# BASE METAL AND TRACE ELEMENT CONCENTRATIONS IN STREAM SEDIMENTS ALONG THE PECOS RIVER, FROM THE SOUTHERN PECOS WILDERNESS TO BRANTLEY DAM, NORTH OF CARLSBAD, EASTERN NEW MEXICO<sup>1</sup>

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Abstract. Since reclamation of the Pecos mine waste pile, area roads and campgrounds, and the Alamitos Canyon mill was begun in 1991, there has been continued monitoring of metal and trace element concentration in stream sediments and water along the Pecos River, extending from the upper Pecos River to below Brantley Dam, north of Carlsbad. In 1992, 1996, and 2000, surface water and stream sediments were sampled and analyzed for the entire reach of the Pecos River. Between 1992-1996 the upper reach of the river between the Pecos Wilderness and Villanueva was sampled on 8 occasions as part of a multidisciplinary study. These efforts were initiated so that point and non-point sources of contamination associated with the areas of concern could be identified and the effects of reclamation examined. The Pecos mine generated approximately 70,000 m<sup>3</sup> of waste rock, which was piled at the mine site on a slope above the river. The crushed ore from the mine was transported by aerial tramway to the Alamitos Canyon mill 18 km south of the mine. Both mine waste and mill tailings have been sources of acidic drainage contributing elevated concentrations of metals and other trace elements. This paper provides the most recent year's sample data for the stream sediments and compares the data to the earlier year's data. In this study, the <63µ fraction was digested with aqua regia and analyzed for Cd, Cr, Cu, Fe, Mn, Pb, and Zn using flame atomic absorption spectroscopy. Geochemical trends over the period 1992-2000 confirm a decrease in concentrations with time since reclamation began, especially in the immediate vicinity of the Pecos mine and below the confluence of Alamitos Creek which drains the mill site area. In 2000, a sharp increase was noted in Cu and Pb levels in stream sediments immediately below the fish hatchery, 19 km below the Pecos mine.

Additional Key Words: Mine reclamation; mill reclamation; copper; lead; zinc; chromium; flame atomic absorption spectroscopy; X-ray fluorescence.

### Introduction

The Pecos River originates in the Pecos Wilderness in the southern Sangre de Cristo Mountains and flows in a southerly direction through eastern New Mexico to the New Mexico-Texas border and enters the Rio Grande in Texas (Fig. 1). In 1991, it was reported that fish, waterfowl, and small mammals from along the upper Pecos River displayed elevated levels of Se, Hg, Pb, Cd, Cr, and other pollutants (U. S. Bureau of

<sup>1</sup>Paper presented at the 2001 National Meeting of the American Society for Surface Mining and Reclamation, Albuquerque, New Mexico, June 3-7, 2001. Published by ASSMR, 3134 Montavesta Rd., Lexington, KY 40502.

<sup>2</sup> New Mexico Bureau of Mines and Mineral Resources, New Mexico Institute of Mining and Technology, 801 Leroy Place, Socorro, NM 87801. Reclamation, written comm. 1992; S. J. Haness, U.S. Department of Health and Human Services, written comm. 1991).

The Lisboa Springs Fish Hatchery (New Mexico Game and Fish Department, NMGFD), above the Village of Pecos (Fig. 2), reported fish kills beginning in 1991 that were attributed, in part, to heavy metals in water (McLemore et al., 1993). Possible point sources were the waste piles from the Pecos mine located along the river 19 km upstream from the fish hatchery. When the mine was in operation (1902–1904, 1927–1939, and1943 – 1944) ore was crushed at the mine and mine waste piled on the hillside above the river. During 1950-1980 material from the mine waste pile was used as surfacing material in the area campgrounds and roads. The ore was transported by aerial tramway to the Alamitos Canyon mill, 18 km south of the mine. The mill employed flotation-processing techniques and

Proceedings America Society of Mining and Reclamation, 2001 pp 246-254 DOI: 10.21000/JASMR01010246



