Long-term monitoring of the geochemistry of surface water and stream-sediment samples from the Upper Pecos Wilderness to Brantley Dam, north of Carlsbad, eastern New Mexico: Year nine

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LONG-TERM MONITORING OF THE GEOCHEMISTRY OF SURFACE WATER AND STREAM-SEDIMENT SAMPLES FROM THE UPPER PECOS RIVER, FROM THE SOUTHERN PECOS WILDERNESS TO BRANTLEY DAM, NORTH OF CARLSBAD, EASTERN NEW MEXICO: YEAR NINE

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Abstract.—Since reclamation of the Pecos mine waste piles, area roads and campgrounds, and the Alamitos Canyon mill area began in 1990-1991, there has been continued monitoring of base metals and trace element concentrations in stream sediments along the Pecos River, extending from the upper Pecos River to below Brantley Dam, north of Carlsbad. In 1992, 1996, and 2000, water and stream sediments were sampled and analyzed for the entire reach. Between 1992-1996, the upper reach of the river between the Pecos Wilderness and Villanueva was sampled on eight occasions as part of a multi-disciplinary study. Five areas of concern included the Pecos mine waste pile (a volcanogenic massive-sulfide deposit containing Pb, Zn, Cu, Ag, and Au), the Alamitos Canyon mill tailings (El Molino site 18 km south of the mine), roads and campgrounds north of Terrero (mine waste material from the Pecos mine waste pile was used as fill), and the Lisboa Springs Fish Hatchery (where several fish kills in 1991-1995 have been attributed to drainage from the mine site and contaminated campground sites). Geochemical analyses of surface-water samples indicate that drainage from the Pecos mine is not significantly affecting the composition of the surface water in the area, except in the immediate vicinity of the mine and mill site. Elevated concentrations of Cu, Pb, Zn, and Cd occurred in stream sediments below both the Pecos mine and Alamitos Canyon mill sites, before reclamation began. Collectively, multi-disciplinary studies suggest that Cu, Pb, Zn, and other metals were eroded and leached from the Pecos mine waste pile and the tailings piles in Alamitos Canyon. These geochemical trends confirm a decrease in concentrations with time since reclamation began, especially in the immediate vicinity of the Pecos mine (where Cu levels decreased from 310 to 92 ppm; Cd from 17 to 4.7 ppm; Pb from 300 to 160 ppm; and Zn from 3100 to 2080) and below the confluence of Alamitos Creek (Cu decreased from 270 to 30 ppm; Pb from 590 to 93 ppm; and Zn from 990 to 287 ppm). The overall metal concentrations dramatically decrease in stream sediments below Pecos Village, mostly due to dilution of sediment derived from the red bed sedimentary units.

INTRODUCTION

Water quality of the Pecos River has regional and international concerns as the population in eastern New Mexico increases (Fig. 1). The Pecos mine and Alamitos Canyon mill in the upper Pecos River area had been identified by state and federal agencies as point sources for metals contamination for Pb, Zn, Cu, Al, Se, Cd, and Cr (Fig. 2, 3; Johnson and Deeds, 1995a, b). Material from the mine waste pile had been used as fill in the campgrounds and roads north of Terrero and these areas had been also identified as point sources for metal contamination. Furthermore, the Lisboa Springs Fish Hatchery (New Mexico Game and Fish Department) experienced several fish kills from March 1991 through 1995 that may be attributed to contamination from the Pecos mine. Reclamation of the campgrounds, roads, and Alamitos Canyon mill site began in the early 1990s and is nearly completed. Reclamation of the Pecos mine began in 1999 and is on going. The Lisboa Springs Fish Hatchery closed, temporarily, in 2000 because the fish were diagnosed with Whirling disease, which is not related to the metals contamination from the Pecos mine.

In September 1992, the New Mexico Bureau of Geology and Mineral Resources (NMBGMR) personnel sampled and analyzed surface water and stream sediments from the Pecos River at sites near the Pecos Wilderness boundary southward to below Brantley Lake, north of Carlsbad (McLemore et al., 1993). Subsequently, the U.S. Bureau of Reclamation, in cooperation with the New Mexico Institute of Mining and Technology (NMIMT) and NMBGMR, initiated a three-year multi-disciplinary study of the headwaters of the Pecos River (Pecos Wilderness boundary to Villanueva) in order to identify and prioritize point and

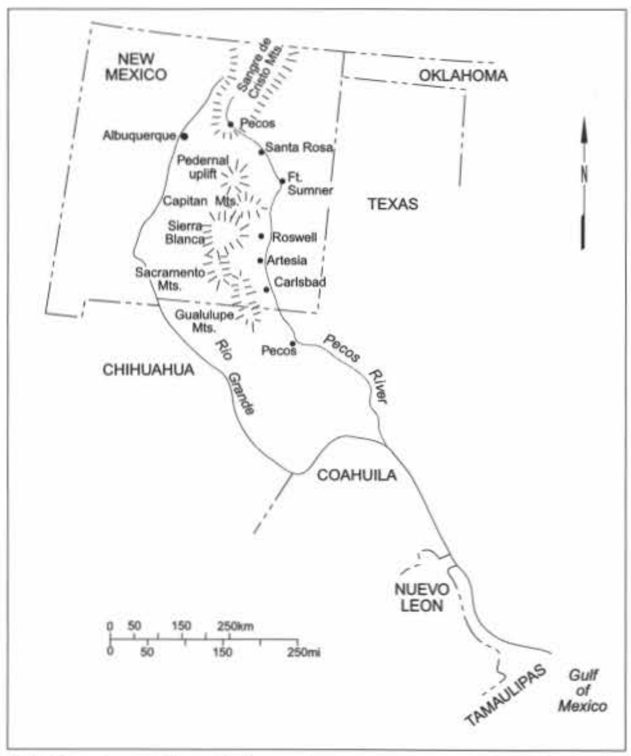
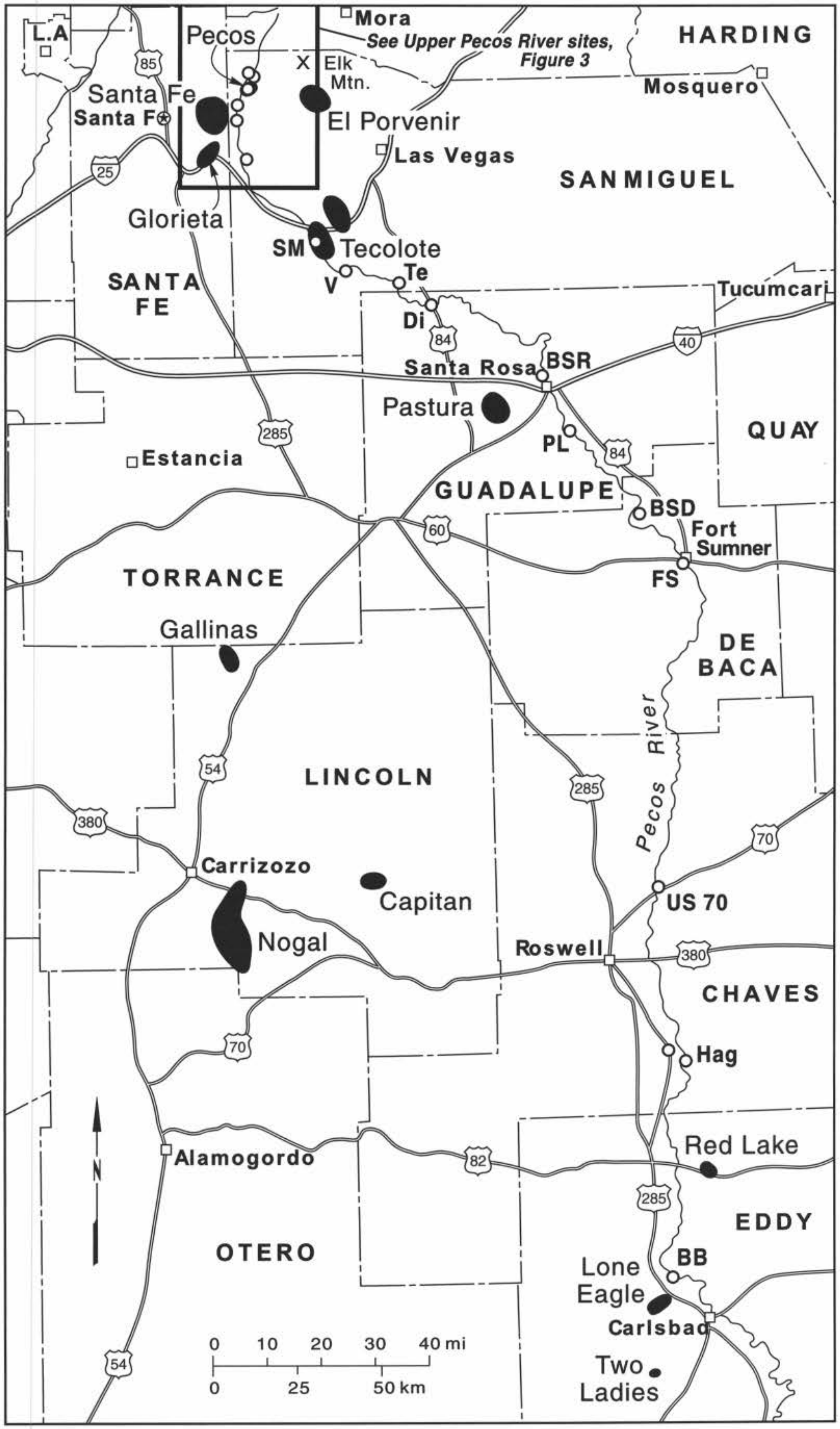


