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Geochemical processes contributing to the contamination of soil and surface waters in the Rio Conchos basin, Mexico

Melida Gutierrez

Carlos Martinez-Pina

Jun Luo

Kevin L. Mickus
Missouri State University

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Mélida Gutiérrez
Geography, Geology and Planning, Missouri State University, Springfield, Missouri 65897, USA

Carlos Martinez-Pina
Department of Geosciences, University of Texas at El Paso, El Paso, Texas 79968, USA

Jun Luo
Kevin Mickus
Geography, Geology and Planning, Missouri State University, Springfield, Missouri 65897, USA

ABSTRACT

A geochemical characterization of the middle Rio Conchos basin is presented based on two contaminants, salts (Ca and Na) and toxic metalloids (As and Sb). Their content in surface water and sediment samples was determined, and their spatial distribution was mapped to show the relationship to each other, to the geology and hydrology, and to other potential factors affecting their distribution (i.e., prevailing winds). Correlation analyses between salts, toxic metalloids, and associated elements, and their spatial distribution aided in determining their sources, which included mines, rock outcrops, urban centers, irrigation waste water, and agricultural runoff. The salinity of the Rio Conchos reached a critical level after receiving waters of its contaminated tributary Rio Chuviscar and irrigation drain returns from the Irrigation District 005, but further downstream the water quality improved when it mixed with Ca-rich water, significantly reducing its Na concentration. Based on its spatial distribution, the content of As in alluvial material was found to be associated with the presence of Ag-Pb mines and to a lesser degree to Oligocene ignimbrites. A correlation of As with Sb, Cu, and Bi suggests that natural sources are the dominant contribution of As within the area, although concentrations above permissible level for water were found in river water samples at a few places where sewage was also present, suggesting an additional (anthropogenic) important source of As. A characterization of natural sources affecting the chemistry of surface waters is a first step toward understanding the natural processes taking place and for documenting natural background levels that are needed to predict the response of the environment to various human activities.

Keywords: arsenic, Chihuahua, Chihuahuan Desert, Rio Conchos, salts, metalloid, water chemistry, water resource, water pollution.

INTRODUCTION

The Rio Conchos is an important river within the Chihuahuan Desert and the largest tributary of the Rio Grande in spite of its relatively modest discharge (Hudson et al., 2005; International Boundary and Water Commission [IBWC], 2007a). The Rio Conchos provides surrounding communities with surface water for irrigation, habitat for wildlife, recharges aquifers, and (unfortunately) it is also used as a medium to dispose of domestic wastewater and irrigation drain returns. The latter degrade its water and habitat quality (Kelly and Arias Rojo, 2007).

Efforts toward a sustainable management of the Rio Conchos basin have emerged in the past few years, as evidenced by contributions presented at international scientific conferences hosted in Delicias (May 17–18, 2007) and Chihuahua City (June 6–8, 2007) and workshops offered on sustainability of natural resources (Center for Research in Water Resources, 2005; Secretaria de Medio Ambiente y Recursos Naturales, 2007; World Wildlife Fund, 2007). A notable example discussed in both of the congresses mentioned above is Caudal Ecologico, a plan to maintain a minimum amount of water in the river to help the survival of aquatic organisms (Zapata, 2007). In order for these and other remediation efforts to succeed, a characterization of major sources affecting the chemistry of the surface waters is an important step toward understanding the natural processes occurring and to document natural background levels. Once this characterization is complete, the response of the environment to possible scenarios of human activities could more easily and reliably be predicted.

The objective of this study was to determine the main geochemical processes taking place in a river in an arid environment and to find a plausible explanation for the presence of calcium and sodium (main components of water salinity) and toxic metalloids (arsenic and antimony). For this purpose, surface-water data collected by Gutiérrez were complemented with sediment geochemical data acquired from the Servicio Geologico Mexicano (SGM). The spatial distribution of the elements was tied to the geology, hydrology, and other factors presumed to affect their presence using geographic information system (GIS) and satellite images. The results fill an important gap in knowledge about the extent to which water composition is affected by geological factors, e.g., the composition of rock outcrops and the presence of mine tailings. We used a variety of methods to perform these characterizations, described in more detail in the following.

Water Quality

Water quality data for the Rio Conchos are scarce and at the present time there is no monitoring of water quality. Until 2002, the International Boundary and Water Commission (IBCW) monitored water quality at a station near Ojinaga as it entered the Rio Grande, but sampling stopped in 2003. Five other water quality stations on the Rio Conchos purportedly exist (Kelly, 2001), but these data are not publically available. A limited number of studies have been conducted, each with a specific goal and small number of samples (Gutiérrez and Borrego, 1999; Rubio-Arias et al., 2005; Holguín

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et al., 2006; Gutiérrez-Espinoza et al., 2007). Additional data are included in hydrologic maps (Instituto Nacional de Estadística, Geografía e Informática [INEGI], 1984a, 1984b).

Salinity variations within the entire Rio Conchos with time have not been reported, except for a study in the lower Rio Conchos by Gutiérrez and Carreón (2004) using IBWC data. This study found that the salinity of the river increased during dry years but the relation between salinity and precipitation was nonlinear, indicating that factors other than precipitation affect salinity.

Remote Sensing, GIS, and Sediment Geochemistry

Satellite imagery data can offer a useful tool in the determination of salt-affected soils, vegetation growth, and land use, as they allow remote areas to be accessible and facilitate the temporal analysis of quality parameters (Jensen, 2007). The spatial and spectral resolution of satellite imagery data resolution varies depending of the instrument utilized; some of the imagery data most commonly used in environmental and geologic work are Landsat thematic mapper (TM) and enhanced (ETM) mapper (30 m spatial resolution and 7 spectral bands), Spot (10 m spatial resolution and 4 spectral bands), and Quickbird (4 m spatial resolution and 4 spectral bands). In spite of its lower resolution, Landsat remains a popular type of image used in these studies because of its low cost, number of years of operations (>30 yr), and relatively high spatial and spectral resolution. Numerous investigations have focused on soil salinity in arid areas using remote sensing (Metternicht and Zinck, 2003) and in combining GIS and remote sensing for watershed assessment (e.g., Basnyat et al., 2000; Perez-Gonzalez et al., 2006).

Numerous investigators have used geochemical analyses of sediment to study contaminant impact on streams (Vincent et al., 1999; Hudson-Edwards and Taylor, 2003; Box et al., 2005). National geochemical databases consisting of chemical composition of a grid of samples became available to the U.S. in 1994 (Hoffman et al., 1994) and in Chihuahua, Mexico, in 2001 (SGM, 2001). Although these databases were originally intended for geochemical exploration purposes, they were later found to provide an inexpensive and accessible information source for conducting geochemical characterization (Borrego and Gutiérrez, 2000; Xuejing and Hangxin, 2001).

