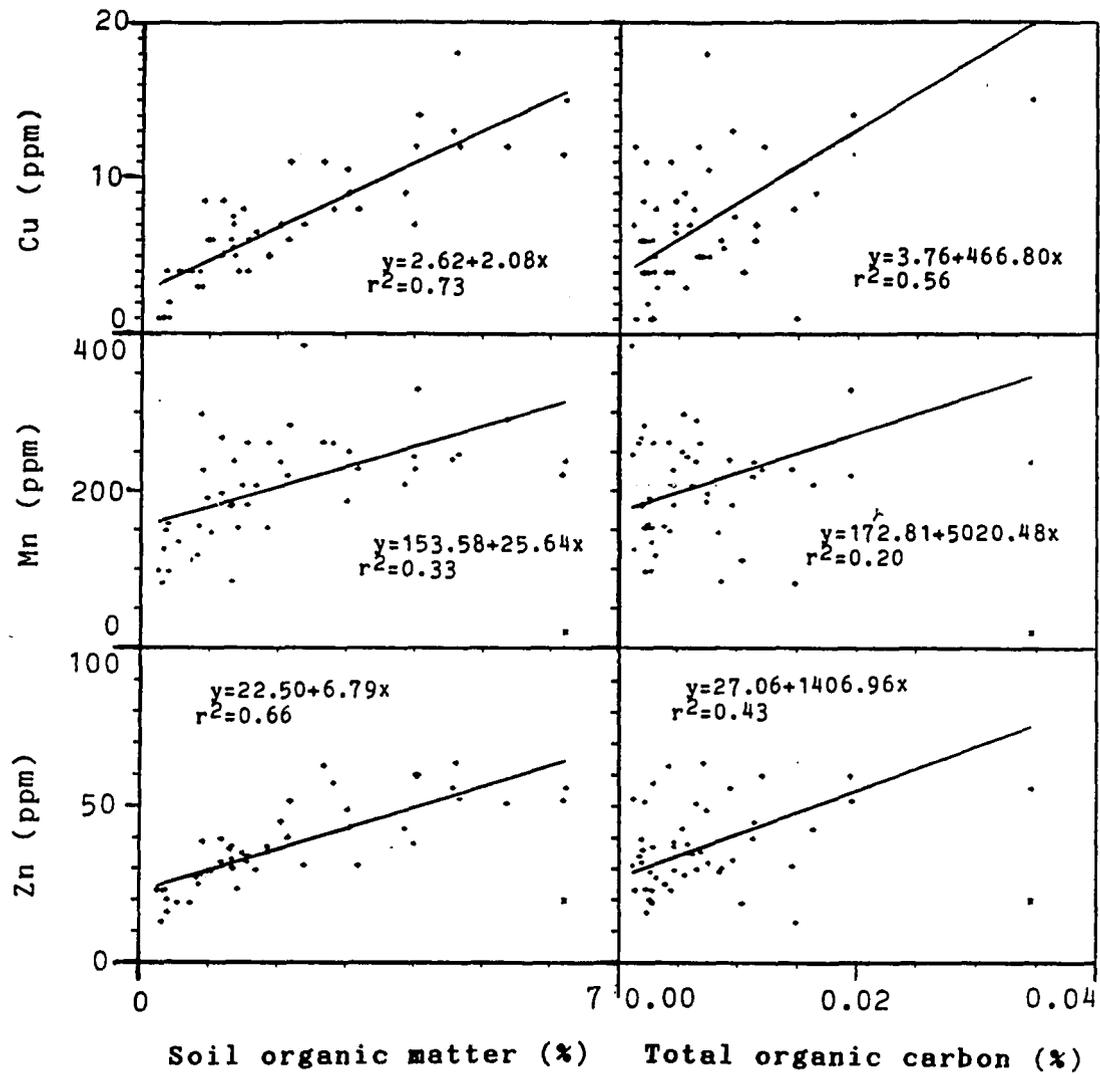


Figure 9. Relation between metal concentration of sediments and soil organic matter and total organic carbon

Table 7. Coefficients of correlation between soil properties that are potential covariates

	Clay plus silt	Total organic carbon	Soil organic matter	Carbonates
TOC	0.62	----	----	----
SOM	0.79	0.84	----	----
Carbonates	0.78	0.53	0.69	----

(Significant values: $r > 0.57$)

TOC, with a coefficient of correlation of 0.84) that are highly correlated with metal concentrations and also with each other might be measuring the same sediment properties. However, properties that show high correlation with metals and low intercorrelation (e.g., TOC and carbonates with a coefficient of correlation of 0.53) might be indicative of two distinct confounding variables, and hence may be more useful in a covariate analysis.