FIGURE 1. Pecos River drainage basin, eastern New Mexico and western Texas.

non-point sources of contamination so that measures could be taken to protect water supplies for municipal, irrigation, and recreational use and to protect wildlife habitat (Brandvold et



KEY TO SITES

Symbol	Description
SM	San Miguel
V	Villanueva
Te	Tecolotito
Di	Dillia
BSR	Below Santa Rosa Dam
PL	Puerto del Luna
BSD	Below Sumner Dam
FS	Fort Sumner
US 70	Highway U.S. 70 bridge
Hag	Hagerman
BBR	Below Brantley Dam

FIGURE 2. Location of sample sites and mining districts along the Pecos River, eastern New Mexico.

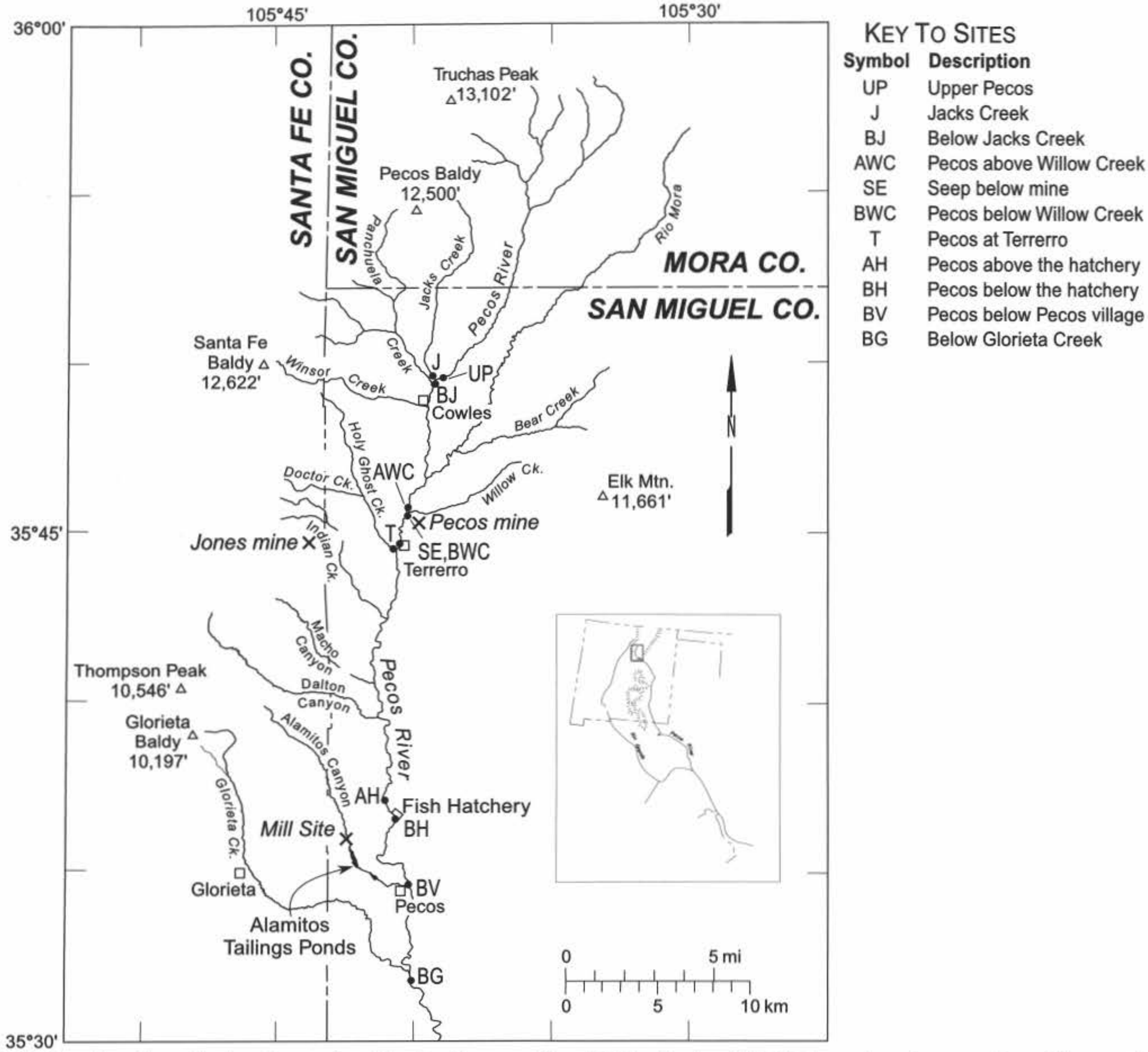


FIGURE 3. Location of sample sites, Pecos mine, Alamitos Canyon mill, and Lisboa Springs Fish Hatchery along the upper Pecos River, northeastern New Mexico.

al., 1995; Brandvold and McLemore, 1999; McLemore et al., 1995a, b; Popp et al., 1996). In September 1992, 1996, and June 2000, the NMBGMR sampled water and stream sediments from the entire Pecos River from the Pecos Wilderness southward to below Brantley Lake. This report presents a summary of the first nine sampling trips in 1992-1995 (McLemore et al., 1993; Popp et al., 1996) and presents new data from the sampling trips in 1996 and 2000 (Fig. 2, 3).

