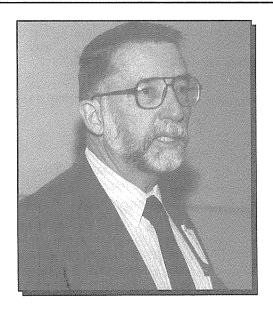
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A REGIONAL PERSPECTIVE ON ARSENIC IN WATERS OF THE MIDDLE RIO GRANDE BASIN, NEW MEXICO

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INTRODUCTION

The objectives of this paper are to provide a concise summary and a regional perspective on the geochemical characteristics and occurrence of arsenic in waters of the Middle Rio Grande Basin. The initial intent was to discuss arsenic in groundwater, but, because of interrelationships between ground and surface waters, the need to research arsenic variations in both soon became apparent. A second realization is that some arsenic analyses reported in the literature are erroneous. Samples *must* be filtered at the time of collection to determine arsenic dissolved in the water. Arsenic has a strong tendency to sorb onto iron and manganese oxides and other particulate matter and if these particles are not removed the arsenic analyses will be high

and erratic. Some analyses reported as dissolved arsenic were obviously performed on unfiltered samples or on samples acidified before filtration. The senior author thanks Dr. Fraser Goff of Los Alamos National Laboratory for alerting him to this problem.

To develop a regional perspective on natural variations in arsenic in ground and surface waters of the western U.S. we obtained all the arsenic analyses in the STORET data base of the U.S. Environmental Improvement Agency for the Rio Grande, Colorado and Snake rivers, and a more limited data set for some of their tributaries, some wastewater treatment plants along their drainages, and for some springs and wells. We thank Dr. Jim Piatt of the New Mexico Environment Department for acquiring the data and for his encouragement in

pursuing this study. We also thank the Public Works Department of the City of Albuquerque for access to their data and to consulting reports by CH2M HILL completed for the City in 1989 and 1990.

GEOCHEMICAL CHARACTERISTICS OF ARSENIC

Arsenic is a metalloid that sublimes to vapor at 613 °C. Its enthalpy of vaporization (ΔH vap/kJ $mol^{-1} = 31.9$) is among the lowest of common elements, being lower than mercury and intermediate between iodine (41.67) and bromine (30.5) (Emsley 1991). Arsenic has several valence states, of which +3 (arsenite) and +5 (arsenate) are the most common in nature. Arsenic trioxide (As₂O₃) sublimes at only 193°C and the pentasulfide (As₂S₅) sublimes at 500°C. Consequently, arsenic is strongly enriched in volcanic gases as compared to magma, with an enrichment factor of 103 to 106 (Table 1). The crustal abundance of arsenic is estimated at 1500 ppb (Emsley 1991), but its abundance in common rocks (Table 1) varies widely. Of particular importance to ground and surface waters in the western U.S. is the relative abundance and mobility of arsenic in silicic volcanic rocks, in volcaniclastic sediments derived from them, and in the hydrothermal systems commonly associated with silicic volcanism.

Arsenic has chalcophile, siderophile, and oxyphile characteristics, meaning that it tends to follow sulfur, iron, and oxygen in geochemical processes. In aqueous systems, the two common oxidation states are arsenite (+3) and arsenate (+5). Arsenite is the common form under reducing conditions, such as in deep groundwater and magmatic and hydrothermal systems, whereas arsenate dominates in most surface waters and shallow groundwater. Arsenite (As+3) is not easily sorbed onto any compound or mineral and is thus very mobile. Arsenate (As⁺⁵), however, is easily sorbed onto iron, manganese, and aluminum oxides and fine-grained sediments. The Mn⁺⁴ ion, which is widely distributed as a coating on fracture surfaces and mineral grains, is an efficient oxidizer of As⁺³ to As⁺⁵. Note in Table 1 the enrichment of arsenic in iron-rich and clay-rich rocks.

Both arsenite and arsenate are equally soluble in aqueous fluids where they commonly are present as oxyanions. In an oxidizing environment (0.2–0.5 V), as in most river waters, both H₂AsO₄⁻² and HAsO₄⁻² occur in appreciable proportions, while under reducing conditions (0–0.1 V) H₃AsO₃ is the dominant species (Mok and Wai 1994). Arsenite forms complex ions with chloride in the pH range 6 to 12 and forms both complex ions and colloids with sulfur in hydrothermal systems. Arsenite also forms complex anions with fluoride. Organic complexes with arsenite can greatly increase its mobility (Mok and Wai 1994).

