GEOCHEMICAL DISPERSION IN SOILS ON THE ALAMOSA RIVER FLOODPLAIN, SAN LUIS VALLEY, COLORADO

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INTRODUCTION[1]

Acid-mine drainage has been identified recently as an environmental issue in Colorado (Plumlee and others, 1993) because of the downstream impacts on fisheries, on drinking-water quality, and on agricultural uses of water for irrigation and animals. The Summitville Mine, an open-pit, cyanide heap-leach gold mine, located in the San Juan Mountains of southwest Colorado is one source of acid-mine drainage that has received considerable attention (Posey, Pendleton, and Van Zyl, 1995). The mine site was declared a Superfund cleanup site by the U.S. Environmental Protection Agency in 1994.

What is important here is that drainage from the mine enters Wightman Fork, a tributary of the Alamosa River, which then flows into the San Luis Valley and joins the Rio Grande. The San Luis Valley has a significant agricultural industry that could be adversely effected by that drainage. Because of this perceived impact on agriculture in the San Luis Valley, the Alamosa River was an important focus for this study for two reasons: (1) the river is a source of water used for irrigation and (2) soils on the Alamosa River floodplain that developed on sediments partly derived from mineralized source rocks are widely used for agriculture. Much of the sediment carried in the Alamosa River is intercepted in Terrace Reservoir, which is one of the major water sources for agricultural irrigation in the valley.

The identification of element dispersion patterns in transported sediments on alluvial fans is a common tool used in geochemical exploration to search for potential mineral deposits located upstream within a watershed. In the present study, the application of this technique was reversed to examine the extent of downstream effects from metal-laden sediments derived from a known source, such as, the Summitville Mine. The Creede Mining District located west of the study area is also an upstream source of metal-laden sediments on the Rio Grande. The downstream effects could include excessive acidity of irrigation water, elevated concentrations of dissolved metals in the water, and elevated concentrations of metals in alluvial soils that are developed from the sediments. This report addresses the latter effect.

Nearly 1000 soil samples were collected from throughout the San Luis Valley to determine a geochemical baseline against which any sedimentation effects along the Alamosa River could be judged (Tidball and others, 1995). The present report is based on a subset of those soil samples collected only from the southwestern part of the valley, namely those collected south and west of the Rio Grande including the alluvial fans of the Alamosa River and adjacent drainages from the Conejos River on the south to the Rio Grande on the north. The purpose is to determine the magnitude and extent of dispersion of selected anomalous metals in alluvial soils and overbank sediments.

These results should be judged in their proper perspective. Basin fill materials are of course chronologic in deposition, and the near surface sampling represents comparatively recent erosional and depositional episodes. Even so those episodes could span one to several millennia, and thus could represent the cumulative effects of the following: natural erosional processes occurring during Holocene time, outwash from historical mining during the past 120 years, and outwash from the open-pit mining at Summitville Mine during the most recent decade. The sediment transport load into the valley has surely diminished since 1912 when Terrace Reservoir first began to intercept some of the sediment load of the Alamosa River.

Acknowledgments

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[1] The use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the U.S. Government.

GEOLOGIC SETTING

The San Luis Valley is an intermontane structural depression, the northern extension of the Rio Grande Rift system (Tweto, 1979; Burroughs, 1981). The depth of basin fill material ranges from near zero on the western side of the valley to about 19,000 feet near the eastern margin (Burroughs, 1981). The San Juan volcanic field borders the entire western side of the valley and constitutes the source rock for sediments in much of the valley. Steven and Lipman (1976) identified 15 calderas in the field, and 3 more were postulated by Steven and others (1974) based on the complex stratigraphy of 18 major ash flows sheets. Of particular concern here, the Platoro caldera complex lies partly within and adjacent to the Alamosa River watershed (Lipman, 1975). The Summitville caldera is defined by Lipman as a probable late collapse of only the northwest part of the Platoro caldera. Hydrothermal alteration and mineralization developed at intersections of intrusive and extrusive centers with the marginal ring fracture structures during subsidence of the Platoro complex. Thus the possible sources of metal-rich acid waters in the watershed are multiple (Kirkham, Lovekin, and Sares, 1995). Wightman Fork, a tributary of the Alamosa River, is a major source of both solid-phase and water-extractable Cu, extractable Zn, and total As in overbank sediments (Stewart and others, 1995). Alum Creek, a tributary above Wightman Fork, was identified as a major source of Pb.