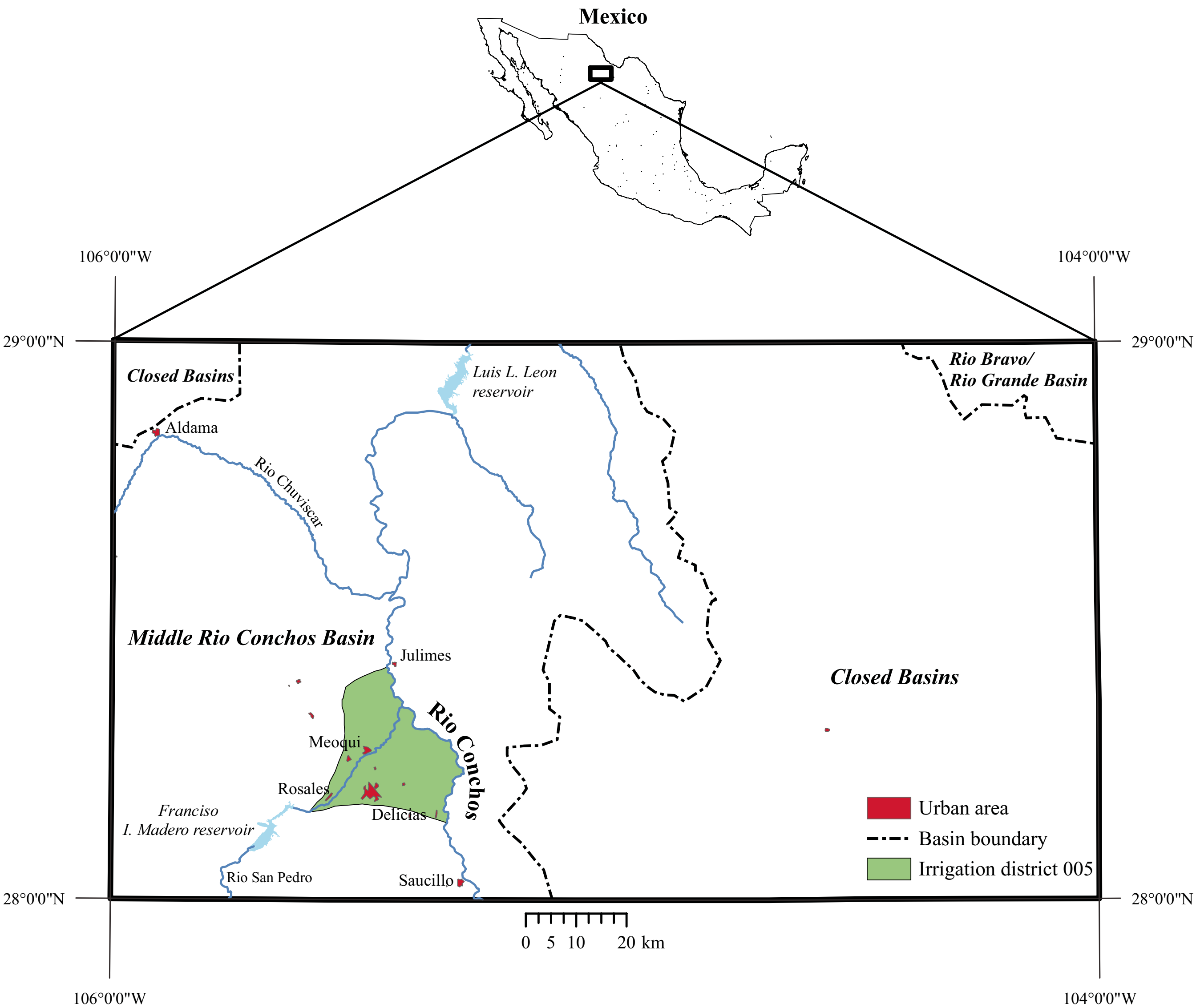

Figure 1. Location of the study area showing the major hydrological basins, rivers, and urban areas.

Within the Rio Conchos basin, sediment geochemistry and geospatial (GIS, remote sensing) studies are just as scarce as those of water quality. Among these, Carreón-Hernandez et al. (2001) classified riparian quality using Landsat TM imagery, and Gutiérrez et al. (2004) used Landsat TM data to report the temporal variation in the size of reservoirs and the amount of cultivated land along a section of the Rio Conchos.

STUDY AREA

The study area comprises a 1° × 2° quadrangle between 28°–29°N and 104°–106°W (Figs. 1 and 2). The area is in an elevated plateau that is part of the Chihuahuan Desert. The largest city within this area is Delicias (population 127,200); other towns are Meoqui, Saucillo, Rosales, Aldama, and Julimes. The study area is crossed by the Rio Conchos and tributaries Rio Chuvíscar and Rio San Pedro. Important reservoirs on these rivers are the Luis L. León (296×10^6 m^3 storage capacity) and Francisco I Madero (343×10^6 m^3) (INEGI, 1999). Along the Rio Conchos and near Delicias, Irrigation District 005 was created in 1932 to irrigate 105,000 ha of desert land (Fig. 1). The amount of cultivated land during most years is significantly less due to water shortages. Modernization and technical improvements of the water distribution system were recently implemented in this irrigation district to increase crop production while using a minimum of water and the same acreage of cultivated land (Comisión de Cooperación Económica Fronteriza, 2002). Three of the most important aspects that cause and help distribute the natural contaminants are described in the following.

Geology

The geologic history of the study area is diverse, as evidenced by a wide variety of geologic units (Fig. 2). Except for two locations in the north-central and northwest section of the study area, where Paleozoic sedimentary rocks (limestones) crop out, the units exposed are primarily Cretaceous limestones with smaller amount of shales and evaporites, Tertiary conglomerates, and Tertiary volcanics (Oligocene ignimbrites and minor amounts of basalts and Eocene andesites and rhyolites) (INEGI, 1984a; Alam-Hernández et al., 1998; Ferrari et al., 2007). The Cretaceous limestones and evaporites were deposited in the Chihuahua trough, a deep asymmetric basin built upon the fossil Triassic–Jurassic magmatic arc that slopes gently basinward to the west (Coney and Reynolds, 1977). However, at the end of the Mesozoic, major magmatic activity that is commonly associated with the Laramide magmatic arc (Clark et al., 1982; Ferrari et al., 2007) began to occur throughout western Mexico (McDowell and Keizer, 1977). This magmatic arc produced large volumes of plutonic and volcanic rocks within the Sierra Madre Occidental during the