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

was designed to treat 544 metric tons of ore per day (Bemis, 1932; Martin, 1931). Only the foundations remain on the east slope of Alamitos Canyon (Popp et al., 1996). After milling, the tailings were placed behind an earthen dam on the canyon floor. Over time, the dam had been breached. A small perennial stream flowed through the tailings, and entered the Pecos River just below the Village of Pecos. In 1991 and 1992, state and federal agencies identified the Pecos mine, area roads, campgrounds, and Alamitos Canyon mill as point sources of contamination for Pb, Zn, and Cu (McLemore et al., 1993; Johnson and Deeds, 1995a, 1995b). Reclamation began in 1991 and at Alamitos Canyon was completed by 1996. Reclamation was completed for the roads and campgrounds by 2000, and is still on going for the Pecos mine waste piles.

In 1992, 1996, and 2000, water and stream sediment samples were collected along the Pecos from the Pecos Wilderness area to below Brantley Dam. In 1992-1994, a multidisciplinary study was completed in cooperation with the U. S. Bureau of Reclamation, New Mexico Institute of Mining and Technology (NMIMT) and New Mexico Bureau of Mines and Mineral Resources (NMBMMR), in order to identify and prioritize point and non-point sources of contamination in the upper Pecos area above Villanueva (McLemore et al., 1995; Popp et al., 1996).

This paper presents geochemical analyses of sediment samples from the most recent sampling period (2000) and investigates trends with the prior sampling periods (1992-1994 and 1996). Three trips along the entire reach were made in 1992, 1996, and 2000. The multidisciplinary study included eight sampling trips in the upper Pecos area above Villanueva.

The study area encompasses the Pecos River from the southern Pecos Wilderness to below Brantley Dam, north of Carlsbad. The Pecos River supplies a significant amount of water to eastern New Mexico, west Texas and Coahuila, Mexico (Fig. 1) (McLemore et al., 1993). Elevations within the study area range from 1000 to almost 4000 m (McLemore et al., 1995). The climate varies from semiarid in the valleys to more humid in the mountains (McLemore et al., 1995). Currently there is no metal mining within the Pecos drainage basin.



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

The geology of the Pecos drainage basin is diverse and includes rocks ranging in age from Proterozoic to recent (New Mexico Geological Society, 1982). Lithologies are also diverse ranging from metamorphic volcanics to granites to syenites to shales, limestones, and sandstones (McLemore et al., 1993). The Proterozoic rocks are the oldest and consist of mafic metamorphic and volcaniclastic rocks comprising the Pecos greenstone belt (McLemore et al., 1995). Sedimentary rocks overlying the Proterozoic rocks include limestone, sandstone, and shale. For a more detailed description of the geology see McLemore et al. (1995).

Mining has occurred throughout the Pecos drainage basin with the largest mining district being the Pecos mining district, however total production in this district has been insignificant when compared to production in other parts of New Mexico (McLemore et al., 1993). The majority of deposits within the Pecos mining district consist of precious- and base-metal vein deposits and sedimentary-copper deposits (McLemore et al., 1993; McLemore, 1995; McLemore, in press). The Pecos mine is a volcanogenic-massive sulfide deposit that was the largest Pb and Zn producer in New Mexico from 1927 to 1939 and is one of the top ten Pb and Zn producers in New Mexico (McLemore et al., 1995).

#### Procedures

# Sampling

Twenty-one sediment samples were collected along the Pecos River (Table 1, Fig. 2, 3) from sites that correspond to sites from previous trips.

Since the river is typically shallow, grab samples were collected from the center (<0.5 m depth) of the riverbed when possible and generally consisted of a heterogeneous mixture of gravel sized (> 2mm) to clay sized ( $< 63\mu$ ) material. These samples were air-dried, homogenized using the cone and quarter method, and then screened in order to obtain different size fractions. For this study only the  $< 63\mu$  fraction was analyzed. The metals that were analyzed include; Cd, Cr, Fe, Pb, Zn, Cu, and Mn, but only Cr, Cu, Pb, and Zn are reported here. A portion of this fraction was also used for X-ray fluorescence (XRF) analysis. These values have been tabulated along with the values obtained from flame atomic absorption spectroscopy (FAAS) for the same four metals, in order to compare the acid extractable fraction with the total amount.