COVARIATE ANALYSIS

The sediment properties identified above as potential covariates were then used in covariate analyses to adjust observed metal concentrations of samples. Covariate analyses were executed with a computer model that adjusted the observed metal concentrations for the partial effects of various combinations of the potential covariates (Montgomery, 1984). The usual assumptions were made for the analysis of variance.

Results of the covariate analyses of observed values of Cu, Mn, and Zn with various combinations of the possible covariates, (for surface and subsurface samples separately) are shown in Tables 8-10. All four possible covariates were used in the first trial for each sample set. In subsequent trials, covariates with a non-significant regression coefficient in the first trial were removed from the

Table 8. Regression coefficients for copper with respect to partial effects of various combinations of covariates

Cu						
Layer	Analysis	Covariate	Regression coefficient	Sign. of regression coefficient (P<0.10)	R ²	
Surface	1	Clay + silt	0.11	0.00	0.86	
		TOC *	0.28	0.82		
		SOM **	0.94	0.22		
		carbonates	-2.58	0.04		
	2***	Clay + silt	SOM	0.11	0.00	0.86
			carbonates	0.99	0.00	
				-2.59	0.03	
	3	Clay + silt	TOC	0.13	0.00	0.83
			carbonates	2.21	0.05	
				-2.56	0.05	
	4	Clay + silt	carbonates	0.16	0.00	0.80
				-2.70	0.06	
Subsurface	1	Clay + silt	0.18	0.02	0.86	
		TOC	2.35	0.17		
		SOM	0.45	0.65		
		carbonates	-24.13	0.09		
	2***	Clay + silt	TOC	0.20	0.00	0.86
			carbonates	2.81	0.04	
				-23.79	0.08	
	3	Clay + silt	SOM	0.16	0.03	0.83
			carbonates	1.34	0.12	
				-25.20	0.09	
	4	Clay + silt	TOC	0.13	0.00	0.81
				2.87	0.05	
5	Clay + silt	carbonates	0.24	0.00	0.79	
			-24.55	0.11		
6	Clay + silt		0.17	0.00	0.74	

* Total organic carbon
 ** Soil organic matter
 *** Selected covariates

Table 9. Regression coefficients for manganese with respect to partial effects of various combinations of covariates

Layer	Analysis	Covariate	Mn		R ²
			Regression coefficient	Sign. of regression coefficient (P<0.10)	
Surface	1	Clay + silt	1.48	0.04	0.65
		TOC *	11.91	0.78	
		SOM **	7.05	0.60	
		carbonates	115.20	0.01	
	2	Clay + silt	1.53	0.03	0.65
		SOM	9.38	0.36	
		carbonates	114.71	0.01	
	3	Clay + silt	1.61	0.02	0.64
		TOC carbonates	26.38 115.34	0.43 0.01	
	4***	Clay + silt	1.96	0.00	0.63
		carbonates	113.68	0.01	
	Subsurface	1	Clay + silt	1.51	0.49
TOC			17.69	0.74	
SOM			7.94	0.81	
carbonates			-0.60	1.00	
2		Clay + silt	1.85	0.25	0.47
		TOC carbonates	28.85 5.42	0.52 0.99	
3		Clay + silt	1.39	0.50	0.47
		SOM carbonates	14.66 -8.58	0.55 0.98	
4		Clay + silt	1.86	0.06	0.47
		TOC	25.84	0.50	
5		Clay + silt	2.25	0.13	0.45
		carbonates	-1.49	1.00	
6***		Clay + silt	2.24	0.01	0.45

* Total organic carbon
 ** Soil organic matter
 *** Selected covariates

Table 10. Regression coefficients for zinc with respect to partial effects of various combinations of covariates