In rivers such as the Rio Grande, arsenic in unfiltered samples is appreciably higher than in filtered samples (Table 2) because of sorption on, and coprecipitation with, hydrous oxides of iron, manganese, and aluminum as well as attachment to sediment grains. The scavenging power of these particles for arsenic is further evident in the dramatically higher arsenic content of sediment from the river bed (Table 2). Arsenic in sediment samples (dry weight) is commonly reported in parts-permillion (ppm) instead of parts-per-billion (ppb), a thousand times higher than typical values from water samples. In tables 2, 7, and 8, we have listed arsenic content of sediment in the same units (ppb) as in the water to emphasize the contrast in concentration. Mok and Wai (1994, p. 101) state that "In a river, arsenic is predominantly bound to sediments." Arsenic can be released from the sediments if the pH becomes acidic or if the pH becomes very high (>8.5). At high pH levels, hydroxide ions compete with arsenic anions for sorption sites. Arsenic can also be released if the Eh becomes reducing. Reduction of ferric ions to ferrous ions liberates sorbed arsenic as As⁺³, which is highly mobile.

EXAMPLES OF GEOLOGICAL CONTROLS ON ARSENIC DISTRIBUTION IN WATER

Arsenic Enrichment during Potassium Metasomatism

Potassium metasomatism is a type of low-temperature alteration common in closed hydrographic basins in arid or semiarid climates (Chapin and Lindley 1986). As basin waters become more alkaline and saline, sediments and inter-

TABLE 1. ARSENIC CONCENTRATIONS IN SELECTED NONBIOLOGICAL MATERIALS. ALL ARSENIC CONCENTRATIONS IN PARTS PER BILLION (PPB) TO FACILITATE COMPARISON. MODIFIED FROM EISLER (1994) UNLESS OTHERWISE NOTED

	Concentration			
Material	Dissolved (ppb)	Total [mean, (range)](ppb)		
Rain Canada New Mexico, USA	0.7 (<0.5-1.2)1	(0.1–5)		
Drinking Water Nationwide, USA		2.4 (0.5–214)		
Groundwater USA USA		usually <10 ² 17.9 (0.01–800) ³		
River Water Nonpolluted, USA Mainstem rivers in SW Tributaries in SW	(0.5–8) ⁴ (<1.0–52) ⁴	usually <5 (1.0–14) ⁴ (<1.0–55) ⁴		
Lake Water (ppb) <2000 ppm TDS >2000 ppm TDS		(<1.0–100) (<1.0–2000)		
Volcanic Gases		enriched 10 ³ -10 ⁶		
Thermal Waters Worldwide		(20–3800 usually) max. 276,000		
Sea Water Worldwide		2 (0.15–6)		
Rock Limestone Sandstone Shale and Clay Phosphate Iron-rich sedimentary rocks Volcanic Metamorphic		1700 (100–20,000) 2000 (600–120,000) 14,500 (300–490,000) 22,600 (400–188,000) (1800–2,900,000) 1500–3000 (60–113,000) (50–143,000)		
Sediments Upper Mississippi River Lake Michigan Oceanic Lacustrine		2600 (600–6200) (5000–30,000) 33,700 (<400–455,000) (usually 5000–26,900)		
Soil Porewaters Unmineralized areas Arsenate Arsenite		(18–49) (1–7)		
Soils USA, uncontaminated		7400		
Synthetic Detergents Household, heavy duty		(1000-73,000)		
Crustal Abundance		1500		

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TABLE 2. AVERAGE ARSENIC CONCENTRATIONS IN WATER AND SEDIMENT OF THE RIO GRANDE AND SELECTED TRIBUTARIES (INCLUDING SOME WASTEWATER TREATMENT PLANT DISCHARGES). ALL ANALYSES FROM STORET DATA BASE AS OF 11/7/94. NUMBER OF SAMPLES GIVEN IN PARENTHESES. RIO GRANDE SAMPLES CAPITALIZED; TRIBUTARIES AS NAMED