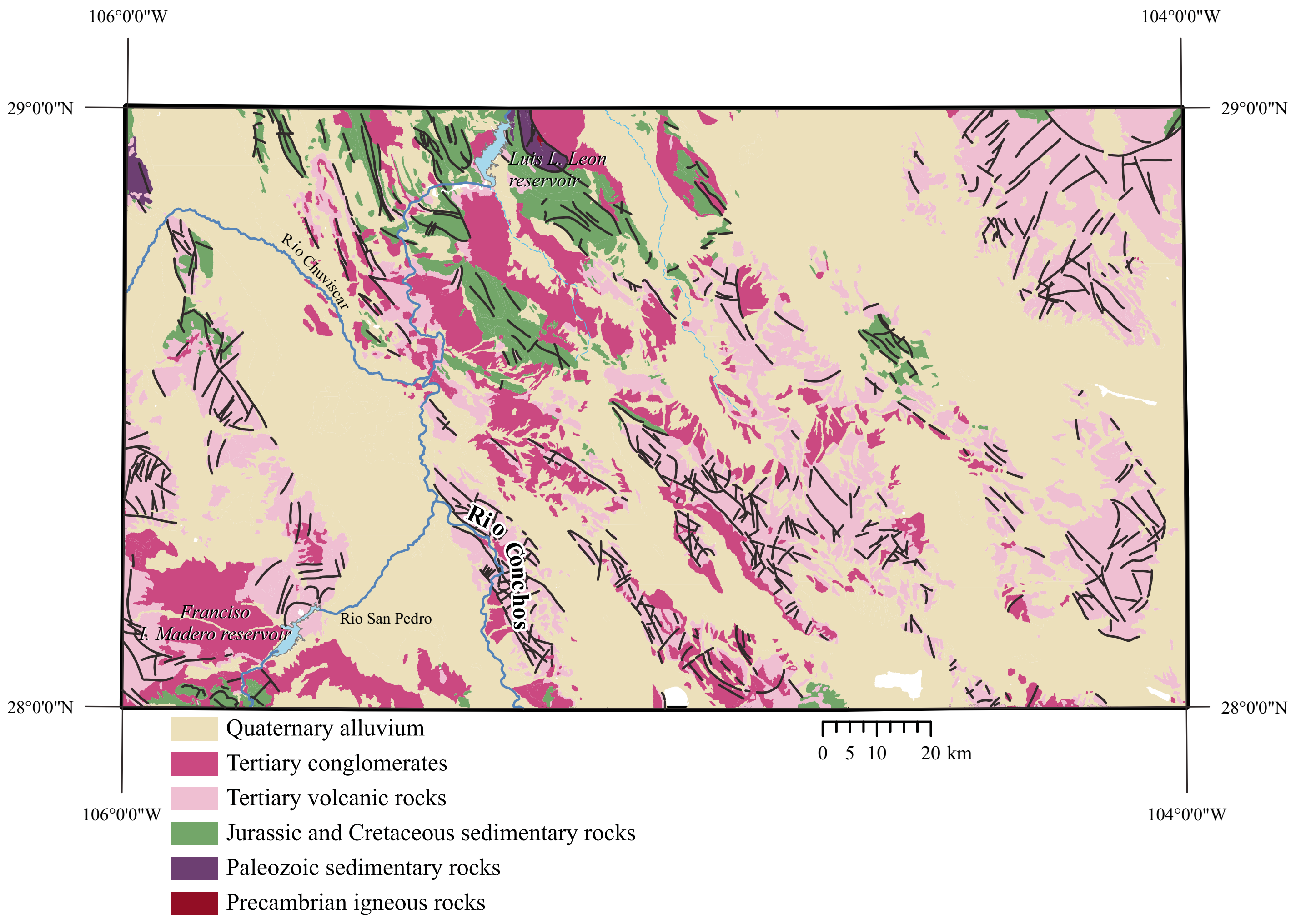

Figure 2. Geologic map of the study area. Thin black lines represent mapped faults. Adapted from Servicio Geologico Mexicano (2001).

Late Cretaceous–Paleocene and was collectively grouped as the Lower Volcanic Complex by McDowell and Keizer (1977). A distinct Eocene magmatic episode is evidenced as various types of ignimbrites within the study area (Megaw, 1990; McDowell and Mauger, 1994). The main Laramide magmatic event (ignimbrite flare up; McDowell and Clabaugh, 1979) deposited thick layers of Oligocene–early Miocene ignimbrites that were related to the magmatic arc that moved from west to east (Clark et al., 1982; Ferrari et al., 2007). These ignimbrites in the Sierra Madre Occidental have thicknesses that exceed 1 km; within the study area they are less massive and occur as either silicic ignimbrites or basaltic to andesitic lava flows (Ferrari et al., 2007).

The compressional forces associated with the Laramide orogeny produced thrust faults within the Chihuahua tectonic belt that were probably soled in incompetent evaporates, with the Cretaceous limestones above the décollement surface being folded (Sedlock et al., 1993). These limestones were transported as much as 80 km to the northeast from central Chihuahua (Sedlock et al., 1993). The magmatic arc migrated from the Sierra Madre Occidental to the Trans-Pecos region in Texas between 100 Ma and 40 Ma, after which it migrated back west. The ignimbrites found in the study area vary in composition from calc-alkaline in the Sierra Madre Occidental in Chihuahua to alkaline volcanic rocks of the Trans-Pecos region (McDowell and Clabaugh, 1979).

From the middle to late Tertiary to the early Pleistocene, extensional forces acting parallel to the Laramide compressional structures produced grabens of the Chihuahua basin and range that gradually filled with sediments derived from the surrounding rocks (Clark and Ponce, 1983; Sedlock et al., 1993). During the Pleistocene, melting of ice and cooler climate conditions were conducive to the formation of lakes (Ortega-Ramirez et al., 1998; Allen, 2005) that occupied in topographically closed basins. Lacustrine deposition in Chihuahua has been reported for the interval ca. 11–2.5 ka (Metcalfe et al., 1997). A decrease in precipitation was evident ~5 k.y. ago, followed by an onset of semiarid conditions a few thousand years ago (Ortega-Ramirez et al., 1998). Evaporation and changes of the hydraulics of the river systems have caused most of the Pleistocene lakes to dry up; pluvial sediments are evidence of their former presence.

Ore Deposits

One important potential source for contaminants within the Rio Conchos basin is ore deposits. Both active and abandoned mines contain potential contaminants (e.g., heavy metals, As, sulfuric acid) from the underground and surface workings, tailings piles, and other waste near the mined areas. The state of Chihuahua contains many types of metallic ore deposits, ranging from porphyry-type systems in the Sierra Madre Occidental to hydrothermally related deposits (including skarn and fissure vein) to magmatic segregation deposits in the Chihuahua trough (Clark and De la Fuente, 1978; Ruiz, 1986; Megaw et al., 1996).

Within the study area there are 34 known mines, and 3 are currently operating (Fig. 3) (SGM, 2001). The ore deposits are mostly associated with the Laramide orogeny, specifically the Eocene and Oligocene volcanic activity related to the formation of the Sierra Madre Occidental (Megaw et al., 1996). This volcanic activity formed the carbonate-hosted lead-zinc deposits (that may also contain Ag, Cu, Au, Fe) that are the most common ore deposits in the study area, in the Santa Eulalia district (San Antonio mine) (Megaw et al., 1996; Alam-Hernández et al., 1998), and at the Carrizalillo, La Negra, and Chorreras mines (SGM, 2001). The other common ore-deposition mechanism is magmatic segregation of iron at the La Perla and La Cantera, associated with volcanic units (Clark and De la Fuente, 1978; Alam-Hernández et al., 1998). Other economically important minerals present in the study area include altered clays and zeolites, which are associated with clay hydrothermal alteration and occur as fissure-vein deposits (Clark and De la Fuente, 1978).

The minerals associated with the sulfide mineral deposits include arsenopyrite (iron-arsenic sulfide), stibnite (antimony sulfide), and pyrite (iron sulfide) (Megaw et al., 1996; Clark and De la Fuente, 1978); As, Sb, and Fe are elements commonly found in soils and groundwater where this type of mineralization occurs (Mueller et al., 2001). Rodriguez-Pineda et al. (2005b) reported a Tertiary rhyolitic tuff with high arsenic content exposed at Sierra El Cuervo, and associated this mineralization with the presence of As in the Aldama aquifer, located in the northwest corner of the study area.

Environmental studies on tailings of mines and mine prospects within the study area are lacking, but studies (Puga et al., 2006) in southern Chihuahua report high concentrations of metals near the source and a strong relationship to the distance away from the tailings. Puga et al. (2006) reported a decrease of As content in the soil around mining tailings, from 2687 mg/kg to 1118 mg/kg to 388 mg/kg at distances of 0, 1500, and 3000 m, respectively, from the tailings. Flores-Tavizón et al. (2003) reported As-contaminated soils near mines and hot springs, and recommended growing arsenic-tolerating plants as a soil remediation treatment.

Hydrology

Groundwater tables range between 50 and 130 m depth between western and eastern parts of the area, respectively (INEGI, 1983a, 1999). The groundwater quality is also quite variable depending on the location and depth of extraction, ranging from good (<525 mg/L total dissolved solids) to saline (>1400 mg/L total dissolved solids) (INEGI, 1983a).

The central part of the study area is drained by the Rio Conchos, flowing in a northwest direction toward its confluence with the Rio Grande at the Ojinaga on the U.S.-Mexico border, and henceforth referred to as middle Rio Conchos basin. The main Rio Conchos tributaries within the study area are the Rio San Pedro and Rio Chuviscar (Fig. 1), but many ephemeral streams (arroyos) also drain the area (Fig. 3). The majority of the water within the above channels is derived from the monsoon season that occurs from June to August and is characterized by intense rains of short duration that produce flash floods in the generally dry beds of ephemeral streams. Because of this climate pattern, the major purpose of all reservoirs in the area is flow regulation. Within the study area there are several closed hydrological basins (Fig. 1) surrounding the middle Rio Conchos basin. A group of several adjacent closed basins located west of the middle Rio Conchos basin belongs to the Cuencas Cerradas del Norte, while the group of closed basins east of the middle Rio Conchos basin is known as Llanos de los Gigantes. At the northwest edge of the study area and within the Cuencas Cerradas del Norte, there is a playa lake, El Cuervo, with a salt content as high as 3450 mg/kg Na and 13,040 mg/kg Ca (INEGI, 1984b). The most important recent hydrological event within the state of Chihuahua was an extended drought from 1993 to 2002, when most of the reservoirs dropped to 20% of their capacity and only 25% of the irrigated lands were cultivated (Rodriguez-Pineda et al., 2005a). During this drought, the playa lakes dried out, increasing the salinity of the topsoil and facilitating the transport of these salts (as aerosols) by wind.