Layer	Analysis	Covariate	Zn		R ²
			Regression coefficient	Sign. of regression coefficient (P<0.10)	
Surface	1	Clay + silt	0.51	0.00	0.89
		TOC *	0.62	0.88	
		SOM **	2.59	0.05	
		carbonates	-14.59	0.00	
	2***	Clay + silt	0.51	0.00	0.89
		SOM	2.71	0.01	
		carbonates	-14.62	0.00	
	3	Clay + silt	0.56	0.00	0.88
		TOC	5.95	0.09	
		carbonates	-14.54	0.00	
	4	Clay + silt	0.64	0.00	0.86
		carbonates	-14.92	0.00	
Subsurface	1	Clay + silt	0.64	0.01	0.85
		TOC	2.38	0.67	
		SOM	0.20	0.95	
		carbonates	-36.25	0.43	
	2	Clay + silt	0.65	0.00	0.85
		TOC	2.59	0.54	
		carbonates	-36.10	0.40	
	3	Clay + silt	0.63	0.01	0.84
		SOM	1.11	0.66	
		carbonates	-37.33	0.39	
	4	Clay + silt	0.54	0.00	0.84
		TOC	2.68	0.52	
	5	Clay + silt	0.69	0.00	0.84
		carbonates	-36.79	0.38	
	6***	Clay + silt	0.58	0.00	0.83

* Total organic carbon

** Soil organic matter

*** Selected covariates

equation and the R^2 (multiple correlation coefficient) was examined for change in magnitude. If the R^2 did not change substantially in magnitude, the non-significant covariate from the previous trial was omitted from the analysis. This process was continued with the remaining covariates until a substantial change in R^2 was observed. The models with the highest R^2 and the fewest covariates, all of which had significant regression coefficients, were selected. For surface samples, clay and silt, SOM, and carbonates fit the criteria of the best covariates for Cu and Zn from surface samples, while clay and silt, and carbonates were the best covariates for Mn. For subsurface samples, clay and silt, TOC, and carbonates were the best covariates for Cu, while clay plus silt alone was the best covariate for Mn and Zn.

ANALYSIS OF ADJUSTED DATA

Means of the adjusted metal concentration values and their standard errors are shown in Table 11. These means remained fairly similar to means of observed metal concentrations (Table 6) for river and control samples. Standard errors decreased slightly for Mn from those for the means of observed metal concentrations (Table 6). T-tests showed that means of adjusted metal concentrations from Puerco River samples were not significantly different from means of controls, with one exception. The mean adjusted Mn

Table 11. Mean adjusted metal concentrations of sediments from Puerco River and tributary (control) locations

Layer	Metal	Location		Probability of significant difference
		River	Control	
Surface	Cu	6 ± 1 *	7 ± 1	0.31
	Mn	185 ± 10	230 ± 23	0.04
	Zn	33 ± 3	37 ± 4	0.40
Subsurface	Cu	8 ± 1	9 ± 4	0.81
	Mn	229 ± 14	242 ± 45	0.73
	Zn	41 ± 4	44 ± 12	0.73