ORE MINERALS AND ELEMENT ASSOCIATIONS

The ore deposit at Summitville Mine is a low-grade gold-silver-copper deposit developed in an epithermal acid-sulfate system (Gray and Coolbaugh, 1994). A diversity of sulfide minerals at Summitville Mine is hosted among rocks with very limited acid neutralizing capacity. During weathering of these minerals there is a potential to generate large amounts of acid drainage enriched with metals (Plumlee and others, 1995). Sulfide minerals include marcasite (FeS_2), pyrite (FeS_2), enargite (Cu_3As_4), luzonite (Cu_3AsS_4), native sulfur (S), covellite (CuS), chalcopyrite ($CuFeS_2$), tennantite (($Cu, Fe, Zn)_{12}As4S_{13}$), plus minor amounts of sphalerite (ZnS), galena (PbS), and the sulfate, barite ($BaSO_4$).

What sort of metal dispersion could be expected from such an assemblage? Multivariate analysis based on soil sample compositions that included 31 elements showed two significant element associations in the soils developed on Alamosa River sediments (Tidball and others, 1995): (1) As-Cu and (2) Pb-Zn. Sulfur was primarily associated with the alkaline-earths, Ca, Mg, and Sr, which are most prominent as evaporites in the northeastern part of the valley

METHODS

Soil samples were collected in 1993 from 762 sites in the southwestern part of the San Luis Valley encompassing the Alamosa River floodplain and adjacent drainages between the Conejos River and the Rio Grande (Tidball and others, 1995). Each sample was collected from a depth of 0-12 inches (0-30 cm) using a stainless steel auger. Samples sites were located on a grid with approximately one-mile intervals. Each site was near the section corner but at least 200 feet (60 m) away from roads or farm buildings to minimize the possibility of contamination. Many sites were in cultivated fields and pastures that had been variously subjected to irrigation using either Terrace Reservoir or Rio Grande water or both.

All samples were sieved through a 2-mm stainless steel screen and the -2 mm fraction was saved. A representative subsample was ground to -100 mesh and decomposed with multiacids—HNO_3, $HClO_4$, and HF. The solution was analyzed for *total* concentrations of 40 elements including Cu, P, Pb, and Zn by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Lichte, Golightly, and Lamothe, 1987). Total S was determined by combustion with detection by infrared absorption (IR) (Curry, 1990). Total As and Se were determined by flow injection hydride-generation-atomic absorption spectroscopy (HGAAS) (Crock and Lichte, 1982; Welsch, Crock, and Sanzolone, 1990). Total Hg was determined by continuous flow-cold vapor-atomic absorption spectrophotometry (CVAA) (O'Leary, Crock, and Kennedy, 1990). Lower limits of detection for the methods used is shown in Table 1.

Color-filled contour maps of single element distributions were created to summarize and smooth the scattered data observations using the computer software, Earthvision[©], version 2.0, by Dynamic Graphics. The gridding algorithm is a minimum tension procedure. Because our interest lies in the more elevated concentrations as viewed against a background of lower values, only the 50th, 90th, 95th, and 99th percentiles of the frequency distributions are contoured.

Table 1.—Lower limits of determination for analytical methods used in this study

Element	Lower limit of determination	Method [1]
As, ppm	0.6	HGAAS
Cu, ppm	2	ICP-AES
Hg, ppm	.02	CVAA
P, percent	.005	ICP-AES
Pb, ppm	4	ICP-AES
S, percent	.05	IR
Se, ppm	.1	HGAAS
Zn, ppm	2	ICP-AES

[1] HGAAS—hydride-generation atomic spectroscopy
ICP-AES—inductively-coupled argon plasma-atomic emission spectroscopy
CVAA—cold vapor atomic absorption
IR—combustion/infrared detection

For purposes of this study, anomalous concentrations of an element are defined as those equal to greater than the 95th percentile of the frequency distribution for that element. Thresholds at the 95th percentile for the several elements are shown in figures 1-8, respectively.

RESULTS AND DISCUSSION

The distribution patterns of selected metals as illustrated in figures 1-8 clearly distinguishes both the Alamosa River and the Rio Grande from among the several drainages which emerge from the San Juan volcanic field. Copper, Pb, and Zn (Figures 1-3) exhibit distinctive dispersion trains that confirm an upstream source, but different metals characterize the two rivers. Arsenic, P, S, and Se have accumulated along the lower part of the Alamosa River floodplain. A few samples containing slightly elevated concentrations of Hg and Se are also clustered on the mid part of the Alamosa River floodplain. Ranges of concentrations for several elements are compared in Table 2 with the geometric means of soils within the greater San Luis Valley and the western U.S. These means may be taken as estimates of background values.