METHODS

Geochemical Data

Water that we collected from the Rio Conchos and its tributaries in 1997 and 2001 consisted of 104 river water and 5 spring samples, respectively. The former were analyzed in the field for temperature, electrical conductivity (EC), and pH, and in the laboratory for 64 elements using an HP 4500 inductively coupled plasma mass spectrometer (ICP-MS) at the Department

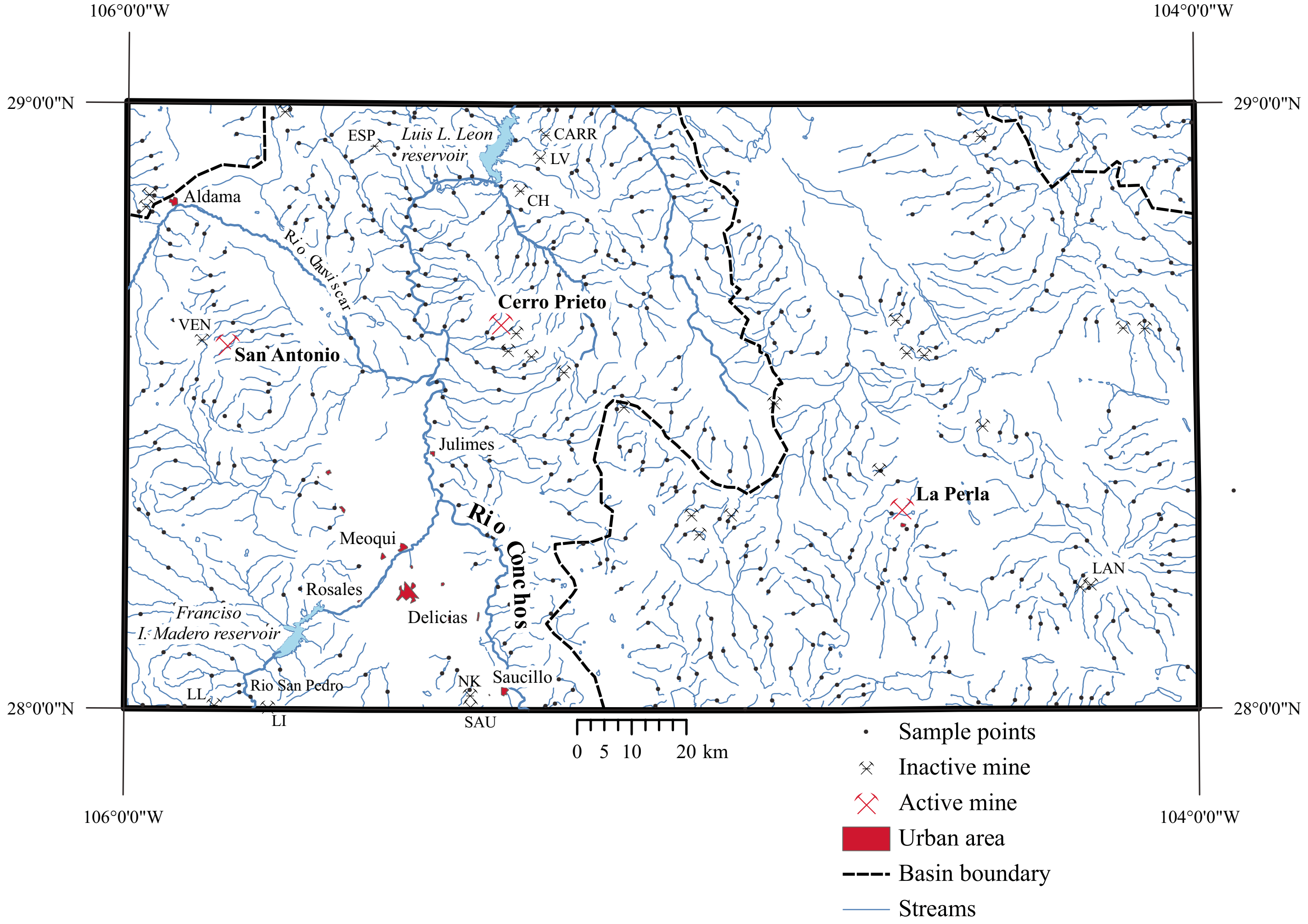

Figure 3. Location of soil samples (circles), and active and abandoned mines (CARR—Carrizalillo, CH—Chorreras, ESP—Esperanza, LAN—La Negra, LI—La India, LL—La Licha, LV—La Verde, NK—Niko, SAU—Saucillo, VEN—La Ventura) within the study area.

of Geosciences, University of Texas El Paso. The general downstream concentration pattern was reported by Gutiérrez and Borrego (1999). Five spring samples collected in 2001 were analyzed for seven elements using a Liberty 150 AX Turbo ICP emission spectrometer. EC was determined in the field for all samples using a conductivity meter and the values were reported in dS/cm (dS—deciSiemens per meter). These values were further transformed to total dissolved solids (TDS) by a conversion factor of 659 mg/L per dS/cm reported by Miyamoto et al. (1995) for the Rio Conchos.

The above data were complemented with data reported on hydrological maps for the area (INEGI, 1983a, 1983b) that contain concentration of cations (sulfate, carbonate, chloride) in addition to five elements (Ca, Na, Mg, K, and Si). Sediment chemistry data (SGM, 2001) and a soil map (INEGI, 1984b) were also utilized in this study. The SGM data for this quadrangle consist of 540 stream sediment samples collected in 1999 from surficial material of dry arroyos. According to SGM protocols, the samples were digested in aqua regia and analyzed for 32 different elements using ICP-MS spectrometry at their laboratory facilities in Pachuca, Mexico. The locations of sediment samples and arroyos are shown in Figure 3. The arroyos were omitted from other figures for simplicity.

Remote Sensing

For this study, we utilized three 1997 Landsat TM (row 40, path 33; row 40, path 32; row 41, path 41), and three 1998 Landsat TM (row 39, path 32; row 41, path 32; row 39, path 33) data. Before applying any type of transformations to the data, the above data sets were rectified to the Universal Transverse Mercator projection system using NAD83 as a datum using ground control points collected by us using a handheld global positioning system receiver. Common image enhancement methods included Gaussian contrast stretching, haze correction, and sun angle removal, and were applied to each data set. In order to enhance areas with higher amounts of surficial gypsum, a false color composite with red (ratio of bands 5 and 4), green (ratio of bands 3 and 1), and blue (ratio bands 7 and 5) was applied (Fig. 4), as determined from laboratory spectral studies of gypsum (Howari et al., 2002). The locations of gypsum highlighted in Figure 4 agree with our field checking.

RESULTS AND DISCUSSION

The quality parameters discussed below are based on chemical elements selected according to their environmental significance. Elements were grouped as salts (Ca, Na, and associated elements Al, Ba, As, Sr, Fe, Mg, K, Se, and U) or toxic metalloids (As, Sb, and associated

elements Al, Bi, Cd, Cu, Cr, Fe, Mn, Ag, Pb, and W).

Salts

Water samples showed a significant increase in the salinity as the river received irrigation drain returns from Irrigation District 005 (Fig. 1), from 250 µS/cm (165 mg/L TDS) to ~1400 µS/cm (920 mg/L TDS), while the Na concentration increased from 25 to 280 mg/L. Nevertheless, the maximum detected salinity of 1400 µS/cm was less than the conventional upper limit for irrigation waters of 2000 µS/cm (Rhoades et al., 1992). A drop in the concentration of Na and concurrent increase of Ca were observed ~60 km downstream from the irrigation district and just before the river reached the Luis L. Leon reservoir. This indicated that Ca-laden waters must be reaching the river. Ca concentrations of nearby springs reported by INEGI (1983a) and Gutiérrez and Carreón (2004) were not high enough to account for the change in chemistry of the river water, suggesting instead Ca-rich runoff during rain events and Ca-rich groundwater flowing into the river as possible sources. Gypsum outcrops along a valley that drains toward the river and one unnamed spring in these outcrops with high Ca concentration was considered to be evidence supporting this assumption. The enhanced Landsat TM image (Fig. 4) highlights the regions with exposed gypsum as bright yellow. Weathered rhyolite is shown as a tan color, while the red to yellowish colors correspond to clayish soil and/or oxidation of the iron minerals, and limestone outcrops are shown as dark purple. The image shows the places where gypsum is exposed and where gypsum-rich sediments accumulate based on geology maps and our field checking.