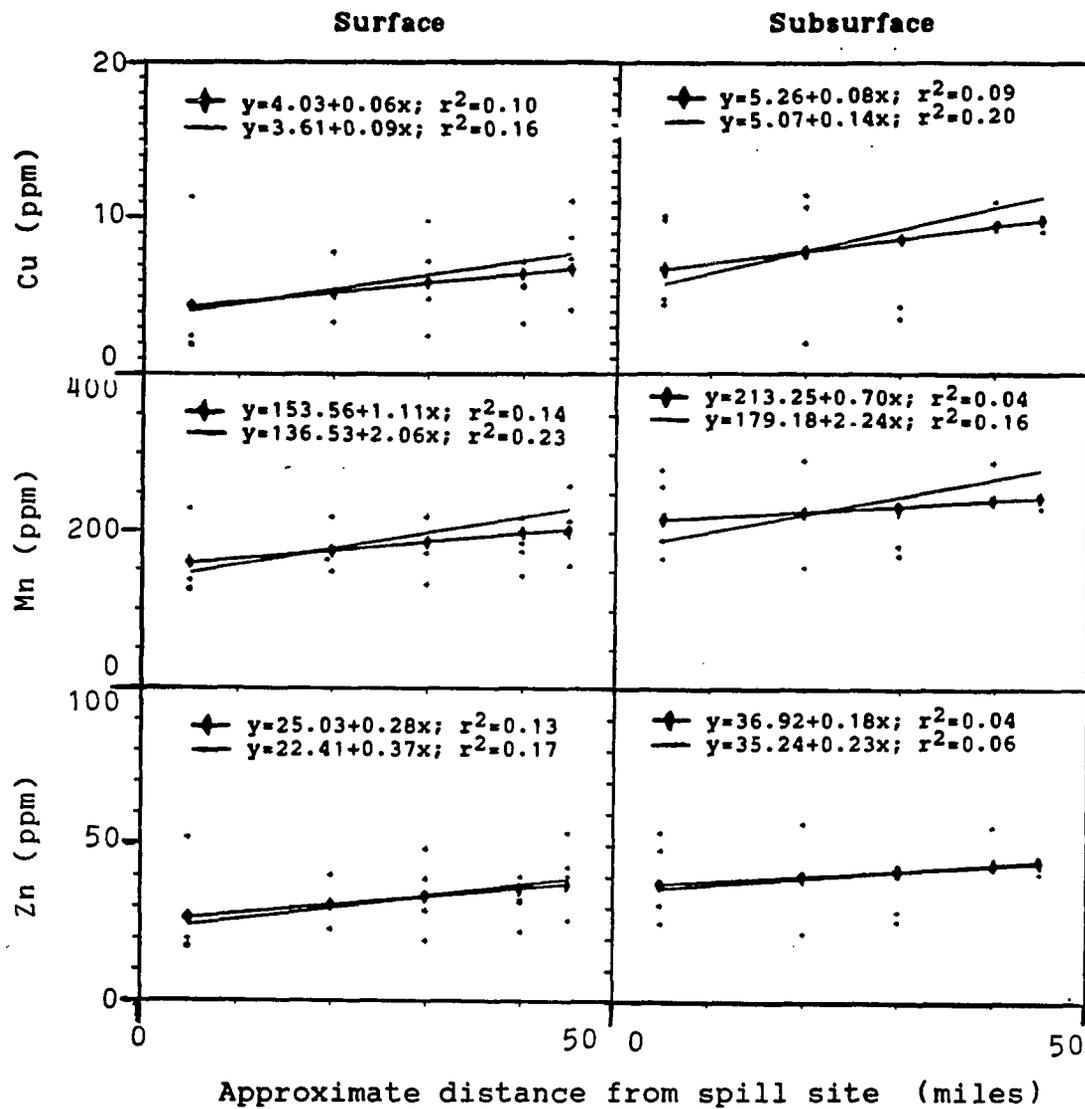
* means plus or minus standard error

concentration of river surface sediments was significantly less ($P < 0.05$) than that for control sites (Table 11). The reason for this significant difference is unknown.

Adjusted metal concentrations regressed on approximate distance downstream are shown in Figure 10. Significance of the relationship was determined by a test of the hypothesis that regression coefficients differed from zero. Probability values for the t-tests:

	<u>Cu</u>	<u>Mn</u>	<u>Zn</u>
Surface	0.17	0.10	0.13
Subsurface	0.32	0.52	0.52

indicate that slopes of regression equations representing adjusted surface and subsurface metal concentrations were not significantly different from zero ($P < 0.10$). However, the regression coefficients of equations for observed surface metal concentrations were significantly different from zero ($P < 0.10$). Ordinarily, the slope of the regression line for adjusted data is expected to match that of the regression for observed data; i.e. the adjustment procedure is not expected to change the slope or intercept of the equation. Therefore, the regression lines from adjusted and observed data should be further compared with each other. This was done by a test of the hypothesis (t-test) that regression coefficients for equations with observed and adjusted data



◆ Regression lines from adjusted metal concentrations
(plotted points are adjusted metal concentrations)

— Regression lines from observed metal concentrations

Figure 10. Relation between adjusted metal concentration of sediments and approximate distance downstream from spill site.

were equal. As expected, regression coefficients for observed metal concentrations on distance did not differ from those for adjusted metal concentrations ($P < 0.10$).