STUDY AREA

The study area covers the southern Pecos Wilderness to south of Brantley Lake and includes many tributaries and the main stem of the Pecos River. The headwaters of the Pecos River are in the southern Sangre de Cristo Mountains, with additional drainages from the Pedernal uplift, Capitan Mountains, Sierra Blanca, and Guadalupe Mountains (Fig. 1). Elevations range from 1000 to over 3600 m. The river flows southward through the towns and cities of Pecos, Santa Rosa, Fort Sumner, Roswell, Artesia, and Carlsbad into west Texas and finally enters the Rio Grande at the international border with Coahuila, Mexico (Fig. 1). The Pecos River flows through the Santa Fe National Forest and the Pecos National Historical Park (U.S. National Park Service) and four state parks. Water from the Pecos River is stored in three main reservoirs: Santa Rosa, Sumner, and Brantley Lake. Eastern New Mexico is predominantly a rural agricultural area, but the larger cities have some light industry. Petroleum and potash production is important in southeastern New Mexico near Artesia and Carlsbad. There is currently no metals mining within the Pecos drainage basin.

REGIONAL GEOLOGY

The geology of the Pecos River drainage basin is complex with rocks ranging in age from Proterozoic to recent. Lithologies are likewise diverse, ranging from metamorphic volcanic rocks to granites to syenites to shales, limestones, and sandstones (Anderson et al., 1994). Proterozoic rocks crop out along the upper Pecos River and several tributaries north of Pecos. The oldest rocks are mafic metamorphic and volcaniclastic rocks that comprise the Pecos greenstone belt. The most abundant Proterozoic rocks are the plutonic rocks that consist of granite, tonalite-trondjemite, gabbro, diabase, and ultramafic rocks. Overlying sedimentary rocks consist of Mississippian limestone, sandstone, and shale of the Arroyo Penasco Group (Espiritu Santo and Terrero Formations) and unconformably overlie the Proterozoic rocks. Pennsylvanian siltstones, sandstones, shales, thin coals, and limestones overlie the Mississippian and, locally Proterozoic rocks in the Pecos River area. The Pennsylvanian-Permian rocks consist of the Magdalena Group and the Sangre de Cristo Formation. Permian siltstones, limestones, and sandstones overlie the Pennsylvanian-Permian rocks and consist of the Yeso, San Andres, and Bernal Formations and Artesia Group. Triassic sandstones and shales crop out in the area south of Pecos and consist of the Chinle Group. Permian evaporites that comprise the Permian Basin section crop out south of Roswell. Quaternary rocks are found throughout the area and consist of Pleistocene to recent alluvial, terrace, and floodplain deposits.

Mining began in the late 1880s in the southern Sangre de Cristo Mountains (Harley, 1940; McLemore, 1995). The largest of these deposits is the volcanogenic massive-sulfide deposit containing Pb, Zn, Cu, Ag and Au at the Pecos mine in the Willow Creek district, which produced during 1902-1904, 1927-1939, and 1943-1944. The Pecos mine was the largest lead and zinc producer in New Mexico from 1927 to 1939 and was one of the top ten past producers of lead and zinc in New Mexico. Production from other deposits in the southern Sangre de Cristo Mountains is minor and insignificant (McLemore, 1995).

DESCRIPTION OF PECOS MINE WASTE PILE AND ALAMITOS CANYON TAILINGS PILE

The waste rock generated during mining activities was piled at the Pecos mine site and consists of several mine waste piles within an area of approximately 7.7 ha. Estimates of the volume of waste rock vary from 66,151 to 72,630 m^3 of material and it varies in thickness from 3.1 to 13.7 m. The waste pile is underlain by a layer of colluvial materials less than 5 m thick and consists of clay and sedimentary rock fragments (limestone, shale, sandstones; Johnson and Deeds, 1995 a, b). Mineralogically and chemically the mine waste pile is very heterogeneous (Tables 1, 2). The Pecos River flows less than 152 m west of the mine site and Willow Creek flows west along the northern edge of the mine waste pile.

Numerous discrete and diffuse seeps occur along the base of the mine waste pile. The number of seeps and amount of water flow varies according to storm events and snowmelt as well as yearly fluctuations in precipitation. During August 1994 many seeps were dry and the total amount of flow was lower than on previous visits in 1992 and 1993. White and brown precipitates or froths are present along the course of the seeps that drain into Willow Creek. X-ray diffraction and chemical analyses (Table 3; Popp et al., 1996) of the precipitates from the seeps indicated that they are a mixture of Fe, Cu, and Zn sulfates, and Fe and Al oxides and hydroxides including goslarite ($ZnSO_4 \cdot H_2O$). Chemical analyses of water samples from the seeps indicate a low pH and high total metals (Table 4; Berger et al., 2000). The main controls on pH of the water is controlled by reaction between the water from the mine waste piles and local bedrock (i.e. limestone) and mixing with water from Willow Creek (Berger et al., 2000). Neutral pH waters were collected from the Jones Hill mines (Table 4).

The ore was crushed at the mine and then transported by aerial tramway to the Alamitos Canyon mill (El Molino site) 18 km south

TABLE 1. Mineralogy of the ore deposits at the Pecos mine and vicinity, in order of perceived abundance (Stott, 1931; Krieger, 1932; Northrop, 1959; Fulp, 1982; Fulp and Rensaw, 1985; Popp et al., 1996). * Found on mine waste piles at Pecos mine (Popp et al., 1996).

Major Ore Minerals
*sphalerite ZnS
*galena PbS
*chalcopyrite CuFeS2
Minor Ore Occurrences
*bornite Cu5FeS4
tetrahedrite (Cu,Fe)12Sb4S13
native gold Au
argentite Ag2S
proustite Ag3AsS3
Oxidized Minerals
*malachite Cu2CO3(OH)2
*azurite Cu3(CO3)2(OH)2
*angelsite PbSO4
*smithsonite ZnCO3
*chalcocite Cu2S
cerussite PbCO3
*chalcanthite CuSO4 _ 5H2O
Selected Gangue Minerals
*pyrite FeS2
*pyrrhotite Fe1-xS
*quartz SiO2
*chlorite (complex silicate)
*actinolite Ca2(Mg,Fe)5Si8O22(OH)2
*tourmaline (complex silicate)
*epidote Ca2(Al,Fe)2(Al,Si3,O12)(OH)
*Fe and Mn oxides
*arsenopyrite FeAsS
*biotite K (Mg,Fe)3AlSi3O10(OH)2
*fluorite CaF2
*kaolinite Al2Si2O5(OH)4
*sericite KAl2(AlSi3O10)(OH)2
*calcite CaCO3
Additional Minerals in the Jones Hill, Dalton Canyon and Macho Canyon Areas
molybdenite MoS2
scheelite CaWO4

TABLE 2. Chemical analyses of waste rock at the Pecos mine in ppm (* from S. M. Stoller Corp., 1993; — no data).

Element	*Average	*Standard deviation	*Maximum	*Minimum	*Number of samples	NMBMMR sample of Pecos mine piles (Pecos)
Cu	1,840	1,960	7,140	40	25	11,810
Pb	9,380	10,400	33,100	41.8	25	238
Zn	17,330	30,600	150,000	204	25	31,350
As	25	23	101	1	20	—
Cd	68	136	607	0.65	20	7.5
Hg	0.65	0.81	2.49	0.033	10	<0.10
Ag	10	11	32.6	0	20	—
Al	13,740	9,880	27,000	23	5	—
Fe	52,650	35,120	129,150	10,960	12	5.3
Co	18	14	59.5	3.2	13	—
Cr	18	13	52.4	2.4	20	—
Ni	12	6	23.3	1.7	13	29

TABLE 3. Chemical analyses of sediment and precipitate from seeps along the base of the mine waste pile at the Pecos mine. Samples were digested using agua regia and analyzed by FAAS (NMBMMR Chemistry laboratory). (— no analyses)