Copper exhibits a distinctive dispersion train singular to the Alamosa River floodplain (see figure 1). Anomalous values are judged to be greater than about 47 ppm, and the maximum Cu concentration found was 140 ppm. Based on evidence found in overbank sediments for both water-extractable Cu and total Cu (Stewart and others, 1995), the principal source of the Cu is the Summitville Mine.

Lead (Figure 2) is dispersed on the floodplains of both the Rio Grande and the Alamosa River. Metal sources in the Rio Grande watershed, for example the Creede Mining District, probably represent a more significant source of Pb than anything in the Alamosa watershed. Highly anomalous samples along the Rio Grande have Pb values of 120-280 ppm whereas anomalous samples along the Alamosa have a lower range of 34-74 ppm. Most of the Pb in the Alamosa watershed appears to come primarily from the Alum Creek drainage and secondly from Wightman Fork (Stewart and others, 1995).

Table 2—Comparison of element concentration ranges and geometric means between soils of the Alamosa study area and soils of the wider San Luis Valley and the western U.S.

Element	Range in study area	Mean, soils in study area	Mean, soils of San Luis Valley[1]	Mean, soils of western U.S.[2]
As, ppm	4.9-26	5.2	4.6	5.5
Cu, ppm	7-140	24	22	21
Hg, ppm	<.02-.77	<.02	--	.046
P, percent	.05-.62	.12	.11	.032
Pb, ppm	2.8-380	19	19	17
S, percent	<.05-9.4	.083	.073	.13
Se, ppm	<.1-2.9	.21	.33	--
Zn, ppm	40-590	92	86	55

[1] Tidball and others, 1995
[2] Shacklette and Boerngen, 1984

Zinc tends to occur with Pb as shown by multivariate factor analysis (Tidball and others, 1995), and this element association was found on both the Rio Grande and the Alamosa River. When viewed as a single element (Figure 3), however, Zn is anomalous (greater than 130 ppm) on the Rio Grande but only slightly elevated above background (92 ppm) on the Alamosa River. Concentrations of Zn range from about 300-590 ppm on the Rio Grande floodplain and 120-140 ppm on the Alamosa floodplain.

Arsenic, P, S, and Se all exhibit accumulations near the mid part of the Alamosa River floodplain (see Figures 4-7), but any continuous dispersion train extending from the mountain front is absent. The dispersion patterns suggest that these elements have moved and accumulated in dissolved form. A model for the weathering and transport of Se as described by Presser and others (1990) in California's San Joaquin valley may well apply on the Alamosa River fan.

This model is described in terms of Se, but it could extend to other similar elements. Selenium can substitute for S in insoluble selenides resident in rocks in the Coast Range mountains. The selenide upon exposure to surface weathering becomes oxidized to the soluble selenate form, which is then carried down gradient in the shallow groundwater moving through basin-fill materials dipping toward the valley center. Dissolved salts then accumulate as evaporites near the lower extremity of the fan where the water table is close to the surface and warm, arid conditions enhance evapotranspiration.

The setting in the San Luis Valley is similar to that of the San Joaquin wherein the hydrologic gradient follows the sedimentary beds that dip downward from the western mountain front toward the valley center (Emery and others, 1971). Following such a gradient, dissolved salts have indeed accumulated as evaporites in the northeastern part of the San Luis Valley in an area of internal drainage (Edelmann and Buckles, 1984; Tidball and others, 1995). Artesian wells are common in various parts of the study area attesting to the pressure of the shallow groundwater. The climate is arid though not as warm as California. The soils are commonly alkaline, and precipitates in the soils are widespread particularly where irrigation is insufficient to leach the soils.

Arsenic tends to be associated with Cu (Tidball and others, 1995). Anomalous values are those greater than about 10 ppm. The maximum value found was 26 ppm. Arsenic could originate from any of several As-bearing minerals noted by Plumlee and others (1995) in the Summitville deposit for example. Stewart and others (1995) reported a significant increase in As and Cu in overbank sediments along the Alamosa river below Wightman Fork, which drains Summitville Mine.