Returning to the regression lines themselves, those for adjusted metal concentration on distance showed more variation about regression and lower r^2 values than those for observed metal concentrations. This is not the result that is usually expected from the adjustment procedure. Ordinarily, a decrease in variation about regression and an increase in r^2 values is expected. This increase in variation and decrease in r^2 values accounts for the lack of significant difference from zero of the regression coefficients from regression lines of adjusted metal concentrations. However, since these regression lines did consistently show slightly lower slopes than those for observed metal concentration on distance downstream, further analysis was pursued to determine what characteristics of the covariates may have led to increased variation. The first step was to determine whether or not the covariates themselves showed a detectable relation with distance downstream. For surface samples, the amount of clay and silt, SOM, TOC, and carbonates each were plotted on distance downstream (Figure 11). Of these only the clay and silt particle size fraction showed a regression coefficient that was significantly different from zero ($P < 0.10$).

Covariates were assumed to be randomly distributed with

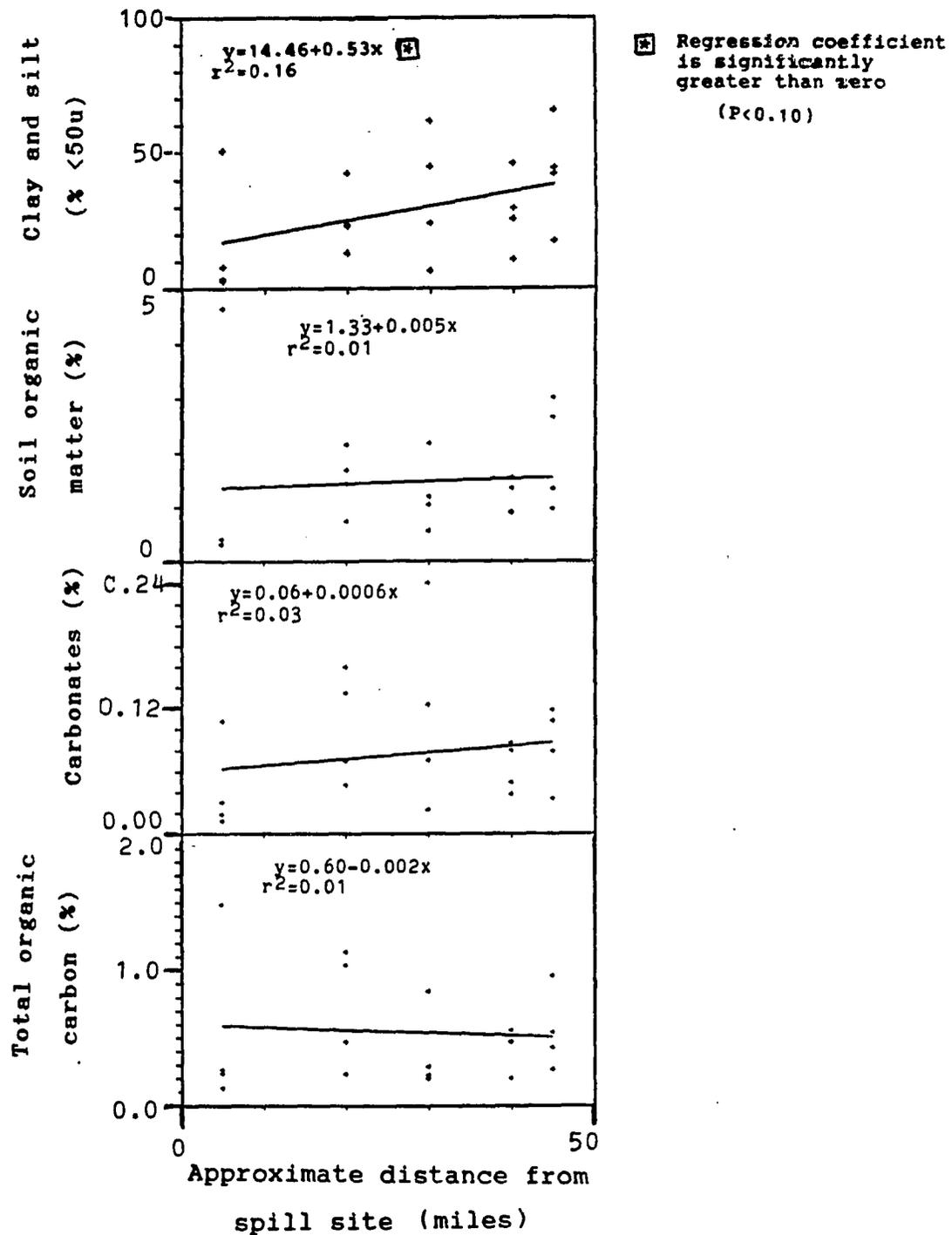


Figure 11. Relation between covariates and approximate distance downstream from spill site for surface samples.

respect to distance for the covariate analyses executed in this study, but clay and silt concentration increased downstream. Therefore, the decrease in regression coefficients for adjusted metal concentrations was due to the functional relationship that the covariate (clay and silt) had to distance downstream. Thus, the covariate analyses may have overcorrected the observed data, producing higher and lower values of clay and silt. This overcorrection caused slopes for regression lines from adjusted metal concentrations to be lower than those for regression lines that would have been obtained had the covariates been randomly distributed. Such a covariate analysis should yield regression lines for adjusted metal concentrations with regression coefficients that are closer to those for regression lines of observed metal concentrations and with lower r^2 values than those obtained here (Figures 7 and 10). This type of complex adjustment is unnecessarily cumbersome and no significant change in results would be expected.

Thus, two possibilities are available: adjusted metal concentrations can be left intact, or they can be re-adjusted to reflect the problem of the functional relationship that the covariate (clay and silt) has to distance downstream. This study presents the first option (leaving the adjustments intact) because of the difficulty alluded to above involved in attempting such a complex re-