Lab No.	Sample name	Date collected	Cu ppm	Pb ppm	Zn ppm	Cd ppm	Fe%
—	Seep 1 white	9/92	4,700	1,500	12,700	—	4.09
—	Seep 1 brown	9/92	1,000	600	12,000	—	4.9
360	Seep 1 (at pipe)	5/94	1,279	461	3,455	16	—
361	Seep 2 (at confluence with Willow Creek)	5/94	1,933	1,340	5,900	15	—
2523	Seep	6/93	1,630	490	38,000	31	—
—	Seep	7/7/93	680	310	70,000	40	—

TABLE 4. Chemical analyses of water samples from seeps at the Pecos and Jones Hill mines (in mg/L). Analyses by NMBMMR Chemical Laboratory. (— no analyses)

	SEEP 1 5/3/94	SEEP 2 5/3/94	SEEP 1 7/1/94	SEEP 2 7/1/94	UPPER JONES ADIT 5/3/94	LOWER JONES ADIT 5/3/94
pH	3.7	4.1	3.6	—	7.0	6.9
TDS	14,405	8,614	14,148	—	79	223
conductivity (umhos/cm)	11,000	7.7	10,300	—	139	312
HCO3	0	11	0	—	53	75
Cl	23	25	23	—	3.1	1.1
SO4	13,000	7,660	13,000	—	17	113
Na	11	25	9.8	—	1.1	5.4
K	13	11	5.1	—	2.1	2.5
Mg	950	475	800	—	7.2	14.5
Ca	380	400	310	—	14	40
Al	630	8.1	—	—	<1.0	1.1
Cd	16.5	8.6	15	0.06	<0.03	<0.03
Co	2.1	1.2	1.5	0.39	<0.03	<0.50
Cu	80	35	65	0.07	<0.10	0.14
Fe	1.2	0.38	2.7	0.24	0.13	0.7
Pb	1.3	0.04	0.8	<0.002	0.022	0.017
Mn	27.8	18.4	45	1	<0.10	<0.10
Hg (ppb)	1.5	<1.0	—		1.5	<1.0
Si	28	12	—	10	5.4	8.1
Zn	19,500	2,000	3,460	26	0.17	1.2

of the mine. The sulfide grains entering the mill were as large as 3 mm. A typical analysis of the mill feed was reported at 4.9% Pb, 15.4% Zn, 0.8% Cu, 113 ppm Ag, and 3.4 ppm Au (Bemis, 1932). Mill recoveries were good by the standard of the day although variable (Bemis, 1932). The rejected waste material was conveyed to the tailings pond in Alamitos Canyon and held in place by two earthen dams, 0.7 km and 1.5 km downstream of the mill site.

Today the tailings piles occupy approximately 14 ha in the bottom of Alamitos Canyon (Sidle et al., 1991) and have been covered with an impermeable cover. The depth varies from 0 to 20 m and averages 9-12 m. The tailings consist of predominantly sand size material (Table 5; Sidle et al., 1991). More silt is found in the southern, lower end of the pile than the north end. Higher concentrations of metals are found in the lower end as well. Discharge from the tailings pile enters Alamitos Creek, was acidic before reclamation, and contained elevated levels of metals (Table 6; Sidle et al., 1991; Brandvold et al., 1995). Wet meadows with pockets of water covered some of the tailings. Reclamation consisted of construction of a stream channel through the tailings pile and stabilization of the tailings by covering with clay, gravel, and soil (Johnson and Deeds, 1995a, b).

From 1950 through 1980, various state and federal agencies used the mine waste material from the Pecos mine as fill in various campgrounds (Jacks Creek campground and trailhead, Panchuela Creek campground), Winsor Trailhead parking area and the access roads to these sites from the Pecos mine. Mine waste rock from the Pecos mine was used as fill in these areas and the U.S. Forest Service had determined that erosion from these areas are point sources of Cu, Pb, Zn, and other metals (Table 7; Koch and Barkmann, 1995; Science Applications International Corp., 1995). All of these areas, except for Panchuela campground, have been reclaimed by removing the material to the Pecos mine waste pile.

TABLE 5. Selected average physical and chemical properties of the tailings pile (from Sidle et al., 1991).

Property	Upper, northern portion of pile	Lower, southern portion of pile
% Sand	65.7	37.7
% Silt	22.9	46.5
% Clay	11.3	15.8
% Organic matter	0.91	1.61
pH	3.41	3.71
Cu mg/kg (total)	586.9	1,873.0
Pb mg/kg (total)	4,154.4	7,225.4
Zn mg/kg (total)	245.6	1,572.2
Cd mg/kg (total)	0.6	5.9

TABLE 6. Summary of chemical analyses (mg/L) of water samples from the Alamitos Canyon mill site (El Molino)(from Johnson and Deeds, 1995b). (— no analyses)

Element (mg/l)	Range of Ground Water Analyses	Range of Surface Water Analyses
Cd	<0.0001-3.4	<0.1-8.4
Cu	<0.001-0.13	<1.0-205
Fe	<0.02-13,000	0.042-7.3
Mn	<0.01-150	—
Pb	<0.001-0.85	<1.0-18
Ag	<0.0001-0.015	<0.1-3.0
Zn	<0.01-3,500	0.016-1.8
SO4	33-90,200	—
pH	9.62-4.2	8.36-4.95

SUMMARY OF PREVIOUS RESULTS

Results from the first sampling trip in September 1992 (McLemore et al., 1993) found that samples below the Pecos mine waste pile were elevated in Hg, Pb, Cu, and Zn. Multi-disciplinary studies reported by Popp et al. (1996) and McLemore et al. (1995b) confirmed these results.

Chemical analyses of six sediment size-fractions from six sites suggested that the metals were predominantly traveling both as suspended and/or absorbed material and as larger minerals or other grains weathered from the mine waste pile and the tailings pile (McLemore et al., 1995a). Statistical analyses of XRF data indicated that Cu, Pb, and Zn had a high correlation with Fe and Mg (Popp et al., 1996), suggesting that these metals were associated with iron-bearing and ferro-magnesium minerals such as magnetite, pyrite, biotite, pyroxene, hornblende, etc. In addition, Cu, Pb, and Zn in the small size fraction (< 63 microns) had a high correlation with Al, suggesting that these metals were also associated with clay minerals. The weight percent of the size fraction had a high positive correlation with SiO_2 and Na_2O and a high negative correlation with TiO_2 and Al_2O_3, indicating that SiO_2 is concentrated in quartz in the large-size fraction and that TiO_2 and Al_2O_3 are concentrated in the small-size fraction, probably as clay minerals. Cu, Pb, and Zn also had a high correlation

TABLE 7. Geochemical analyses (FAAS) in mg/kg of background soils and soils from the contaminated campgrounds and roads that used mine waste pile material as fill (from Science Applications International Corp., 1995).

Element	Background Soils Range	Background Soils Mean	Environmental Site Range	Environmental Site Mean
Ag	0.5-5.0	1.3	1.0-38	4.4
Al	10,850-32,050	18,015	7,400-28,350	15,178
As	1.3-4.7	2.5	0.9-9.3	3.2
Be	0.5-0.9	0.7	0.4-0.9	0.6
Ca	1,575-10,15	3,518	427-100,000	3,491
Cd	0.1-1.2	0.2	0.7-124	8.3
Cr	20-63	37	12-66	26
Cu	10.5-26.5	14.7	25-1,311	245
Fe	20,550-31,750	25,227	11,800-41,050	25,222
Hg	<0.01	<0.01	0.02-0.35	0.05
K	1,135-7,500	2,337	805-4,275	2,206
Mg	1,945-5,660	2,831	1,825-23,250	5,779
Mn	271-960	590	251-1,060	494
Na	30-111	53	29-225	68
Pb	10-41	18	37-10,600	702
Se	0.9-1.0	0.9	0.8-6.7	1.9
Si	1,375-3,070	2,052	1,110-3,365	2,034
V	25-70	46	25-85	42
Zn	60-129	96	485-33,550	2,417

with each other and with Ga and V, and Pb had a high correlation with Ni. These elements are probably elevated in the ore and waste material at the Pecos mine.