GIVEN IN LANGINITIES			<u>Water</u>		<u>Sediment</u>
Location	Geologic setting	When sampled	Dissolved arsenic (ppb)	Total arsenic (ppb)	Dry wt. arsenic (ppb)
NEAR LOBATOS, CO	San Luis Basin	3/75–8/91	2.3 (52)	2.7 (20)	
Rio Lucero near Arroyo Seco	Taos Plateau	3/87–3/92	<1 (32)	<1 (32)	
Rio Pueblo de Taos near Taos	Taos Plateau	3/87–1/92	<1.0 (25)	<1 (25)	
Below Taos Junction Bridge	Taos Plateau	4/80–11/91	2.3 (28)	2.4 (20)	3400 (8)
Embudo Creek at Dixon	Española Basin	8/71–5/74	2.0 (10)		
Above San Juan Pueblo	Española Basin	7/87–11/87	2.0 (2)	2.0 (2)	
Rio Chama near Chamita, NM	Española Basin	8/71–11/91	1.8 (16)	2.2 (5)	
SANTA CLARA PUEBLO	Española Basin	7/87–11/91	1.8 (6)	2.0 (6)	
Otowi Bridge	Española Basin	8/71–11/91	1.8 (57)	3.1 (20)	2400 (11)
Santa Fe River above Cochiti Reservoir	Santo Domingo Basin	6/74–2/75	8.5 (2)		
Cochiti Reservoir near Cochiti Pueblo	Santo Domingo Basin	6/81–6/91	2.2 (10)	2.2 (10)	9400 (11)
San Felipe Pueblo	Santo Domingo Basin	2/74-1/92	1.9 (24)	2.2 (32)	3300 (12)
Jemez River below Jemez Dam	Albuquerque Basin	1/74–5/80	28.1 (17)	39.5 (6)	
Bernalillo wastewater treatment plant	Albuquerque Basin	7/88–9/91	38.3 (6)		
Rio Rancho utilities wastewater treatment plant #3	Albuquerque Basin	7/88–9/91	12.3 (6)		
Rio Rancho utilities wastewater treatment plant #2	Albuquerque Basin	6/91–9/91	17.8 (6)		
Alameda north floodway channel	Albuquerque Basin	5/82–7/83	3.4 (15)	9.5 (26)	
Albuquerque waste drain	Albuquerque Basin	3/74	17.0 (4)		
Albuquerque	Albuquerque Basin	5/81–11/88	3.3 (8)	4.1 (8)	
Tijeras Arroyo above 4-Hills Bridge	Albuquerque Basin	10/88–9/91	<1.0 (11)	1.3 (10)	

A Regional Perspective on Arsenic in Waters of the Middle Rio Grande Basin, New Mexico

			<u>Water</u>		Sediment Dry wt.
Location	Geologic setting	When sampled	Dissolved arsenic (ppb)	Total arsenic (ppb)	arsenic (ppb)
Rio Bravo Bridge	Albuquerque Basin	4 <i>/</i> 79			3400 (l)
Albuquerque wastewater treatment plant #2	Albuquerque Basin	11/815/94	7.3 (10)	8.4 (7)	
Interstate 25 Bridge	Albuquerque Basin	11/83–5/94	4.7 (9)	4.6 (5)	3200 (1)
Los Lunas Bridge near Isleta	Albuquerque Basin	8/75–2/92	4.1 (41)	5.4 (41)	1900 (9)
Los Lunas wastewater treatment plant	Albuquerque Basin	5/94	12 (1)	16 (1)	
Near Bernardo floodway	Albuquerque Basin	5/82–3/92	4.3 (10)	5.3 (10)	
SAN ACACIA CONVEYANCE CHANNEL	Socorro Basin	9/7711/84	5.3 (6)	6.6 (14)	1500 (2)
SAN ACACIA FLOODWAY	Socorro Basin	11/81–4/92	5.0 (18)	5.8 (18)	3700 (7)
SAN MARCIAL CONVEYANCE CHANNEL	San Marcial Basin	9/77–11/84	5.3 (6)	6.6 (14)	2600 (9)
SAN MARCIAL FLOODWAY	San Marcial Basin	4/73–3/88	4.6 (31)	12.7 (19)	2700 (6)
BELOW ELEPHANT BUTTE DAM	Palomas Basin	2/80–9/82	4.2 (9)	4.7 (9)	
T or C Sewage Treatment Plants	Palomas Basin	3/74–12/74		6.0 (10)	
Below Truth or Consequences	Palomas Basin	3/74–12/74		7.0 (5)	
JUST BELOW CABALLO DAM	Palomas Basin	3/74–12/74		4.8 (5)	
Hatch Sewage Treatment Plant	rift basin	3/74–12/74		5.4 (5)	
Below Leasburg Dam	Mesilla Basin	3/74–12/91	2.0 (5)	4.0 (4)	,
Las Cruces Sewage Treatment Effluent	Mesilla Basin	3/74–12/74		4.8 (5)	
ANTHONY TO LAS CRUCES, NM	Mesilla Basin	3/74-11/93	1.9 (19)	6.8 (21)	
Anthony Sewage Treatment Plant	Mesilla Basin	3/74–12/74		9.8 (5)	
VINTON BRIDGE NEAR ANTHONY, TX	Mesilla Basin	8/75–5/78	2.5 (12)	3.8 (12)	