adjustment. In both cases, the slopes of the regression lines from adjusted data decrease relative to the slopes of regression lines from observed data, though in the case chosen slopes have decreased slightly more than they would have under the second scenario, with properly re-adjusted data.

Because clay and silt as well as metal concentration are functionally related to distance downstream, this in large measure explains why Cu, Mn, and Zn, which are bound to clay and silt, are present in higher quantities downstream than near the spill site. Covariate analyses removed the confounding influence that clay and silt had on metal concentration by partially correcting for the positive relationship that clay and silt had to distance downstream.

DISCUSSION

MOVEMENT OF METALS

The data show that there is an increase in Cu, Mn, and Zn concentrations in Puerco River sediments downstream from the 1979 spill site. However, none of the Puerco River sediments tested had significantly higher mean metal concentrations than the control sediments tested, even though the spill introduced tons of heavy metals and radionuclides into the watercourse. High correlations were detected between metal concentration and organic matter, clay and silt, and carbonates. Where did the heavy metals and radionuclides spilled in 1979 go? One answer lies in understanding the mechanisms of sediment transport in streams like the Puerco River, recalling the correlation between the metals and sediment properties.

According to the ADHS Sediment Loading Model, elements from the spill event may have bound with sediments in the stream bed and settled near the source of the spill.¹² Clay and silt particles of less than 50um, with metals adsorbed

12. Arizona Department of Health Services. Water quality study: Puerco River, Arizona (Draft Report). Ambient Water Quality Unit, Water Assessment Section, Office of Emergency Respose and Environmental Analysis. Pheonix, Arizona. December, 1985.

to them at all but very low pH, could then have been scoured from the streambed in numerous hydrologic events and moved downstream along with unbound tailings solids or slimes. Thus, over time, metals may have been dispersed among sediments in the Puerco River, deposited in high concentrations in some areas of the Puerco River, carried downstream over one hundred miles to the Little Colorado River, or passed along in some combination of the above. Further, distribution patterns may have been complicated by airborne transport of particles with metals sorbed to them by wind and "dust devils" out of the stream channel or by faulty tertiary treatment at the Gallup Wastewater Treatment Plant, which may have increased concentrations of metals downstream from Gallup.¹³