# Sample Preparation and Analysis

The method for acid extraction of metals from the sediment involved digesting 1 gram of the  $<63\mu$  fraction with 15 ml of concentrated HCl and 5 ml of concentrated HNO<sub>3</sub> (*aqua regia*). The samples were refluxed on a hot plate for 1 hour and taken to dryness. The procedure was then repeated a second time.

Soluble salts were dissolved in a solution of 3 ml of concentrated  $HNO_3$  and about 20 ml of distilled water, then filtered and brought to 50 ml volume.

Since it was not possible to digest all 21 samples in one run, four separate digestions were done. Except for the first digestion, two reference standards were also digested with each batch in order to determine the accuracy and reproducibility. Duplicates were included in each batch and duplicates of two of the samples were digested in all four trials. Manufacturer's conditions were followed for FAAS and XRF analyses.

### <u>Error Analysis</u>

Two reference stream sediments (STSD-1 and STSD-4) were digested and analyzed with the samples in order to determine the validity of the data (Table 2). These were obtained from the Canadian Certified Reference Materials Project in Ottawa, Ontario. Duplicates were also analyzed for each digestion and two of the samples were digested and analyzed in each of the four separate trials (Table 3).

### **Results and discussion**

With three complete sets of data now in place (1992, 1996, and 2000), comparisons can be drawn with reference to several of the metals. The 1992 data is an average of the data from the multidisciplinary study that included eight sampling trips in the upper Pecos area above Villanueva and the 1992 data for the same sampling sites. Four of the metals in particular (Cu, Pb, Zn, and Cr) were plotted as a function of distance and time. See Table 1 and Figures 2 and 3 for the location of sample sites. The data for these three sampling periods have been provided in Table 4 for the above mentioned elements. The following trends can be seen over the eight-year time period.

Copper concentrations have decreased with time (Fig. 4). The concentrations also decrease significantly downstream from the Pecos mine. Above the Pecos mine (UP, BJ, AWC) concentrations are significantly lower than in the immediate vicinity of the mine (BWC) where they increase relative to the surrounding sampling sites. However, the concentrations decrease significantly downstream from the mine. Соррег concentrations in the vicinity of the mine have decreased with time in response to ongoing reclamation. Interestingly, Cu concentrations increase just below the Lisboa Springs Fish Hatchery. To confirm this increase and also a noted increase in Pb, samples from this site were re-run and values listed represent an average value.

Symbol	Name	Latitude	Longitude	Description
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.
AWC	Pecos above	35°45′43"	105°40′13"	Along Pecos River on east side at Willow Creek Campground
	Willow Creek			approximately 200 m upstream of Pecos Mine. Pecos River is
· · ·				approximately 9 m wide.
SE	Seep, below	35°45'33"	105°40'7"	From seep along drainage downstream of Pecos mine. White and brown
1	mine			iron and aluminum oxide and hydroxide precipitates containing Cu, Pb, and
BWC	Peace below	35945'27"	105940/108	Zh occur along the course of the seep.
DWC	Willow Creek	33-43 27	105'40 10"	From Pecos River. Sample collected from sand bar or bank (depending
	WINDW CICCK			Willow Creek
T	Pecos at	35°44′35"	105°40′30"	From west side of Pecos River, 30 m upstream of Terrerro campground
	Теггегто			and the control of the second of the second s
	campground			
AH	Pecos above	35°37′00"	105°41′00"	From Pecos River at small diversion dam approximately 1.0 km
	hatchery			upstream of hatchery. Sample from west bank upstream of dam.
BH	Pecos below	35°36′30"	105°41′00"	From Pecos River approximately 10 m below discharge pipes from
	Hatchery			hatchery.
BV	Pecos below	35°34′32"	105°40′10"	From Pecos River at bridge where Highway 223 crosses the river. Pecos
DC	Village	268.271.608	1050 401 001	River is approximately 12 m wide.
DQ	Glorita River	35-31-39	105* 40.00*	From Pecos River, at confluence with Glorieta River.
SM	Pecos at San	35922/00"	105926'45"	From Perces River at large dam south of San Miguel Semples taken
	Miguel		105 20 15	upstream of dam on west side of river
v	Pecos at	35°15'30"	105°20′15"	From Pecos River south end of Villanueva State Park campground
	Villanueva			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 Dilia.
BSR	Below Santa	35° 1' 35"	104° 40' 00"	Pecos River below Santa Rosa Dam.
PI	Rosa dam Puerto del	249 54 00"	1049 271 201	Boood Diver at Diverte del Luce
112	Luna	54 54 00	104 37 50	recos Rivel al Fuerio del Luna.
BSD	Below	34° 35' 30"	104° 23' 00"	Pecos River below Sumner Dam.
	Sumner Dam			
FS	Ft. Sumner	34° 29' 00"	104° 15' 03"	Pecos River at Ft. Sumner bridge.
11670	bridge	220.001.458	1010001000	
US/U Hag	U.S. /U Hagarman	35" 38' 45"	104° 22' 30"	Pecos Kiver at U. S. 70 bridge.
BR	Relow	279 221 26	1042 211 001	Pecos River al Hagerman.
מט	Brantley dam	32" 32" 23"	104*21.00"	recos River below Brantley Dam.