Sulfur most likely occurs in floodplain soils as sulfate precipitates typically associated with alkaline-earth elements (Tidball and others, 1995). There are 30 samples with values greater than one percent and the maximum is 9.4 percent. The sulfate is transported into the valley in part in the acid waters of the Alamosa River. Sulfate arises from the transformation through weathering of native S and sulfide minerals to sulfate from both natural sources (Miller and McHugh, 1994) and mining sources (Plumlee and others, 1993). Valley soils are normally moderately to extremely alkaline, and the presence of sulfate in the soil does little to change the pH.

Phosphorus, Se, and Hg (figure 8) are worthy of mention not so much for the anomalous concentrations found, but rather for the clustered distributions that appear to be related to the Alamosa River. The specific source of these elements is unknown, but they are assumed to be accessory elements in the volcanic centers in the watershed.

Soluble elements such as As and Se could have potential environmental impact, but only if there were circumstances that would cause significant secondary accumulation, such as, evaporation ponds or bioaccumulation by plants. Concentrations of Se found on the Alamosa River fan (1-3 ppm) compare with a maximum of only 4 ppm as found in the San Joaquin Valley (Tidball and others, 1989). In the latter case, Se concentrations were enriched in algal mats and salt crusts in evaporation ponds to 15-20 ppm, and up to 100 ppm were found in dredged sediments (Presser and Barnes, 1985). No similar concentrator is known in the San Luis Valley.