Stream sediment data (sample locations are shown in Fig. 3) were used in order to obtain more quantitative results than those obtained from the satellite images. Calcium concentrations ranged between 0% and 16.88% (g Ca/100 g dry soil), with a median of 1.80% and an 85% percentile value of 9.0%. To depict the spatial distribution of significantly higher Ca concentrations, a map was generated for concentrations higher than the 85% (Fig. 5). The map shows regions with high Ca content that correspond to the areas with gypsum outcrops identified by geologic mapping (INEGI, 1984a) and Figure 4. To estimate the potential dissolution from exposed rocks (gypsum and limestone), we applied Visual MINTEQ version 2.53 mineral equilibrium software (http://www.lwr.kth.se/english/OurSoftware/vminteq/index.htm) to the water at the Luis L. Leon reservoir (INEGI, 1983b). The results showed that the water was saturated with respect to calcium carbonate but undersaturated with respect to gypsum.

One possible explanation of why the concentration of Na decreases near the Luis L. Leon reservoir is that enough gypsum enters the river to offset the Na content, similar to a treatment recommended for Na-affected soils consisting of applying gypsum to soils to effectively remove excess Na (Miyamoto and Enriquez, 1990). The occurrence of gypsum outcrops in the Rio Conchos basin downstream from the point where the river receives Na-rich irrigation drain returns may amend the water quality naturally, rendering river water usable for irrigation of fields downstream from the Luis L. Leon reservoir. During extreme drought conditions, however, there is not enough water to transport gypsum to the river and the water does not get naturally treated. Under these conditions, farmers report that crops irrigated with river water do not grow (Roberto Ortiz, 2007, personal commun.). Monitoring dissolved salts (Na, Ca) in this segment of the river is thus necessary to test that the quality of water is appropriate for irrigation, especially during drought episodes.

A concentration map for Na was generated, as for Ca, to show the spatial distribution of high Na concentrations. The reported range of Na values was 46.4–8651.5 mg/kg with a median of 207.0 mg/kg and an 85% value of 417.3 mg/kg (SGM, 2001); Na >417.3 mg/kg was then used to generate a concentration map (Fig. 6). As expected, some of the points with high Na concentrations are within the Irrigated District 005, which is salt affected as a result of irrigation practices (Barocio, 2000). However, the highest Na concentrations are next to the Rio Conchos downstream from the discharge of irrigation drain returns and after the confluence of the Rio Chuviscar. The distribution of the highest found Na concentrations (1699–8651 mg/kg) indicates clearly their association with irrigation drain returns. The Rio Chuviscar carries Na in large amounts, after receiving discharges of sewage and agricultural wastes from the city of Aldama. Lesser concentrations of Na (but still higher than 85%) that are scattered in the northwest section of the map may be explained by the salts that are windborne from the nearby playa lake El Cuervo. Reported concentrations of the topsoil layer of this playa lake are as high as 3400 mg/kg Na with a pH of 9.1 (INEGI, 1984b). The prevalent westerly winds probably carry the salt particles and are most likely able to cross the relatively low divide into the nearby basin to the east and into the middle Rio Conchos basin. Salt-forming elements generally associated with Ca, Mg, and Sr are present in the river water in relatively high concentrations. The content of these elements in water at various river points is shown in Table 1.

Sediment geochemistry analysis was used to identify the possible natural sources of these salts. A correlation analysis of the salt associated elements in alluvium sediment was performed. The correlation coefficients and correlation significances are shown in Table 2. According to Table 2, Ca and Sr correlate, but it is interesting that no correlation was found between Ca and Mg. Furthermore, Na did not correlate to any other element. These results suggest a different source for Ca and Na; gypsum and limestones that crop out in the middle Rio Conchos basin are likely the source of Ca, and irrigation wastes and windborne salts from adjacent closed basins are likely the source of Na. The smaller concentrations of Sr and relatively high correlation (0.61) with Ca agree with reported substitution of Sr for Ca during and after formation of sedimentary rocks (Kinsman, 1969). Kinsman (1969) reported a Sr^{+2}/Ca^{+2} ratio of 0.038 for carbonates (Bahamas). The Sr^{+2}/Ca^{+2} ratio for Rio Conchos water (Table 1) was 0.012 and for sediments was 0.059; although not conclusive in pointing to a specific origin, these ratios are at least in the same order of magnitude as those reported for carbonate rocks.

The lack of correlation of Mg with Ca or Sr indicates that Mg has a source different than Ca and Sr, and its correlation to Al and K suggests an association instead with intermediate volcanic rocks present in the area, which contain ~2 wt% MgO, 15 wt% Al_2O_3, and 1.5–4 wt% K_2O (Cameron et al., 1980; Nelson et al., 1987). A simple ratio, i.e., Mg/K, to infer its origin does not apply in this case as it did for calcium carbonate due to the incongruent dissolution of silicate minerals.

Toxic Metalloids

The term metalloid is utilized for elements that have properties of both metals and nonmetals. Arsenic (As) and antimony (Sb) are important metalloids for aquatic systems because of their toxicity at even small concentrations: permissible levels in drinking water are 10 and 5 ppb, respectively (World Health Organization, 2006). Arsenic is a toxic substance of concern because concentrations >50 ppb have been detected in wells within the study area (Vega-Gleason, 2002) and in soils near hot springs (Flores-Tavizón et al., 2003; Rubio-Arias et al., 2005). We have water quality data from a previous study, and among these were 32 locations within the present study area. The samples correspond to unfiltered water from rivers and irrigation canals and were analyzed using an