 Table 1. Description of sample sites (shown in Fig. 2 and 3).

Zinc is analogous to copper in that concentrations have also decreased over the sampling period (Fig. 5). Zinc has decreased in the vicinity of the mine from ~3000 ppm in 1992 to ~2000 ppm in 2000.

Lead shares a similar fate to copper in that the concentration not only decreases downstream from the mine but also decreases over time (Fig. 6). Similar to zinc and copper, lead is generally highest in the immediate vicinity of the mine (~300 ppm) and decreases substantially downstream. However, it is

interesting to note that similar to the copper, lead increases dramatically just below the fish hatchery.

Chromium has a slightly different profile than the previously described metals (Fig. 7).

Unlike Cu, Pb and Zn, chromium seems to have leveled off and maintained consistent concentrations not only with respect to specific sampling sites but also over the eight-year period. An interesting feature of Cr is that the concentrations seem to increase slightly downstream although they still remain around or below 50 ppm.



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

Table 2. Analysis of reference materials.	Values in ppm unless otherwise noted.
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Standard	Cu	Pb	Zn	Cr	Fe %	Mn %	Cd
STSD-1							
(Ave <u>+</u> STD)	28 <u>+</u> 2	38 <u>+</u> 4	<u>157 ± 3</u>	33 <u>+</u> 6	3.4 <u>+</u> 0.2	0.31 <u>+</u> 0.02	1.39 <u>+</u> 0.24
Certified Value	36	34	165	28	3.5	0.37	0.8
STSD-4							
(Ave <u>+</u> STD)	57 <u>+</u> 6	18 <u>+ 5</u>	83 <u>+</u> 0.6	42 <u>+</u> 11	2.7 <u>+</u> 0.2	0.1 <u>+</u> 0.006	0.8 <u>+</u> 0.2
Certified Value	66	13	82	30	2.6	0.12	0.6

Sample Symbol	Cu	Pb	Zn	Cr	% Fe	Mn	Cd
SE	121-144	156 - 221	2933 - 3669	47 - 59	3.1 - 3.6	765 - 789	7.7 - 8.6
Ave <u>+</u> STD	132 <u>+</u> 12	181 <u>+</u> 35	3209 <u>+</u> 401	52 <u>+</u> 6	3.4 ± 0.3	773 <u>+</u> 13	8.1 <u>+</u> 0.4
PL	14 - 25	18 - 22	40 - 55	30 - 41	1.8 - 2	281 - 333	0.55 - 0.63
Ave <u>+</u> STD	18 ± 5	$18 \pm 3$	47 <u>+</u> 8	34 <u>+</u> 5	1.8 <u>+</u> 0.07	306 <u>+</u> 23	0.6 <u>+</u> 0.04

 Table 3. Analysis of samples and analytical error. Values in ppm unless otherwise noted. Sample symbols from Table 1.

 Table 4. Comparison of data for the three sampling periods for Cu, Pb, Zn and Cr. Values in ppm of solid. Spaces that have been left blank represent values that were either below detection limits or were not determined.