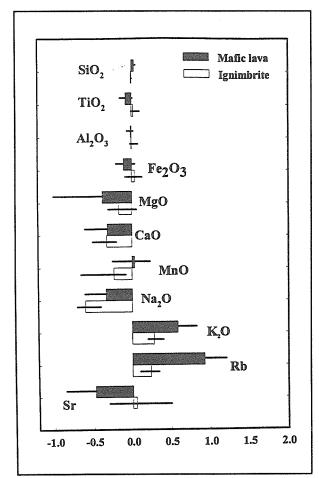


Figure 1. Enrichment-depletion diagrams showing mobility of major elements plus Rb and Sr during potassium metasomatism. The length of the bar repreents \log_{10} of altered rock/fresh rock. The enrichment-depletion factors are based on averages of 5 and 7 altered/unaltered rock pairs for basaltic andesite and rhyolitic ignimbrites, respectively. The range of enrichment factors is shown by the black lines superimposed on the bars. From Dunbar et al. (1994) with permission of the New Mexico Geological Society.

bedded volcanic rocks react with the fluids and are enriched in potassium, rubidium, arsenic, and several other trace elements by volume for volume replacement (figures 1 and 2). At the same time, the rocks and sediments are depleted in sodium, calcium, magnesium, strontium, and manganese (in silicic rocks). These elements become concentrated in the groundwaters and may be involved in other water-rock reactions. Volcanic rocks and volcaniclastic sediments derived from them are particularly susceptible to potassium metasomatism because

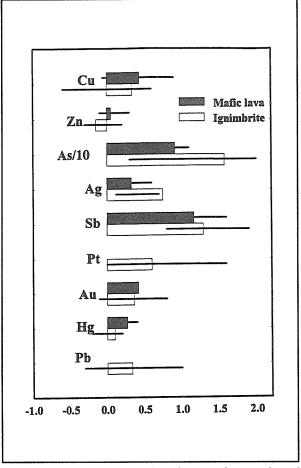


Figure 2. Enrichment-depletion diagrams for arsenic and several elements of economic interest. Diagram construction same as Figure 3. From Dunbar et al. (1994) with permission of the New Mexico Geological Society.

some of their constituent minerals and their finegrained or glassy matrix are unstable in the alkaline, saline, oxidizing geochemical environment. The alteration products consist mainly of adularia (a low-temperature potassium feldspar), hematite, ± quartz, ± clay minerals. Figures 1 and 2 show relative enrichments and depletions of various elements in both mafic lavas and silicic ignimbrites determined during an ongoing geochemical investigation of this phenomenon in a rift basin near Socorro, New Mexico (Chapin and Lindley 1986; Dunbar et al. 1994). Figure 3 shows the magnitude of enrichment for arsenic and several other elements in terms of weight percent, parts per million, or parts per billion depending on the amount of the element present.

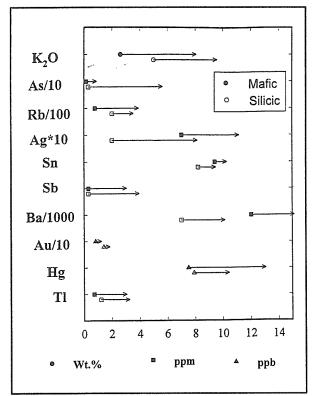


Figure 3. Average absolute enrichments of arsenic and selected elements in silicic and mafic rocks during potassium metasomatism. The symbols (circle for weight percent, square for ppm, triangle for ppb) represent the unaltered rock composition. The length of the line shows the average absolute enrichment.

Potassium metasomatism affects an area of more than 700 mi² (1800 km ²) near Socorro and involves a rock section about 5000 ft (1800 m) thick. The K₂O content of altered rocks can be as high as 13.5 weight percent in rocks which initially contained less than 5 weight percent. The alteration is visually subtle and easily overlooked because rock textures are faithfully preserved and phenocrysts of quartz, sanidine, and biotite are little affected and give the impression that the rocks are fresh. The lack of significant variation in aluminum, silicon, and titanium between fresh and altered rocks (Figure 1) indicates that rock mass was essentially constant during potassium metasomatism.