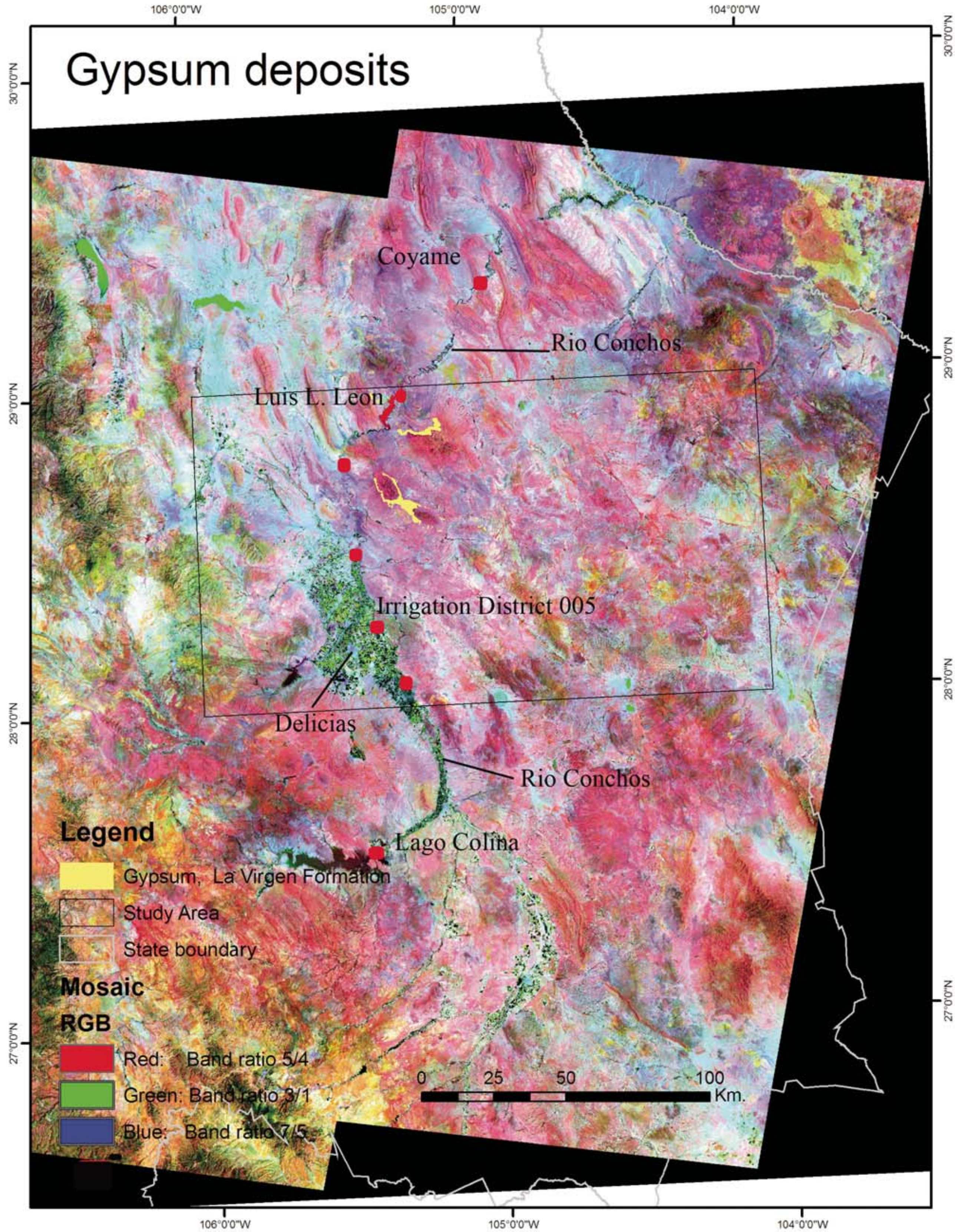

Figure 4. Landsat Thematic Mapper image of the study area shown as a red-green-blue (RGB) composite. Bright yellow areas represent gypsum outcrops or regions with high amounts of gypsum. Red squares along the river show the locations of water samples listed in Table 1.

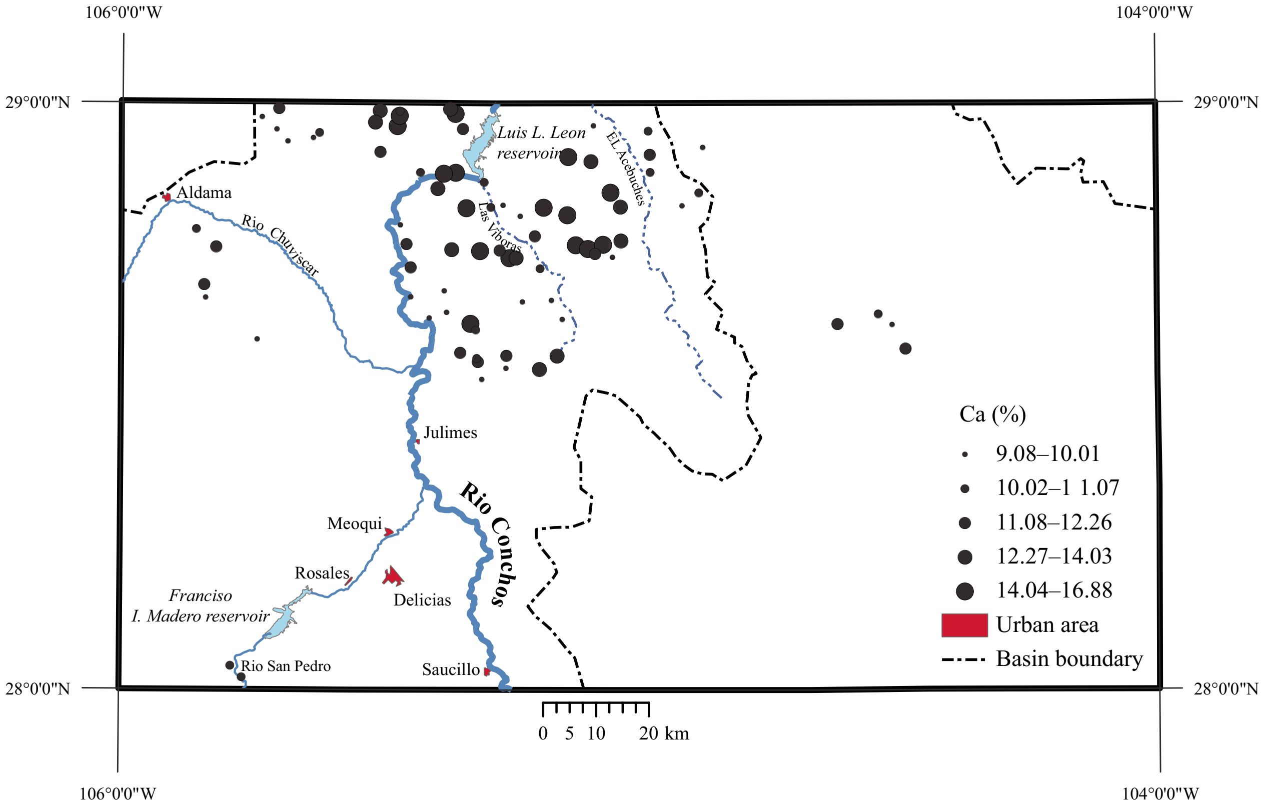

Figure 5. The variation of calcium concentrations (concentrations >85%) in stream sediments.

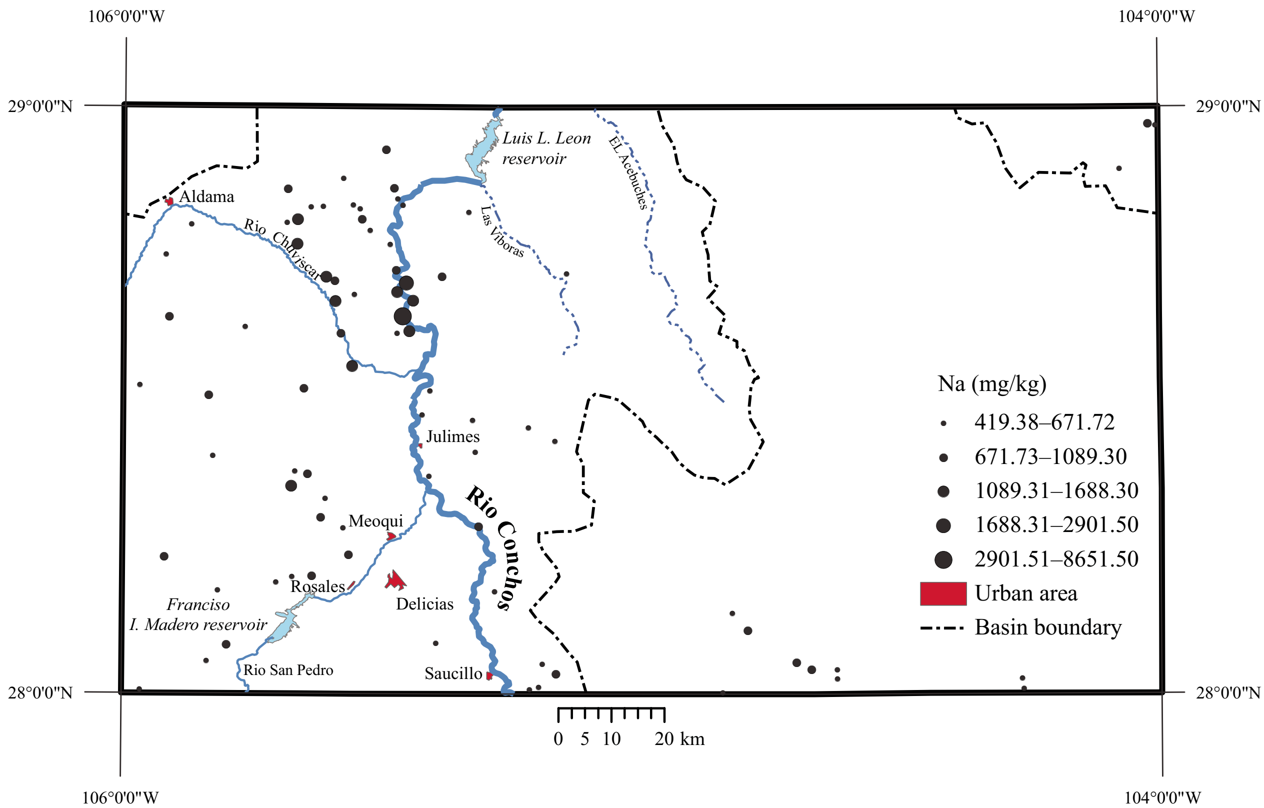

Figure 6. The variation of sodium concentrations (concentrations >85%) in stream sediments.