Nevertheless, applying the ADHS model provides valuable background explanations for the adsorption process. As the tailings solution was diluted and neutralized (the sediment samples in this study had a fairly constant pH of 7.5 to 8.2), dissolved metals were precipitated and sorbed to negatively charged particles. In the case of the 1979 spill two distinct classes of metals are at issue, due to the low pH of the tailings solution and the large amount of solids

13. Shuey, Chris. 1987. Personal Communication. Southwest Research and Information Center. Albuquerque, New Mexico.

spilled. The first class consists of metals that were actually dissolved in the highly-acidic tailings solution and leached into the subsurface of the riverbed. The second class consists of metals that remained on the surface as solids, including those that were not dissolved in the tailings solution and those that precipitated out of solution on or near the surface of the stream channel after the spill. Separate though related pathways for dissolved and precipitated elements contributed to the correlations between metal concentration and other sediment properties that were highlighted by statistical analyses in this study.

The first pathway, for the dissolved materials in the tailings solution, postulates a scenario in which the infiltrating solution saturated a specific layer of alkaline riverbed sediments, becoming less acidic in the process and precipitating elements out of solution. As sediments neutralized a portion of the solution at each layer, they became saturated. The remainder of the solution flowed deeper into the riverbed, taking dissolved elements with it. Since some of the elements dissolved in the tailings solution precipitated out at various depths in the riverbed, this helps to account for the absence of large amounts of metals found in Puerco River bankfull-channel sediments. The second class of materials, comprised of originally undissolved metals and metal precipitates from the neutralized tailings solution, remained on or near the

surface of the riverbed, available for transport downstream by the hydrologic mechanisms outlined above.

Transport of sediments and metals in the river affects the quality of the water. High amounts of suspended sediments in Puerco River water have been correlated with elevated levels of heavy metals, as discussed in the literature. Heightened levels of suspended sediment in ephemeral streams tend to occur in the first flush of water into the channel during a rainstorm and in the sluggish water remaining in the channel after flow has decreased (Forstner and Prosi, 1979). Therefore, potential downstream users of river water with large amounts of suspended sediments may be affected over time by high amounts of heavy metals bound to the suspended sediments.

Inspection showed that the subsurface samples had, overall, higher percentage clay and silt, higher organic matter, and higher concentrations of trace metals than the surface samples (Appendix). This is probably due to the criterion used for selecting subsurface samples (i.e. samples collected from visible clay layer). In contrast, the surface samples were only selected by location, so subsurface samples tended to have a higher percentage of clay and silt and other properties associated with clay and silt than surface samples.

IMPROVED EXPERIMENTAL DESIGN

The most obvious fault of this study stems from the shortage of data. A better experimental design, with a larger data set, might have yielded different results. The following improvements upon the experiment should decrease variations in the data, perhaps influencing the question of whether there is any statistically significant difference between metal concentrations in river and control sediments:

a) Many randomly selected subsamples should be taken to provide one representative sediment sample for each transect, since deposition of particle sizes varies across a transect.

b) Many more randomly selected sites should be sampled to present a more coherent distribution pattern to model the river.

c) Sediment samples should be taken as deep cores to measure concentration of elements within each sediment layer of the sediment profile. The highly acidic tailings spill, with many elements dissolved in it, may have infiltrated into the riverbed to some depth, with the depth function of concentration influenced by several factors.

d) Water, when available, should be tested along with sediments at each transect, to determine concentrations of elements infiltrating through the sediments. Plants should be tested to determine if they are taking up radionuclides

in amounts that might affect the food chain.

e) Radionuclides, as well as other elements that were present in the tailings solution and mining effluents, should be studied. Concentration and location of radionuclides, sulfates, and heavy metals should be investigated, since the fate of the large amounts of toxic elements spilled in 1979 remains unknown.

f) Effluent from the Gallup wastewater treatment plant should be tested to ascertain the contribution of the effluent to elements in the arroyo.

g) Some terraces on the river may be useful as controls. These sites should have been exposed to as few of the treatments that the river was exposed to as possible, while mimicking natural conditions of the river as closely as possible. In contrast, some of the tributaries used as controls were previously exposed to mine wastewater from other sources, even though they were not exposed to the major event of the 1979 tailings spill.