Large areas of the southwestern U.S. have been affected by potassium metasomatism (Chapin and Lindley 1986). Regional extension causes subsidence, which in arid or semiarid climates leads to closed hydrographic basins and alkaline, saline basin waters. Volcanic rocks and volcaniclastic sediments are also abundant in the Southwest and provide unstable parent material to react with the groundwaters. Where volcanic centers and igneous intrusions are also present, local hydrothermal systems often lead to more intense alteration and dramatically higher arsenic content of both ground and surface waters. For example, within the large area of potassium metasomatised rocks near Socorro arsenic in the altered rocks averages 5 ppm arsenic (range 3-10 ppm) compared to 1 ppm in fresh samples of the same rocks (Figure 4). But within this broad anomaly, two areas with arsenic contents between 20 and 200 ppm are associated with fossil hydrothermal systems. These hydrothermally altered areas contain manganese veins and show enrichment in other elements, such as Sb, Zn, Ba, Au, and Hg, that are typically associated with hydrothermal systems. Arsenic has long been used as a "pathfinder" element in prospecting for hydrothermal gold deposits.

Arsenic in the Jemez Volcanic and Geothermal Field

Hydrothermal waters in silicic volcanic fields are usually enriched in arsenic which often results in increased concentration in both ground and surface waters. The Jemez volcanic field, which has been active for at least 13 Ma, was the site of major pyroclastic eruptions between 1.61 and 1.22 Ma (the Bandelier Tuff) and contains rhyolite domes in the moat of the Valles caldera that are as young as 205 Ka (Izett and Obradovich 1992; Spell et al. 1990). Geothermal systems within the Valles caldera are manifested at the surface by high heat flow and several thermal springs (Trainer 1984; Goff et al. 1988). An outflow plume of thermal waters extends southwestward for many miles along the Jemez fault zone, a major pre-caldera zone of faulting marked at the surface by San Diego Canvon which drains the caldera area. Two sets of neutralchloride hot springs, Soda Dam and Jemez Springs, discharge thermal waters in San Diego Canyon about 5 mi (10 km) outside the Valles caldera. These waters are similar in chemical and isotopic composition to thermal waters sampled at depth within the caldera during geothermal exploration by

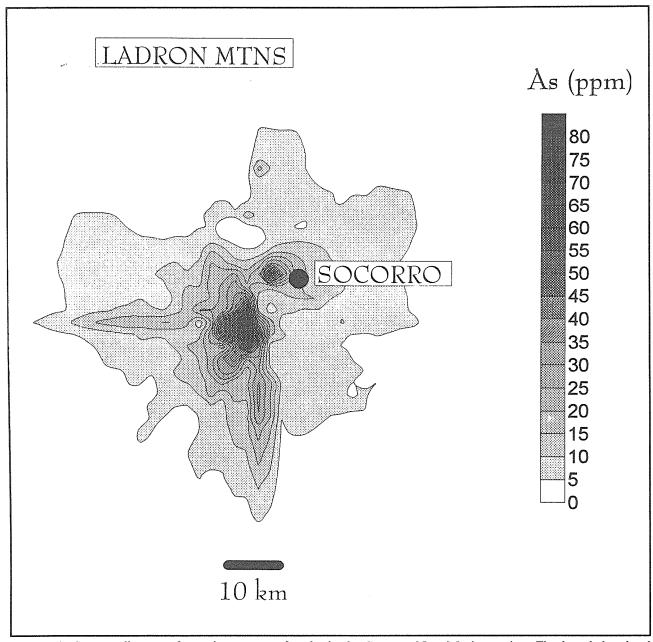


Figure 4. Contour diagram of arsenic contents of rocks in the Socorro, New Mexico region. The broad, low-level enrichment was caused by potassium metasomatism. Two areas of high arsenic associated with hydrothermal mineralization are superimposed.