TABLE 1. WATER QUALITY PARAMETERS DOWNSTREAM OF THE MIDDLE RIO CONCHOS (FROM TOP TO BOTTOM)

Location	Al (mg/L)	Na (mg/L)	Ca (mg/L)	Mg (mg/L)	Sr (mg/L)	As (µg/L)	Sb (µg/L)
Lago Colina (reservoir)	0.176	34.5	31.1	4.0	0.34	40.1	0.07
Rio Conchos south of Delicias	0.240	125.2	163.0	20.1	1.47	30.3	0.50
Rio Conchos after merging with Rio San Pedro	0.300	268.4	134.8	25.7	2.40	80.0	0.50
Rio Conchos after merging with Rio Chuviscar	1.176	307.8	136.0	21.5	2.08	74.8	0.30
El Potrero (October 2001)	n.d.	341.9	148.9	27.1	n.d.	n.d.	n.d.
Luis L. Leon reservoir	0.149	95.5	62.2	12.1	1.26	41.6	0.80
Rio Conchos by Coyame	0.278	68.5	134.0	7.5	1.38	10.2	1.70

Note: Samples collected in June 1997 except when noted otherwise. Values for Lago Colina and Coyame were included as reference even though these sampling locations are outside the study area (see Fig. 4). n.d.—not determined.

ICP-MS. From these 32 samples, the average As concentration was ~25 ppb, with only 4 exceeding the Mexican 100 ppb monthly average for river water (Diario Oficial de la Federación [DOF], 1997). Sewage discharge was evident in all four of these locations; two corresponded to the Rio San Pedro before merging with the Rio Conchos (110 and 104 ppb As), and the other two before and after the Rio Chuviscar merged with the Rio Conchos (136 and 187 ppb As). The relative absence of As in the surface water and concurrent reports of high concentrations of As in wells (Vega-Gleason, 2002) suggest that a possible source of As in these river segments was well water mixed in sewage.

Sediment analyses were used to further identify the sources on the land surface that may contribute to the contamination of the Rio Conchos with As. Sediment As concentrations ranged between 1.95 and 2108.4 mg/kg, with a median of 7.15 mg/kg and an 85% value of 13.3 mg/kg. Permissible limits vary according to land use and soil properties; the U.S. Environmental Protection Agency (2004) recommends a limit of 29 mg/kg for a dilution attenuation factor of 20, while the Mexican permissible value for soils is 22 mg/kg for agricultural and residential use (DOF, 2007). For sediment concentrations that may affect biological communities, Long and Morgan (1990) reported guideline values of effect range-low of 33 mg/kg As and effect range-medium of 85 mg/kg As.

In order to better understand the distribution of high As concentrations, a map for the location of samples containing As >13.3 mg/kg was generated (Fig. 7). The map shows a relatively smaller amount of anomalous points compared to Ca and Na maps; only 24 of 541 samples had concentrations exceeding the Mexican norm of 22 mg/kg As.

The highest As concentrations were found around the San Antonio Ag-Pb mine. The next higher concentrations also plotted near the Ag-Pb abandoned mines La Ventura and La Verde in the northern portion of the map, and La Licha, La India, Niko, and Saucillo in the southern portion of the map. The mineral deposits of San Antonio and La Verde mines contain chalcopyrite (SGM, 2001), for which associated arsenopyrite is most likely present. Other sulfide-bearing mines (La Licha, La India, Niko, and Saucillo) consist of vein deposits mined for Ag and Pb, but their association to anomalously high As concentrations is less clear since they are located in places where concurrent activities (agriculture and urban wastes) could also be contributing As to the streams.

Lesser concentrations of As scattered through the area seem to coincide with Oligocene ignimbrites (rhyolitic tuffs), as suggested by Rodriguez-Pineda et al. (2005b) and shown in Figure 7. The As pattern is, however, not as evident as it is for the mines, and As concentrations are not evenly distributed around ignimbrite outcrops. More studies are needed to confirm the occurrence of As-bearing minerals in Oligocene ignimbrites in the area.

Elements commonly associated with As are Sb, Cu, and Bi. Among these, the relationship between As and Sb has been studied in more detail, as Sb is also toxic at small concentrations (Gebel et al., 1998). The concentrations of Sb and Bi in the study area are approximately one order of magnitude smaller than those of As and

TABLE 2. CORRELATION COEFFICIENTS OF ELEMENTS ASSOCIATED WITH SALTS IN ARROYO SEDIMENT SAMPLES (N = 540)

	Al	Ba	As	Ca	Sr	Fe	Mg	K	Se	Na	U
Al	1.000										
Ba	0.317	1.000									
As	-0.01**	0.01**	1.000								
Ca	-0.130*	0.304	0.078*	1.000							
Sr	-0.03**	0.465	0.01**	**0.605**	1.000						
Fe	0.193	0.103*	0.350	-0.389	-0.188	1.000					
Mg	**0.628**	0.543	0.03**	0.293	0.353	0.189	1.000				
K	**0.814**	0.441	0.05**	0.193	0.126*	0.03**	**0.717**	1.000			
Se	0.05**	0.06**	0.597	0.090*	0.04**	0.211	0.06**	0.187	1.000		
Na	0.05**	0.190	0.01**	0.02**	0.238	0.099*	0.191*	0.01**	-0.02**	1.000	
U	0.433	-0.271	-0.06**	**-0.664**	-0.430	0.256	-0.157	0.04**	-0.152	-0.05**	1.000

Note: Correlation coefficients larger than 0.6 are shown in bold for visualization purposes. The level of significance is shown by asterisks. No asterisk = significant at 99% confidence interval; * = significant at 95% confidence interval but not significant at 99%; ** = not significant at 95% confidence interval.

Cu. Although an association between As and Sb is expected due to their similar chemical characteristics and occurrence in sulfide ores (Gebel et al., 1998; Mueller et al., 2001; Kelepertsis et al., 2006), some investigators have found no relationship between these two elements in alluvial material (McCarthy et al., 2004).

A correlation analysis of elements of concern (Al, Sb, As, Bi, Cd, Cu, Cr, Fe, Mn, Ag, Pb, and W) was conducted to investigate the association of As with other metals and metalloids present in sediment (SGM, 2001; Arzabala-Molina, 2005). The results, compiled in Table 3, show a correlation coefficient of 0.800, 0.667, and 0.913 for As with Sb, Cu, and Bi, respectively. Arsenic also correlated with Cd, Ag, Pb, and W. A strong correlation of As with Bi, Sb, and Cu is indicative of a natural origin (hydrothermal) with As operating as a pathfinder for Au, Ag, vein-type, and complex sulfide ores (Levinson, 1974). This association, however, was unable to explain the high content of As found in water samples in the Rio Chuviscar and Rio San Pedro. Since they do not classify as dry arroyos, SGM did not collect sediment samples in the Rio San Pedro and only three samples were collected in the Rio Chuviscar. The As content of these three samples was 20.99, 12.86, and 12.16 mg/kg sediment (the mean for the study area was 7.15 mg/kg). No other As concentrations have been reported for these rivers' sediments.