McLemore and Brandvold (1997) also concluded that their studies suggested that Cu, Pb, Zn, and other metals are eroded and leached from the Pecos mine waste tailings and the tailings piles in Alamitos Canyon. However, the total metal addition from these sources is insignificant compared to sediment input from the Wilderness Area and drainages south of Pecos Village, especially Glorieta Creek. Zinc concentrations were elevated in samples collected from the dam above the Lisboa Springs Fish Hatchery, especially in the <63 micron size-fraction, and may have contributed to fish kills at the hatchery.

Partial dissolution techniques were employed to determine the following metal forms: (1) exchangeable, (2) organic, and (3) adsorbed to Fe and Mn oxides (Brandvold et al., 1995). The smallest size fraction (<63 micron), which constituted 3% or less of the sample weight, contained the highest concentration of metals. Partial dissolution techniques suggested that for the sites above the mine waste tailings the metals are concentrated in the crystalline or mineral phase as opposed to adsorption to metal hydroxide, organic, clay or dissolved phases. Below the mine waste pile and below the mill tailings there is a marked increase in the amount of Zn adsorbed to clay and hydroxides. This phenomenon changed downstream in both cases to the initial conditions. Copper, Pb, and Zn were higher in samples collected during the Fall of 1992 (low flow conditions) compared to samples collected during the Spring and Summer of 1993 (high flow conditions). This difference, in part, may be due to scouring of the river channel and dispersion of sediment during spring runoff. Partial dissolution techniques designed to estimate exchangeable, organic, and oxide-bound forms indicate that the largest amounts of Cu and Pb were in forms solubilized by *aqua regia* but not by three extraction techniques (Brandvold et al., 1995). The largest amount of Zn was associated with Fe and Mn oxides.

Brandvold and McLemore (1999) used ANOVA statistics on duplicate analyses of stream-sediment samples to study Cu, Pb, and Zn variations. Analytical error was found to be the greatest contributor to total variance. Differences in the adjacent site means were most apparent in the smallest size fraction (<63 micron). But even these differences were shown to be mostly due to random error.

METHODS OF STUDY

Sample sites along the Pecos River and its tributaries were determined prior to collection on the basis of well-maintained roads, easy access by vehicle, and proximity to known mines (Table 8, Figs. 2, 3). Additional sites were added as needed. Samples were collected from the Pecos River during eleven separate trips from September 1992 through June 2000. Not all sites were sampled during each trip. The entire Pecos River reach was sampled only in September 1992 and 1996 and June 2000; the remaining sample trips were in the upper Pecos River from the Pecos Wilderness southward to Villanueva (Fig. 3). Stream-sediment and water samples were taken at each site during each trip. Lake sediments were collected only in 1992 and 1996, but data for lake sediments are not discussed in this report. Outcrops, mine waste piles, and tailings piles were examined and sampled for chemical analyses at various times from 1992 to 1995 (Popp et al., 1996). Water samples were collected at each site and stored in polypropylene bottles. A portion of the water was acidified with trace pure nitric acid for trace metal analysis.

Stream-sediment samples were collected from each site along the Pecos River and adjacent tributaries. The river was typically shallow, enabling the sample collector to sample near the center of the river. During the spring runoff, the river was deeper and safety ropes were used to enable the collector to sample the stream sediments. Samples were stored in plastic bags and air dried and sieved at the laboratory (Fig. 4). Mineralogy is described in Table 9. These samples were homogenized using the cone and quarter method, and then screened in order to obtain different size fractions. Only the <63 micron fraction was analyzed for samples collected in 2000. A portion of the sample was dissolved in acid (*aqua regia*) for analysis using flame atomic absorption spectroscopy (FAAS) (Carey et al., 2001). Pressed powder briquettes were prepared for selected samples for analysis of trace elements by X-ray fluorescence (XRF).

Stream-sediment and rock samples were analyzed for metal concentrations using FAAS; water samples were analyzed using FAAS and graphite-furnace atomic absorption spectroscopy (GAAS). Selected rock, ore, and stream-sediment samples were also analyzed for major and trace elements by XRF and instrumental neutron activation (INAA) (Popp et al., 1996). FAAS and XRF analytical procedures and quality control data are described by McLemore et al. (1993, 1995a), Brandvold et al (1995), Popp et al. (1996), and Carey et al. (2001).

RESULTS AND DISCUSSION

The pH values of Pecos water samples collected in 1996 and 2000 ranged between 7.4 and 8.5 and were similar to samples collected in 1992 (Table 10; McLemore et al., 1993). The metal-content of water samples from the Pecos River is low, in many cases below detection limits (Table 10). Collectively, these data indicate that drainage from the Pecos mine is not significantly affecting the composition of the surface water in the area, except in the immediate vicinity of the Pecos mine site (Popp et al., 1996).

FAAS, XRF, and INAA analyses of samples collected from 1992 through 1994 confirmed that elevated concentrations of Cu, Pb, Zn, Cd, Cs, As, Ag, Au, W, Br, Se, Sb, Co, Al, and Fe occurred in stream sediments below both the Pecos mine (BWC) and Alamitos Canyon mill (BV) sites (Tables 11, 12; Popp et al., 1996; McLemore et al., 1995b). Samples collected in 1996 and analyzed by FAAS for Cu, Pb, Zn, and Cd showed similar results below the Pecos mine (Table 11). Samples collected in 2000 were still elevated in Cu (310 ppm in 1992, 420 ppm in 1996, and 92 ppm in 2000), Pb (300 ppm, 280 ppm, and 160 ppm), Zn (3100 ppm, 2900 ppm, and 2080 ppm), and Cd (17 ppm, 14 ppm, and 4.7 ppm) below the Pecos mine, but not as high as in earlier years (Table 10, 11). This is consistent with the fact that reclamation didn't really begin in this area until after 1996. Metal concentrations are no

TABLE 8. Description of sample sites (collected by NMBMMR). *Sample site consists of predominantly boulders. Sand-sized sediment collected from natural sand traps or bends in river.