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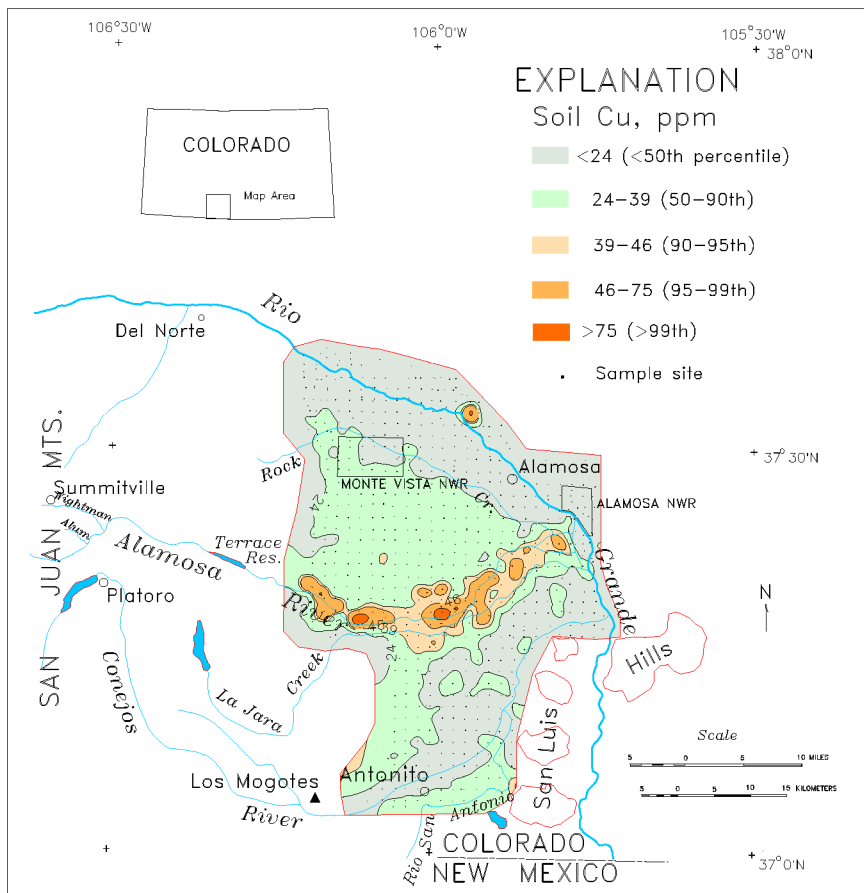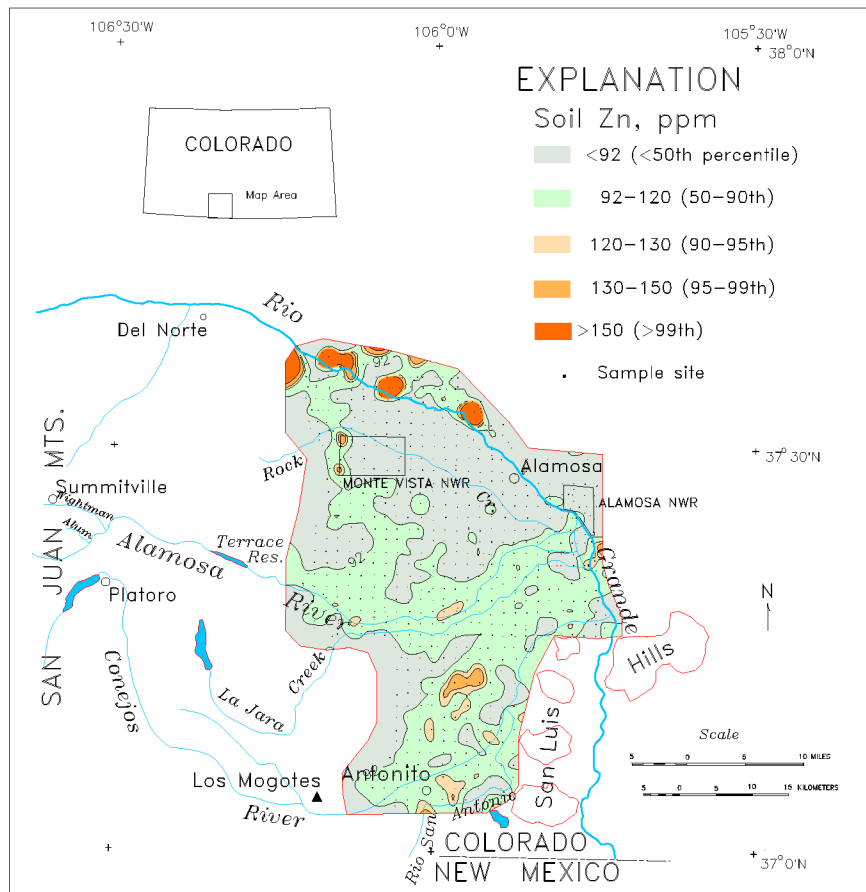
Figure 1.—Copper in soils in the southwestern part of the San Luis Valley, Colorado. Distribution is contoured by percentiles.
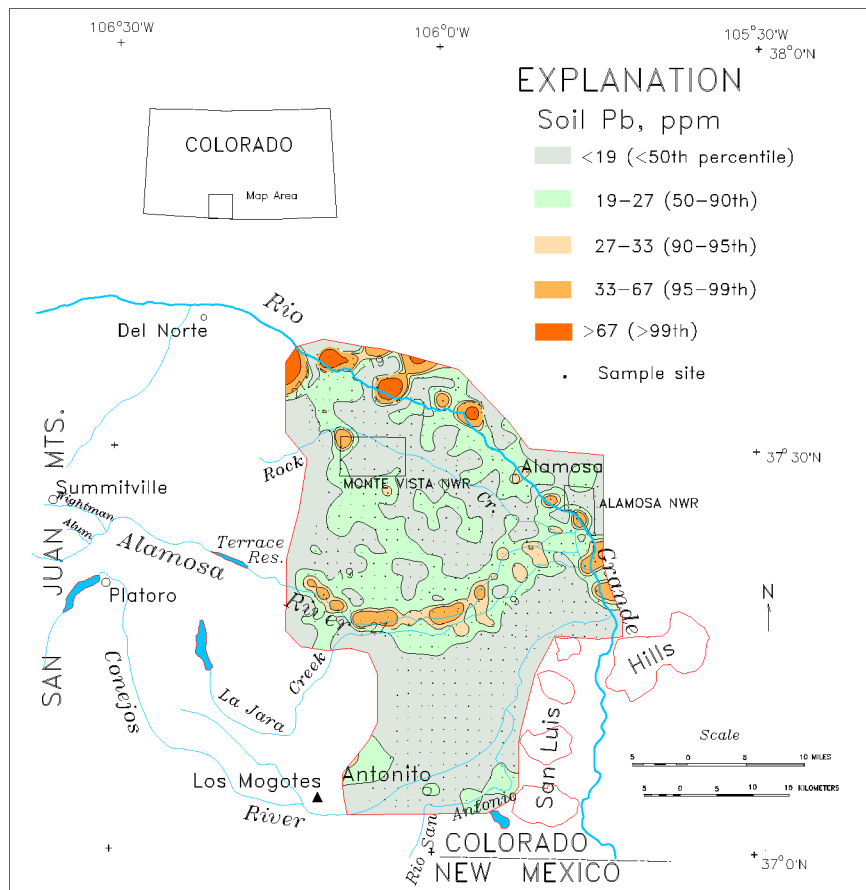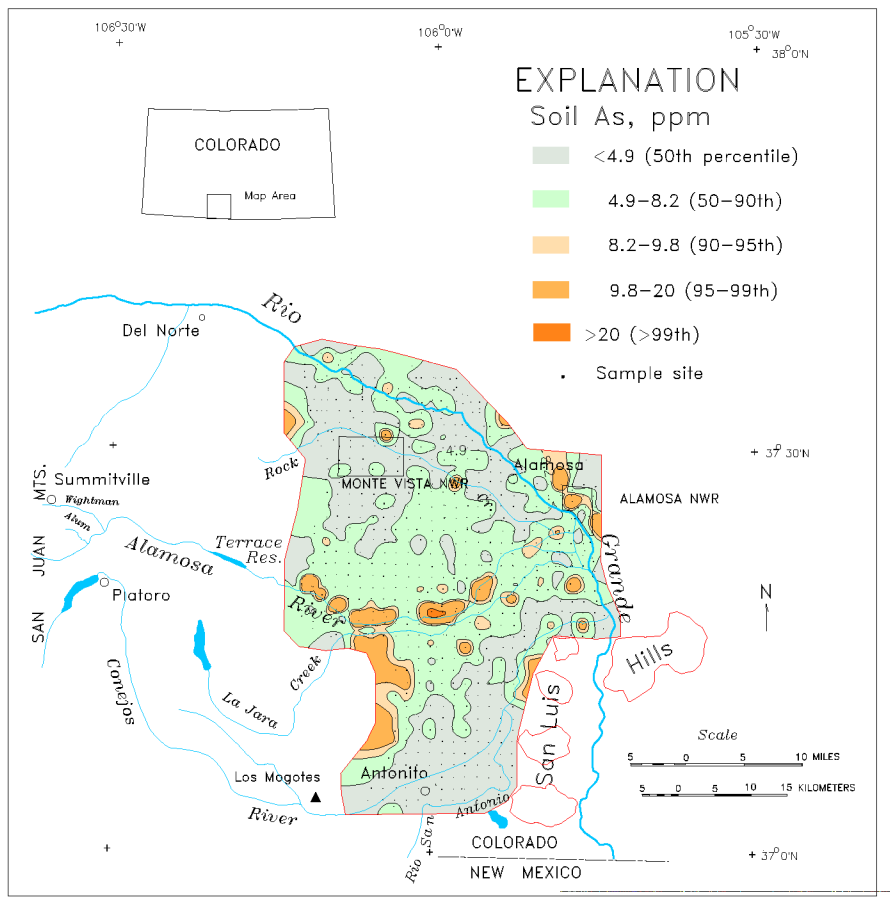