Metal concentrations may be dependant upon many more factors than the parameters tested here, such as the effects of the numerous hydrologic events that have occurred since 1979. In particular, the tailings spill occurred eight years before the samples were taken; numerous storm events probably have dispersed metals and radionuclides over a large area. Likewise, dewatering ceased six months before the samples were taken; rainstorms have brought sediment

down the river since dewatering ceased. Although sampling sediment cores might alleviate the confounding effects of numerous hydrologic events by testing layers of sediment from various deposition events, the effects of specific rainstorm events cannot be taken into account.

CONCLUSION

Observed Cu, Mn, and Zn values from surface samples showed increased concentrations with distance downstream from the site of the 1979 UNC tailings spill. Metal concentrations of each sample varied with percentage SOM, TOC, carbonates, and clay and silt particle sizes. A random distribution of the covariates (sediment properties) was assumed for the covariate analysis that was used to adjust the observed metal concentrations. However, this assumption turned out to be false with respect to clay and silt distribution. Further investigation revealed that amount of clay and silt was increasing with distance downstream in proportion to metal concentration, as might have been expected, due to the relationship caused by the binding of the metals to clay and silt outlined previously. The resulting overcorrection did not, however, invalidate the adjusted metal concentrations.

APPENDIX A

MEASURED VALUES OF SEDIMENT SAMPLE VARIABLES

Layer	Transect	Cu	Mn	Zn	Clay and Silt (<50u)	TOC *	SOM **	Carbonates
		ppm						
Surface	1	2	97	16	3.5	0.24	0.41	0.019
		1	158	20	8.0	0.27	0.41	0.031
		1	82	13	2.8	0.13	0.32	0.012
	2	12	247	53	50.8	1.49	4.66	0.108
		6	219	40	42.5	1.14	2.16	0.160
		7	208	30	23.9	1.04	1.69	0.135
	3	4	111	19	13.1	0.23	0.74	0.047
		4	153	24	23.0	0.47	1.43	0.070
		11	283	52	61.5	0.85	2.18	0.240
	4	9	268	40	44.8	0.29	1.19	0.123
		6	147	29	24.0	0.23	1.04	0.070
		4	134	19	6.4	0.20	0.56	0.023
	5	7	183	37	29.5	0.47	1.35	0.087
		9	227	39	46.0	0.56	0.92	0.080
		3	298	28	10.8	0.20	0.90	0.038
	6	4	183	32	25.8	0.48	1.56	0.049
		11	262	63	65.5	0.96	2.67	0.108
		8	183	33	44.3	0.54	1.34	0.079
	7	6	191	29	17.5	0.27	0.98	0.034
		9	250	43	42.0	0.43	3.05	0.118
		11	187	49	48.5	0.75	3.02	0.121
	8	5	153	37	30.2	0.30	1.86	0.260
		7	197	32	21.2	0.29	1.19	0.072
		1	98	23	7.7	0.12	0.26	0.080
	9	7	385	31	55.3	0.75	2.39	1.301
		4	155	25	31.3	0.21	0.86	0.167
		6	181	36	47.3	0.40	1.31	0.158
Subsurface	1	12	290	51	62.0	1.15	5.35	0.280
		7	237	45	58.8	0.66	2.05	0.222
		8	261	58	63.5	0.87	2.82	0.252
	2	6	85	30	13.1	0.59	1.34	0.020
		5	238	30	23.2	0.30	1.37	0.085
		7	244	38	54.0	0.66	4.00	0.158
	3	1	125	23	7.8	0.15	0.34	0.042
		8	229	31	40.2	1.46	3.18	0.217
		13	240	56	69.0	0.94	4.56	0.249
	4	9	209	43	41.8	1.64	3.86	0.136
		4	149	23	20.0	0.18	0.38	0.081
		6	261	34	14.8	0.45	1.57	0.035
	5	18	390	64	67.5	1.95	4.60	0.159
		14	329	60	67.5	0.72	4.05	0.229
		8	207	35	41.5	0.62	1.49	0.078
	6	12	228	60	66.3	1.21	4.02	0.185
		5	261	36	26.5	0.69	1.88	0.152

* Total organic carbon

** Soil organic matter

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