Symbol	Name	Latitude	Longitude	
UP	Upper Pecos	35°49′30"	105°39′5"	*Near Pecos Wilderness boundary, along of main stream of Pecos River.
J	Jacks Creek	35°49′30"	105°39′7"	*Along Jacks Creek upstream of the confluence with the Pecos River approximately 1 m wide.
BJ	Below Jacks Creek	35°49′28"	105°39′14"	*West side of Pecos River approximately 50 m downstream of the confluence of Jacks Creek (upstream of bridge). Pecos River is approximately 4 m wide.
AWC	Pecos above Willow Creek	35°45′43"	105°40′13"	*Along Pecos River on east side at Willow Creek Campground approximately 200 m upstream of Pecos Mine. Pecos River is approximately 9 m wide.
SE	Seep, below mine	35°45′33"	105°40′7"	From seep along drainage downstream of Pecos mine. White and brown iron and aluminum oxide and hydroxide precipitates containing Cu, Pb, and Zn occur along the course of the seep.
BWC	Pecos below Willow Creek	35°45′27"	105°40′10"	*From Pecos River. Sample collected from sand bar or bank (depending upon water flow) approximately 10 m downstream of the confluence with Willow Creek.
T	Pecos at Terrerro campground	35°44′35"	105°40′30"	*From west side of Pecos River, 30 m upstream of Terrerro campground.
AH	Pecos above hatchery	35°37′00"	105°41′00"	*From Pecos River at small diversion dam approximately 1.0 km upstream of hatchery. Sample from west bank upstream of dam.
BH	Pecos below Hatchery	35°36′30"	105°41′00"	*From Pecos River approximately 10 m below discharge pipes from hatchery.
BV	Pecos below village	35°34′32"	105°40′10"	*From Pecos River at bridge where Highway 223 crosses the river. Pecos River is approximately 12 m wide.
BG	Pecos Below Glorita River	35° 31' 59"	105° 40' 00"	From Pecos River, at confluence with Glorieta River.
SM	Pecos at San Miguel	35°22′00"	105°26′45"	From Pecos River at large dam south of San Miguel. Samples taken upstream of dam on west side of river.
V	Pecos at Villanueva	35°15′30"	105°20′15"	From Pecos River south end of Villanueva State Park campground. Samples taken on north bank or middle of river (depending upon water flow).
Te	Tecolitito	35°20' 20"	105°14' 20"	*From Pecos River at Tecolitito.
Di	Dillia	35°26' 15"	105°11' 25"	From Pecos River at Dillia.
BSR	Below Santa Rosa dam	35° 1' 35"	104°40' 00"	Pecos River below Santa Rosa Dam.
PL	Puerto del Luna	34°54' 00"	104°37' 30"	Pecos River at Puerto del Luna.
BSD	Below Sumner Dam	34°35' 30"	104°23' 00"	Pecos River below Sumner Dam.
FS	Ft. Sumner bridge	34°29' 00"	104°15' 03"	Pecos River at Ft. Sumner bridge.
US70	U.S. 70	33°38' 45"	104°22' 30"	Pecos River at U.S. 70 bridge.
Hag	Hagerman	33° 7' 2"	104°16' 45"	Pecos River at Hagerman.
BB	Below Brantley dam	32°32' 25"	104°21' 00"	Pecos River below Brantley Dam.

longer elevated below Alamitos Canyon (Tables 11, 12). Elevated Cu and Pb concentrations were detected for the first time below the fish hatchery (Table 13), possibly as a result of the cleaning of the raceways and discharging the water into the Pecos River.

XRF analyses are typically higher than FAAS (Table 14). XRF analysis measures the entire solid sample, whereas FAAS measures the amount of dissolved material. Therefore, not all of the sample was dissolved by *aqua regia* dissolution methods used in order to obtain FAAS analyses. However, FAAS probably reflects a better measurement of how much material is available for dissolution and mobility in surface and ground water. XRF is a measurement of the total metal concentrations in the solid.

The metal concentrations of most samples reflect the metal concentrations of the predominant lithology in this area. Stream-sediment samples collected above the Pecos mine contain similar metal concentrations as the Precambrian rocks (Popp et al., 1996). Stream-sediment samples collected below Pecos Village contain similar metal concentrations as the Paleozoic and Mesozoic rocks. These results further confirm that the Pecos mine and Alamitos Canyon mill were point sources of metals contamination.

Zinc is elevated in sediments collected at a dam above the fish hatchery compared to that in sites above the Pecos mine (Fig. 6; Tables 11, 13). Several fish kills have occurred at the hatchery 1991-1995 that have been attributed to drainage from the mine site and the contaminated campground sites. Sediment samples from the dam above the fish hatchery contained elevated concentrations of Zn in 1992 (1300 ppm) and 1996 (944 ppm), which suggested that precipitates formed from the leachate and suspended material eroded from the Pecos mine waste piles could be deposited at the diversion dam above the fish hatchery. During sporadic periods of turbulent flow in the fall, when the Pecos River is at low flow (i.e. low volume), suspended material elevated in Zn could be entering the fish hatchery and contributing to the recent fish kills. After 1995, the fish hatchery personnel established new procedures that reduced the incidence of fish kills. The fish hatchery personnel removed stream sediment above the dam to reduce the amount of Zn entering the hatchery. The fish hatchery personnel also lined the culvert and pumps from the dam to the hatchery with lime.

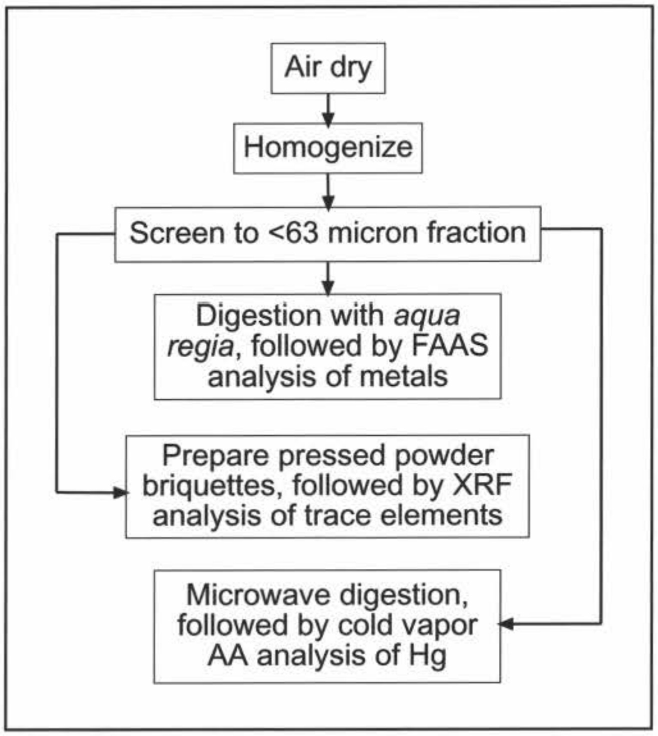


FIGURE 4. Sampling procedures.

TABLE 9. Mineralogy of stream-sediment samples from the upper Pecos River.

Major Constituents (>10% in most samples)
Quartz SiO_2
Lithic or rock fragments
Feldspars
K-feldspar $K(AlSi_3O_8)$
Plagiocalse $(Na,Ca)(AlSi_3O_8)$
Pyroxene (complex silicate mineral)
Hornblende $Ca_2Na(Mg,Fe^{+2})_4(Al,Fe^{+3},Ti)_3Si_8O_{22}(O,OH)_2$
Minor Constituents (<10% in most samples)
Biotite $K(Mg,Fe)_3(AlSi_3O10)(OH)_2$
Chlorite $Mg_3(Si_4O10)(OH)_2Mg_3(OH)_6$
Muscovite $K\ Al_2(AlSi_3O_{10})(OH)_2$
Magnetite Fe_3O_4
Zircon $ZrSiO_4$
Calcite $CaCO_3$
Titanite $CaTiO(SiO_4)$
Apatite $Ca_5(F,Cl,OH)(PO_4)_3$
Clay minerals
Kaolinite $Al_4(Si_4O10)(OH)_8$
Illite (K silicate)
Smectite (complex silicate)
Fe and Mn oxides
Trace Constituents (<1% in some samples)
Garnet (complex silicate)
Monazite $(Ce,La,Y,Th)PO_4$
Rutile, anatase TiO_2
Pyrite FeS_2
Fluorite CaF_2

Finally, the fish hatchery personnel shuts off river water during periods of rain or snow melt and utilizes spring water. Results from sampling in 1996 indicated that Zn was still elevated in stream sediments above the dam, even though the fish hatchery personnel removed material earlier in the year. By 2000, Zn was only slightly elevated in sediments (325 ppm)(Table 13).

During the remediation efforts at Jacks Creek Campground, an erosional event occurred (Richard Koch, personal communication, Sept. 28, 1995) that coincided with an increase in metal concentrations in stream sediments below Jacks Creek (Table 15). This event, in summer 1994, contaminated Jacks Creek with mine waste material, resulting in elevated metal concentrations (Popp et al., 1996). This suggests that remediation efforts can release additional metals to the Pecos River. Reclamation at the Alamitos Canyon mill site is evident in the stream-sediment sampling; metal concentrations decreased during and after reclamation (Tables 11, 14; Popp et al., 1996; Carey et al., 2001). Copper values decreased from 270 ppm in 1992 to 30 ppm in 2000. Lead values decreased from 590 ppm in 1992 to 30 in 2000. Zinc values decreased from 990 ppm in 1992 to 290 ppm in 2000.