	1992	1996	2000	1992	1996	2000	1992	1996	2000	1992	1996	2000
Site	Cu	Cu	Cu	Pb	Pb	Pb	Zn	Zn	Zn	Cr	Cr	Cr
Upper Pecos	17	23	20	30	31	17	110	86	88	28	35	35
Jack's Creek	40	42	14	110	99	21	330	325	97	35		32
Above Willow Creek	52	44	23	113	65	32	371	249	156	220	31	32
Below Willow Creek	310	419	92	300	279	157	3100	2902	2080	62	46	33
Теггего	84	78	48	116	84	80	977	1004	755		34	36
Above Hatchery	55	44	24	94	57	37	1300	944	325	22	21	33
Below Hatchery	35	39	130	67	54	543	830	488	374	19	24	28
Below Village	270	28	30	590	38	93	990	319	287		21	42
Below Glorieta		24	22		39	44		173	213	22		36
San Miguel	19	15	8	27	28	13	51	33	35	24	25	34
Villanueva	17	16	4	44	27	15	75	27	157	28	25	32
Tecolotito	11	14	8	18	20	31	45	25	49	95	95	27
Dilia Stream	15	10	10	21	20	22	32	. 21	62	18	18	69
Below Santa Rosa		12	4		25	32		34	38			46
Puerto Del Luna	<15	12	6	21	24	17	37	30	59	16		31
Below Sumner Dam		18	14		68	31		36	39			35
Fort Sumner	<15	37	9	21	32	28	27	28	· 69	13		59
Hway 70	<15	36	17	114	27	26	66	31	146	80		47
Hagerman	<15	33	9	19	21	16	18	25	60	14		50
Below Brantley Dam	9	32	5	30	24	18	24	27	41	16		38

Data obtained from FAAS and XRF for Cu, Pb, Zn, and Cr are compared in Table 5. Not all of the sampling sites are represented due to lack of sufficient sample. The FAAS and XRF data for Cu and Pb are similar; whereas the Zn and Cr data show deviations between the two techniques.

# **Conclusions**

Sediment concentrations of Cu, Pb, Zn and Cr have decreased over the eight-year sampling period. Reclamation of the Alamitos Canyon mill was completed by 1996 and concomitant with reclamation there was a dramatic decrease in Cu, Pb, and Zn in sediments collected below the confluence of Alamitos Creek



FIGURE 4. Comparison of copper concentrations in stream sediments.



FIGURE 5. Comparison of zinc concentrations in stream sediments.

and the Pecos River in 1996. Reclamation of the Pecos area campgrounds and roads was completed by 2000; reclamation of the Pecos mine is ongoing. The decrease in metal concentrations over the past eight years reflects the reclamation efforts that have taken place.

Sediment concentrations of Cu, Pb and Zn have increased immediately below the Lisboa Springs Fish Hatchery. Prior to the 2000 sampling trip, the hatchery raceways were drained and cleaned in response to a parasitic disease contacted by the fish and were empty at the time of sampling. The elevated concentrations of these metals downstream could have resulted from the draining and cleaning of the raceways. The hatchery depends to a very large extent on river water for the raceways. The high metal sediment washed out of the raceways could have come originally from the river.



FIGURE 6. Comparison of lead concentrations in stream sediments.



FIGURE 7. Comparison of chromium concentrations in stream sediments.

The agreement between the FAAS data and XRF data is quite good for copper and lead. Zinc data is generally lower for FAAS than XRF, with a few anomalous exceptions, which is probably due to the inability to completely acid extract all of the zinc from the sediment. Chromium concentrations are consistently lower, and in some cases, much lower for FAAS than XRF. This may also be a result of incomplete acid extraction of chromium from the sediment sample.

#### **Acknowledgements**

We thank the New Mexico Bureau of Mines and Mineral Resources and associated Chemistry Labs for the continued use of their facilities during this project. We also would like to thank Terry Thomas for his help in the lab and Kelly Donahue for sample preparation. Chris McKee (NMBMMR) analyzed some samples by X-rayfluorescence using the Phillips PW 2400 instrument purchased with funds from NSF grant EAR-9316467.