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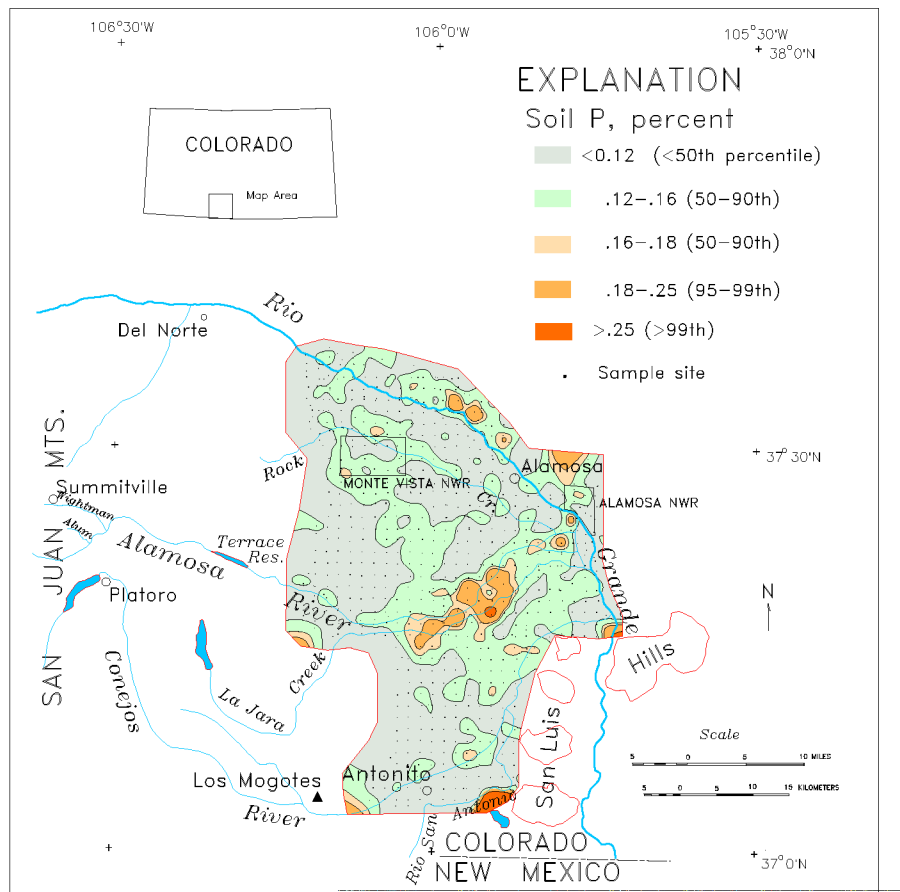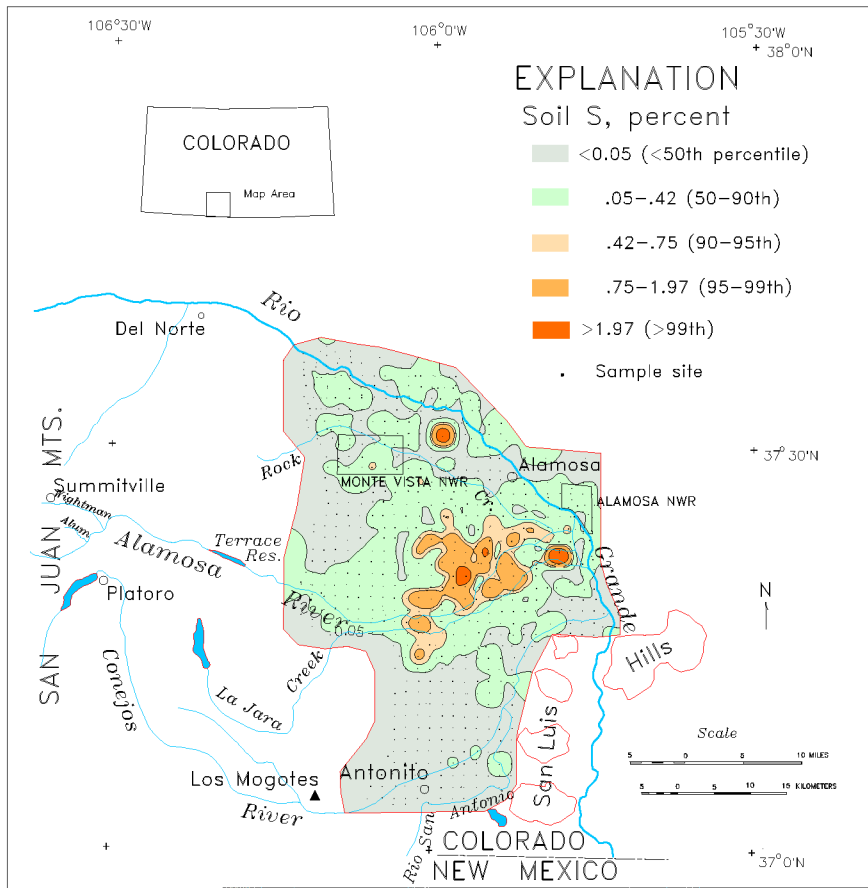
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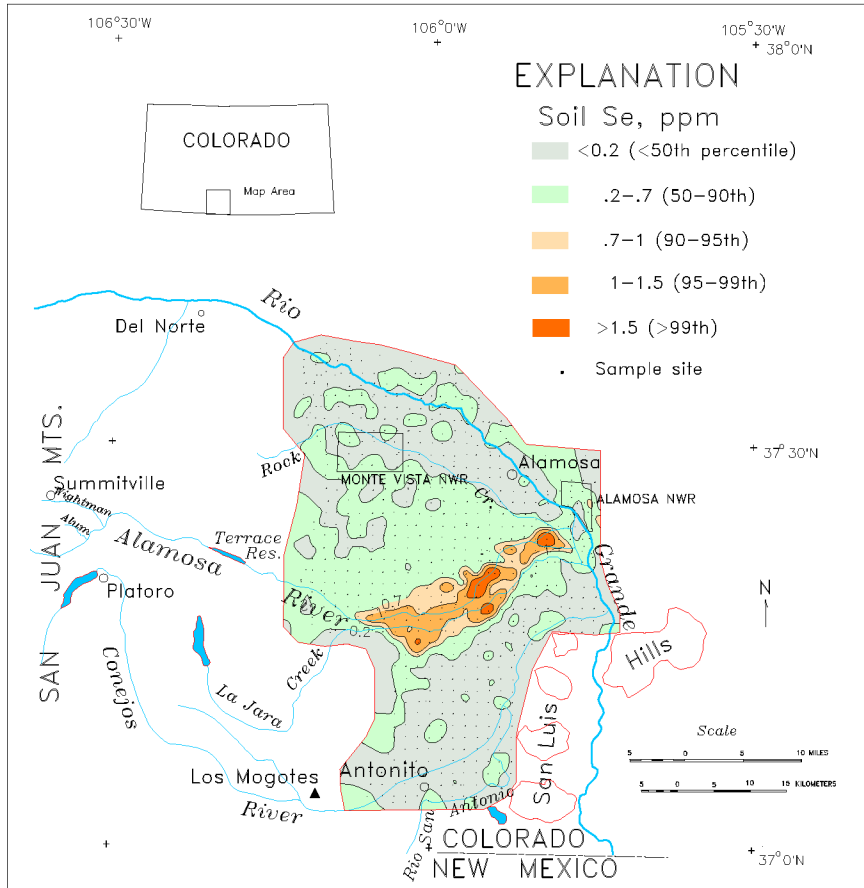
Figure 4.—Arsenic in soils in the southwestern part of the