SUMMARY

Elevated concentrations of Cu, Pb, Zn, Cd and other metals occurred in stream sediments below both the Pecos mine and Alamitos Canyon mill sites before reclamation began. Collectively, multi-disciplinary studies suggest that Cu, Pb, Zn, and other metals were eroded and leached from the Pecos mine waste pile and Alamitos Canyon mill tailings. These studies confirm a decrease in metal concentrations with time since reclamation began, especially in the immediate vicinity of the Pecos mine and Alamitos Canyon. Reclamation efforts at the Alamitos Canyon mill site are successful in that the metal concentrations in both surface water and stream sediments have decreased since reclamation. The overall metal concentrations dramatically decreased in stream sediments below Pecos village in all sampling trips, mostly due to dilution of sediment derived from the red bed sedimentary units. Therefore, the total metals addition from the Pecos mine waste pile and Alamitos Canyon mill tailings is insignificant compared to sediment input from the Pecos Wilderness and drainages south of Pecos village, except in the immediate vicinity of the Pecos mine and mill site. In 2000, a sharp increase was noted in Cu and Pb levels in stream sediments immediately below the fish hatchery. More samples should be taken from this site to confirm the finding.

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TABLE 10. Chemical analyses of water samples collected in 1992, 1996, and 2000. Values in ppm except for conductivity, pH and where noted. Major and trace element analyses by flame atomic absorption spectrometry (FAAS) and graphite-furnace absorption spectrometry (GAAS). (— no analyses)

Site	Date	Temp. C°	Cond. uS	pH	HCO_3	Cl	SO_4	NO_3	F	Na	K	Mg	Ca	As ppb	Hg ppb	Pb ppb	Cu ppb	Zn ppb
UP	9/92	15.0	200	7.60	170	—	—	—	—	—	—	—	—	—	<0.2	<1	3	<50
	9/96	9.6	230	8.27	100	1.4	20	0.7	<0.2	2.8	0.6	4.2	37	<10	—	—	—	—
	6/00	15.3	240	8.10	120	2.0	15	<0.2	0.1	1.4	0.6	4.1	38	<1	—	<5	15	<50
BJ	9/92	12.0	170	8.20	140	—	—	—	—	—	—	—	—	—	<0.2	2	2	<50
	9/96	9.0	270	8.33	146	2.2	22	0.7	<0.2	2.6	0.5	4.5	46	<10	—	—	—	—
J	6/00	13.8	280	8.28	148	2.1	14	<0.2	<0.1	1.4	0.5	3.9	48	<1	—	<5	5	<50
AW	9/96	12.0	140	8.22	73	1.2	8.2	0.4	<0.2	2.5	0.6	2.4	20	<10	—	—	—	—
	6/00	18.2	160	8.13	82	2.0	9.3	<0.2	0.1	1.5	0.5	2.4	25	<1	—	<5	6	<50
BW	9/92	21.5	160	9.10	120	—	—	—	—	—	—	—	—	—	<0.2	6	3	410
	9/96	14.0	130	7.44	73	1.3	8.6	0.9	<0.2	2.6	0.6	2.4	22	<10	—	—	—	—
	6/00	16.1	160	8.16	88	2.0	8.5	0.1	0.1	1.6	0.6	2.5	26	<1	—	<5	5	<50
T	9/96	15.2	130	7.68	73	1.1	8.6	0.5	<0.2	2.5	0.5	2.4	21	<10	—	—	—	—
	6/00	17.5	170	8.02	83	2.0	9.3	<0.2	0.1	1.7	0.6	2.4	25	<1	—	<5	5	<50
AH	9/92	18.0	180	8.30	140	—	—	—	—	—	—	—	—	—	<0.2	2	3	60
	9/96	16.9	160	8.01	91	1.3	9.9	0.4	<0.2	3.0	0.6	2.7	25	<10	—	—	—	—
	6/00	20.6	190	8.12	97	2.3	10	0.1	0.1	2.0	0.7	2.7	30	<1	—	<5	6	<50
BH	9/92	16.5	180	8.05	140	—	—	—	—	—	—	—	—	—	<0.2	2	1	60
	9/96	15.8	190	8.08	100	1.4	9.8	0.6	<0.2	3.0	0.6	2.8	27	<10	—	—	—	—
	6/00	22.6	200	8.18	100	2.2	11	<0.2	0.2	2.1	0.6	2.8	32	<1	—	<5	5	<50
BV	9/92	18.0	200	8.35	140	—	—	—	—	—	—	—	—	—	<0.2	<1	<1	30
	9/96	17.9	180	7.78	100	1.5	11	0.7	<0.2	3.2	0.6	3	30	<10	—	—	—	—
	6/00	22.0	240	8.08	125	2.3	12	0.1	0.2	2.4	0.6	3.2	38	<1	—	<5	4	<50
BG	9/96	18.4	230	8.47	110	5.5	15	0.5	<0.2	6.6	0.8	3.9	34	<10	—	—	—	—
	6/00	25.9	250	8.41	130	2.7	14	<0.2	0.2	3.3	0.7	3.4	40	<1	—	<5	3	<50
SM	9/92	21.5	220	7.95	140	—	—	—	—	—	—	—	—	—	<0.2	9	4	60
	9/96	19.9	220	8.49	120	2.6	13	0.4	<0.2	5.0	0.8	3.8	35	<10	—	—	—	—
	6/00	26.1	290	8.03	140	3.4	19	0.3	0.2	5.3	1.1	4.2	44	<1	—	<5	7	<50
V	9/92	23.0	260	8.20	170	—	—	—	—	—	—	—	—	—	<0.2	<1	2	<50
	9/96	21.8	250	8.46	150	3.1	14	0.6	<0.2	5.5	1.0	4.8	40	<10	—	—	—	—
	6/00	24.5	370	8.21	200	4.0	19	<0.2	0.2	7.3	1.5	7.8	55	<1	—	<5	4	<50
Te	9/92	20.5	250	8.10	170	—	—	—	—	—	—	—	—	—	<0.2	1	2	<50
	9/96	22.4	250	8.45	140	3.7	15	0.9	<0.2	6.4	1.1	5.0	39	<10	—	—	—	—
	6/00	22.6	350	7.90	190	3.9	17	<0.2	0.2	6.8	1.6	7.2	51	<1	—	<5	6	<50
Di	9/92	26.0	310	8.60	220	—	—	—	—	—	—	—	—	—	<0.2	3	3	<50
	9/96	22.8	280	8.47	150	3.6	16	0.4	<0.2	6.0	1.5	6.0	44	<10	—	—	—	—
	6/00	22.8	350	8.08	170	5.2	28	0.2	0.2	8.7	1.4	9.6	45	<1	—	<5	6	<50
BSR	9/92	24.5	590	8.05	170	—	—	—	—	—	—	—	—	—	—	—	—	—
	9/96	26.9	2100	7.68	160	21.1	1320	0.4	0.4	51	14	140	250	<10	—	—	—	—
	6/00	24.6	1550	7.84	200	15	650	0.4	0.2	31	4.3	75	185	<1		<5	16	<50
PL	9/92	24.0	2480	8.00	190	—	—	—	—	—	—	—	—	—	<0.2	<1	1	14
	9/96	23.4	2710	8.05	155	135	1320	0.6	0.4	89	2.4	61	460	<10	—	—	—	—
	6/00	25.1	3060	8.06	140	130	1540	<0.2	0.4	100	2.4	68	550	<1	—	<5	15	<50
BSL	9/92	21.0	1250	8.40	140	—	—	—	—	—	—	—	—	—	—	—	—	—
	9/96	17.7	1960	8.02	100	67	1000	0.9	0.2	62	3.1	41	290	<10	—	—	—	—
	6/00	25.0	1110	8.12	140	30	400	0.2	0.2	28	2.6	21	180	<1	—	<5	6	<50
FS	9/92	20.0	1250	8.10	150	—	—	—	—	—	—	—	—	—	—	—	—	—
	9/96	17.8	1860	7.65	100	69	875	0.5	0.2	65	3.1	44	260	<10	—	—	—	—
	6/00	32.8	1610	8.00	170	70	510	<0.2	0.3	64	2.5	40	210	<1	—	<5	12	<50
US70	9/92	29.0	2000	8.00	120	—	—	—	—	—	—	—	—	—	<0.2	3	4	10
	9/96	18.6	2190	8.05	90	300	610	2.0	<0.2	203	3.8	48	170	<10	—	—	—	—
	6/00	33.5	1780	8.02	110	140	560	3.7	0.4	156	6.0	34	170	<1	—	<5	18	<50
H	9/92	27.0	3490	8.00	150	—	—	—	—	—	—	—	—	—	<0.2	2	<1	8
	9/96	19.3	3150	7.98	130	430	880		0.3	295	4.5	77	250	<10	—	—	—	—
	6/00	31.5	6380	7.88	130	1300	1420	1.8	0.4	790	7.1	130	480	<1	—	<5	18	<50
BBR	9/92	22.0	3250	8.30	120	—	—	—	—	—	—	—	—	—	—	—	—	—
	9/96	22.3	2860	7.70	100	400	770	0.8	<0.2	275	4.9	66	225	<10	—	—	—	—
	6/00	26.5	3880	7.42	110	530	1040	0.2	0.3	345	5.0	85	350	<1	—	<5	<1	<50