Arsenic has a great affinity for iron oxides and clays and tends to remain attached to solid phases that can occur in stream sediments, where they accumulate (Smedley and Kinniburgh, 2002). Reduction reactions under anaerobic conditions can directly affect the mobility of As, facilitating its incorporation to the water column (Smedley and Kinniburgh, 2002). Because of this threat of As remobilization, further work analyzing river sediments is critically needed to determine possible accumulation of As in stream sediments and irrigation canals.

The identification of possible sources of major contaminants to the Rio Conchos abridges recommendations for restoration initiatives; these include improvements in the treatment of wastes (irrigation, sewage), proper containment of mining tailings, and monitoring of salinity (Ca, Na) in river water. The methods utilized here could be applied to other areas in northern Mexico that need studies to identify contamination sources but lack monitoring data of their streams, including Villa de La Paz, San Luis Potosí, a site with

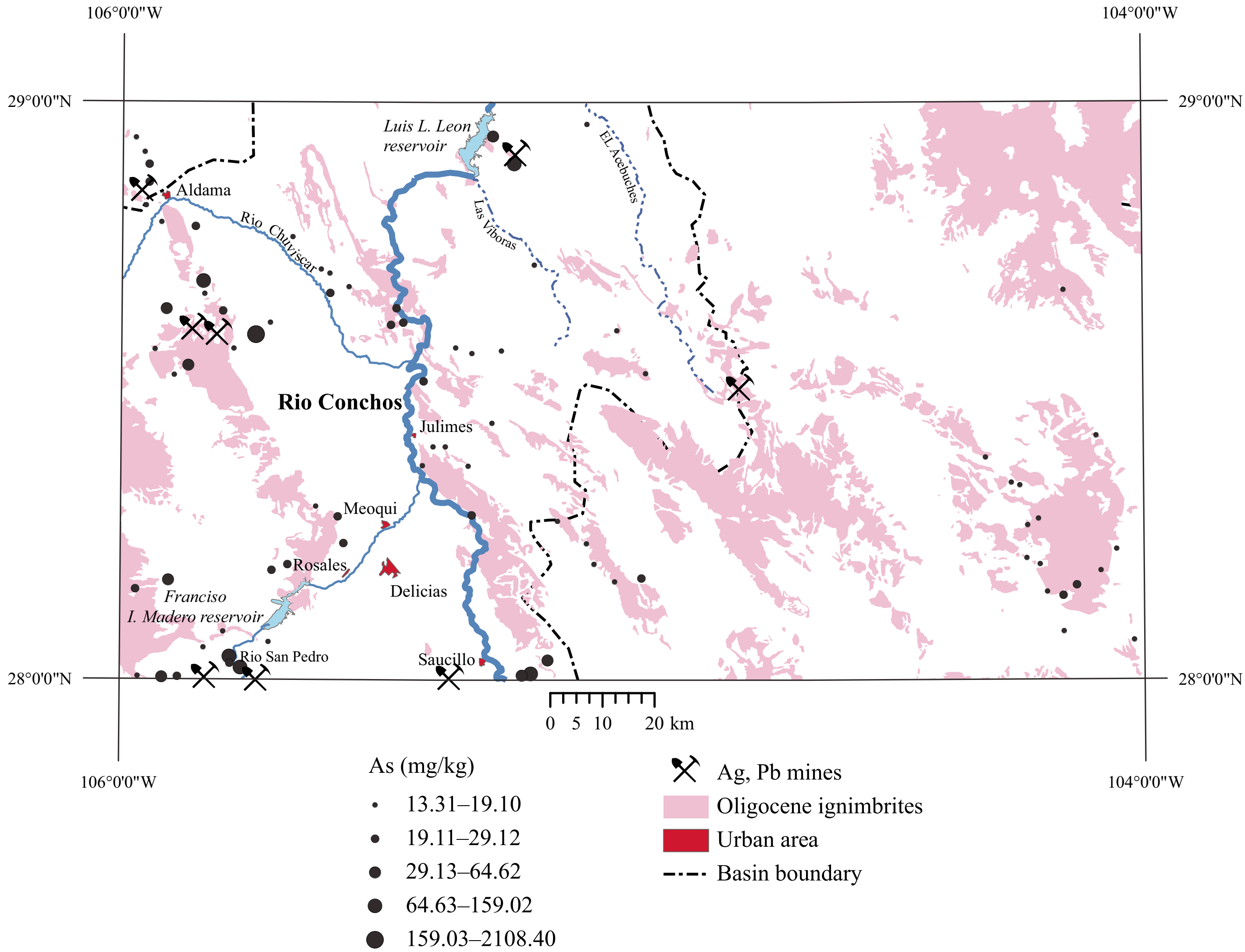

Figure 7. The variation of arsenic concentrations (concentrations >85%) in stream sediments. Also shown are the locations of Oligocene ignimbrites and Ag-Pb mines.

TABLE 3. CORRELATION COEFFICIENTS OF ELEMENTS ASSOCIATED WITH TOXIC METALLOIDS As-Bi-Sb PRESENT IN ARROYO SEDIMENT SAMPLES (N = 540)

	Al	Sb	As	Bi	Cd	Cu	Cr	Fe	Mn	Ag	Pb	W
Al	1.000											
Sb	0.02**	1.000										
As	-0.01**	**0.800**	1.000									
Bi	-0.03**	**0.876**	**0.913**	1.00								
Cd	-0.02**	**0.785**	**0.992**	**0.908**	1.000							
Cu	0.07*	**0.707**	**0.667**	**0.723**	**0.644**	1.000						
Cr	0.225	0.140	0.118	0.12*	0.10*	0.379	1.000					
Fe	0.193	0.307	0.350	0.319	0.337	0.411	**0.756**	1.000				
Mn	0.306	0.379	0.421	0.378	0.435	0.395	0.432	**0.671**	1.000			
Ag	-0.01**	**0.712**	**0.918**	**0.824**	**0.917**	0.592	0.162	0.359	0.420	1.000		
Pb	0.02**	**0.791**	**0.967**	**0.891**	**0.986**	**0.635**	0.110	0.339	0.480	**0.898**	1.000	
W	0.163	**0.613**	**0.769**	**0.750**	**0.765**	**0.605**	0.416	**0.631**	0.535	**0.711**	**0.751**	1.000

Note: Correlation values >0.6 are highlighted in bold to facilitate visual analysis. The level of significance is shown by asterisks. No asterisk = significant at 99% confidence interval; * = significant at 95% confidence interval but not significant at 99%; ** = not significant at 95% confidence interval.

reportedly high levels of As (Pelallo-Martinez et al., 2005), and other sites contaminated with metals (e.g., Puga et al., 2006). Similarly, a geochemical analysis in conjunction with a remote sensing analysis is a cost-effective technique that can be used to monitor soil quality by determining the salt content of irrigated soils that are prone to become salt affected (Metternicht and Zinck, 2003). These include arid areas of countries with limited resources for detailed chemical monitoring (Food and Agriculture Organization of the United Nations, 1988).

CONCLUSIONS

The potential sources of salinity and toxic metalloids (As) within the Rio Conchos were investigated using spatial distribution of pollutants complemented with correlation analyses of these pollutants and their associated elements. The spatial distribution of Ca and Na provided supporting evidence for irrigation drain return as a major source of Na contamination in the river and also revealed the presence of gypsum in the area where Na concentration decreased, suggesting that this decrease was caused by the input of dissolved gypsum. Arsenic within the basin was found to cluster around Ag-Pb-Cu mines and the correlation of As with Sb, Cu, and Bi also pinpointed As-rich mineral deposits as the source of As. However, the highest As concentrations in river water were detected concurrently with sewage discharges, indicating the presence of an important second source of As. The evenly distributed samples of the (dry) stream sediment data were instrumental in identifying the possible sources of the contaminants. In addition to arroyos, stream sediment data within rivers (Conchos, Chuviscar, San Pedro) are needed to determine the worst-case scenario of a release of toxic levels of As to the water column.

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