San Luis Valley, Colorado. Distribution is contoured by percentiles.
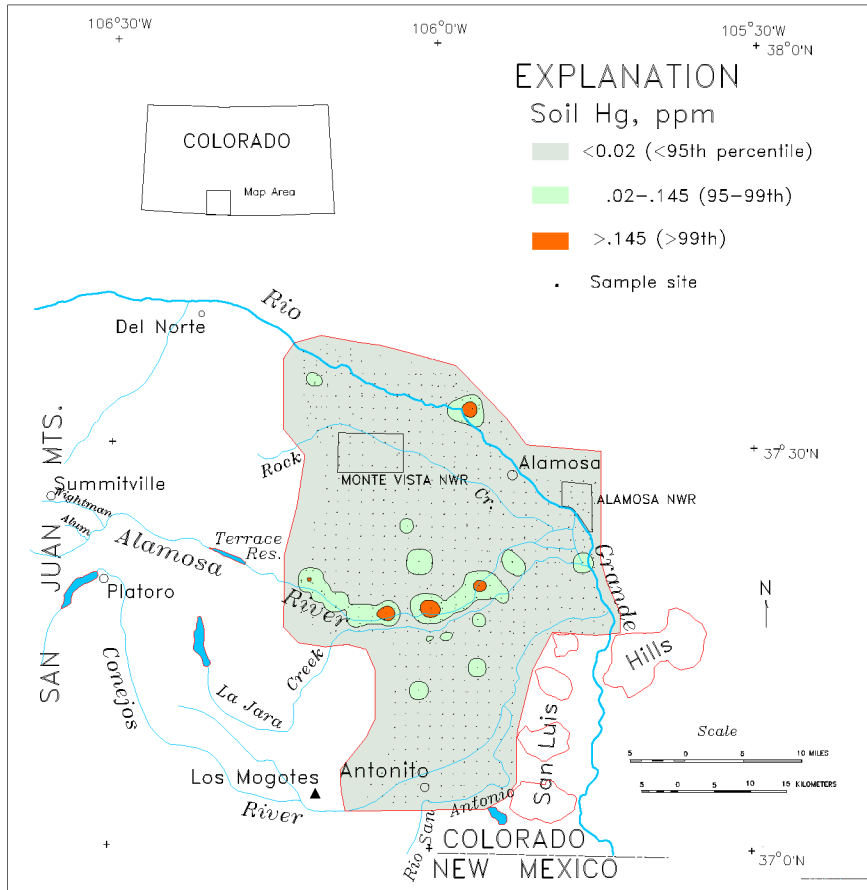
Figure 5.—Phosphorus in soils in the southwestern part of the San Luis Valley, Colorado. Distribution is contoured by percentiles.

Figure 6.—Sulfur in soils in the southwestern part of the San Luis Valley, Colorado. Distribution is contoured by percentiles.

Figure 7.—Selenium in soils in the southwestern part of the San Luis Valley, Colorado. Distribution is contoured by percentiles.

Figure 8.—Mercury in soils in the southwestern part of the San Luis Valley, Colorado. Distribution is contoured by percentiles