TABLE 11. Chemical analyses of stream-sediment samples collected in 1992, 1996, and 2000, as determined by FAAS (<63-micron size fraction). Entire data set can be obtained from the authors.

Site	Cu ppm			Pb ppm			Zn ppm			Cd ppm			Mn ppm			Fe %		
	1992	1996	2000	1992	1996	2000	1992	1996	2000	1992	1996	2000	1992	1996	2000	1992	1996	2000
UP	18	23	20	30	31	17	110	86	88	1.2	1.3	1.2	410		585	2.20		2.28
BJ	40	42	14	110	99	21	330	325	97	1.5	1.0	1.2	400	440	440	2.40	1.70	1.72
AWC	70	44	23	95	65	32	300	250	160	1.7	1.5	1.1	330	370	370	2.20	2.20	2.22
BWC	310	420	92	300	280	160	3100	2900	2080	17	14	4.9	360	425	425	2.05	2.90	2.58
T	92	78	48	125	84	80	1160	1000	755	2.2	5.0	4.7		555	830	1.90	2.00	2.42
AH	55	44	24	94	57	37	1300	945	325	2.2		1.7	310		277	2.00		2.17
BH	35	39	130	70	54	545	830	490	375	2.7		2.0	280		270	1.85		2.49
BV	270	38	30	590	38	93	990	320	290	2.5		2.2	380		320	1.88		2.61
BG		24	22		39	44		175	215			2.0			445			1.93
SM		15	8	29	28	13	51	33	35	0.8		1.1	310		310	1.65		1.89
V	14	16	4	44	27	15	75	27	160	0.7		1.0	310		300	1.80		1.96
Te		14	8	18	20	31	45	25	49	0.7		0.9	280		770	4.00		1.74
Di	15	10	10	21	20	22	32	20	62	0.7		1.0	210		450	1.50		1.71
BSR		12	4		25	32		34	38			1.0			795			2.26
PL		12	6	21	24	17	37	30	59			0.6			275			1.89
BSD		18	14		68	31		36	39			0.9			665			2.83
FS		37	9	21	32	28	27	28	69			0.9			710			2.12
US70		36	17	114	27	26	66	31	145			1.4			410			3.18
Hag		33	9	19	21	16	18	25	60			0.9			380			3.01
BBR	9	32	5	30	24	18	24	27	41			1.0			285			1.50

TABLE 12. Comparison of chemical analyses of stream-sediment samples (<63-micron size fraction, FAAS) Below Pecos Village (BV) before and after reclamation of the Alamitos Canyon mill site.

DATE	Cu ppm	Pb ppm	Zn ppm
9/92	270	590	990
5/94	25	40	290
9/94	22	28	211
9/96	28	38	319
6/00	30	93	287

TABLE 13. Comparison of chemical analyses of stream-sediment samples (<63-micron size fraction, FAAS) above and below the fish hatchery.

DATE	Cu ppm	Pb ppm	Zn ppm
Pecos Above Fish Hatchery (AH)			
9/92	55	94	1300
5/94	33	46	580
9/94	38	77	697
9/96	44	57	944
6/00	24	37	325
Pecos Below Fish Hatchery (BH)			
9/92	35	67	830
5/94	41	74	550
9/94	31	53	373
9/96	39	54	488
6/00	130	543	374

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TABLE 14. Comparison of chemical analyses by FAAS and X-ray fluorescence (XRF) methods for samples collected in 2000 (<63-micron size fraction). As was determined only by XRF methods. (— no analyses).

Site	Cu		Pb		Zn		Cr		Mn		Fe		As
	(FAAS)	(XRF)	(FAAS)	(XRF)	(FAAS)	(XRF)	(FAAS)	(XRF)	(FAAS)	(XRF)	(FAAS)	(XRF)	(XRF)
UP	20	20	17	24	88	106	35	75	585	770	2.27	2.94	5
J	14	21	21	33	97	117	32	63	438	540	1.70	2.21	4
AWC	23	29	32	45	156	180	32	75	369	620	2.20	3.15	4
BWC	92	92	157	143	2080	1600	33	81	424	620	2.91	3.11	3
T	48	58	80	97	755	915	36	78	827	1160	2.41	3.21	4
AH	24	28	37	45	325	432	33	70	284	540	3.44	2.97	3
BH	130	146	543	680	374	599	28	70	283	700	3.81	4.01	<2
BV	30	43	93	103	287	368	42	69	318	460	3.83	3.29	3
BG	22	28	44	51	213	306	36	64	434	620	2.88	2.69	3
SM	8	18	13	13	35	48	34	73	309	390	3.15	2.38	3
V	4	14	15	15	157	57	32	66	305	390	2.90	2.39	3
Tec	8	—	31	—	49	—	27	—	764	—	1.66	—	—
Di	10	—	22	—	62	—	69	—	442	—	1.62	—	—
BSR	4	19	32	32	38	49	46	92	793	930	3.31	2.65	5
PL	6	16	17	17	59	47	31	145	304	390	2.33	2.28	3
BSD	14	—	31	—	39	—	35	—	658	—	2.75	—	—
FS	9	—	28	—	69	—	59	—	701	—	2.03	—	—
US70	17	—	26	—	146	—	47	—	424	—	4.97	—	—
Hag	9	20	16	21	60	54	50	257	370	700	4.80	4.36	7
BBR	5	14	18	18	41	44	38	99	290	390	2.27	1.83	3

TABLE 15. Comparison of chemical analyses of stream-sediment samples (<63-micron size fraction, FAAS) Below Jacks Creek.

DATE	Cu ppm	Pb ppm	Zn ppm
9/92	40	110	330
5/93	23	45	130
5/94	33	100	170
9/94	580	1681	481
9/96	42	99	325

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