Union Oil Company and Los Alamos National Laboratory in the 1980s (Goff et al. 1988). Uranium-thorium disequilibrium dating and field investigations by Goff and Shevenell (1987) have demonstrated that the Valles hydrothermal system is at least 10⁶ yr old, nearly as old as the caldera, and has remained virtually unchanged isotopically during this time. The Soda Dam hot springs

discharge Na-HCO₃-Cl waters at a pH of 6.7 containing 960 ppm Na, 1500 ppm HCO₃, 1500 ppm Cl, about 4600 ppm TDS and anomalous concentrations of arsenic, boron, bromine, and lithium (Goff and Shevenell 1987; Goff et al. 1988).

The discharge rate of thermal water from the Valles geothermal system was estimated by Faust and others (1984) at 3080 L/min. As much as 50%

of this water discharges from the hot springs at Soda Dam and Jemez Springs as well as in the bed of the Jemez River (Goff et al. 1988). From volume calculations and dating of travertine deposits in the Soda Dam area, Goff and Shevenell (1987) concluded that the hot-spring system discharged five to ten times as much fluid in earlier times. The arsenic content of thermal waters at Soda Dam and Jemez Springs is currently 1500 ppb and 700 ppb, respectively; reservoir waters within the caldera geothermal system contain 2800 to 7800 ppb arsenic (Goff et al. 1988). Discharge of large volumes of arsenic-bearing thermal waters into the Jemez River as well as along other subsurface flow paths during at least the past 106 years (Goff and Shevenell 1987), and probably much longer, has increased the arsenic content of much of the groundwater in the northern Albuquerque Basin. The influence of these thermal waters is evident in a north-south belt of higher arsenic and temperatures in groundwaters roughly parallel to, and mainly west of, the Rio Grande and extending southward to beyond the Bernalillo-Valencia County line (CH2M HILL 1990). The presence of playa systems in the western Albuquerque Basin between 4-8 Ma (J. Hawley, personal communication, 1995) may have played a role in evaporatively concentrating waters and further increasing their As contents. Note in Table 2 the relatively high arsenic concentrations in the Jemez River and in effluent from the Bernalillo and Rio Rancho (a northwestern suburb of Albuquerque) wastewater treatment plants. Waters used by these municipalities are drawn from the Asenriched zone west of the Rio Grande.

ARSENIC DISTRIBUTION IN RIO GRANDE VALLEY WATERS

Arsenic Distribution in Riverwater

Dissolved arsenic (filtered samples) and total arsenic (unfiltered samples) have been compiled for selected sample sites along the Rio Grande from southern Colorado to El Paso, Texas (Table 2, Figure 5). The data are from the STORET data base of the U.S. Environmental Protection Agency as of November 7, 1994. Sample sites selected for Table 2 are mainly those reporting both dissolved arsenic

and total arsenic over a significant interval of time (3 months to 21 years); however, some sample sites with less data but key locations are also included as are data for some tributaries and some municipal wastewater treatment plants. The analytical data were taken directly from STORET and no attempt was made to check the data with the reporting agency or original publications. There may be some errors in the data, but by covering a large quantity of data over a large geographical area and a significant interval of time, important trends and relationships should be evident.

The arsenic content of Rio Grande surface waters exhibits systematic geographic variations that can be used, in conjunction with an understanding of local geology, to infer patterns of water flow within the valley (Figure 5). Multiyear averages for dissolved arsenic in the Rio Grande between Albuquerque and Elephant Butte Dam range between 4.1 and 5.3 ppb. This compares to multiyear averages for the Rio Grande in northern New Mexico of 1.8 to 2.3 ppb and for tributaries near their confluences as follows: Rio Chama (1.8 ppb), Embudo Creek (2.0 ppb), Rio Lucero (<1 ppb), Rio Pueblo de Taos (<1 ppb), and Tijeras Arroyo (<1 ppb). The arsenic content of Rio Grande waters increases markedly at the confluence with the Jemez River, due to the input of higharsenic waters from the young Jemez volcanic field. The arsenic content of the river continues to be relatively high from the confluence with the Jemez River, near Bernalillo, New Mexico, to below Elephant Butte Dam. The highest arsenic values are between San Acacia and San Marcial (average about 5 ppb dissolved As) where the Rio Grande flows through an area with abundant rhyolitic volcanic rocks and the potassium metasomatised area around Socorro, New Mexico. The Rio Grande below Bernalillo is an exotic river in this reach, meaning that it flows for hundreds of miles through desert terrane with no perennial tributaries. For most of this distance, it also flows through sedimentary basins within or bordering volcanic fields. The high arsenic values from Albuquerque to Elephant Butte reflect significant contributions of groundwater to the river, from wastewater treatment plants and groundwaters that have circulated through volcanic

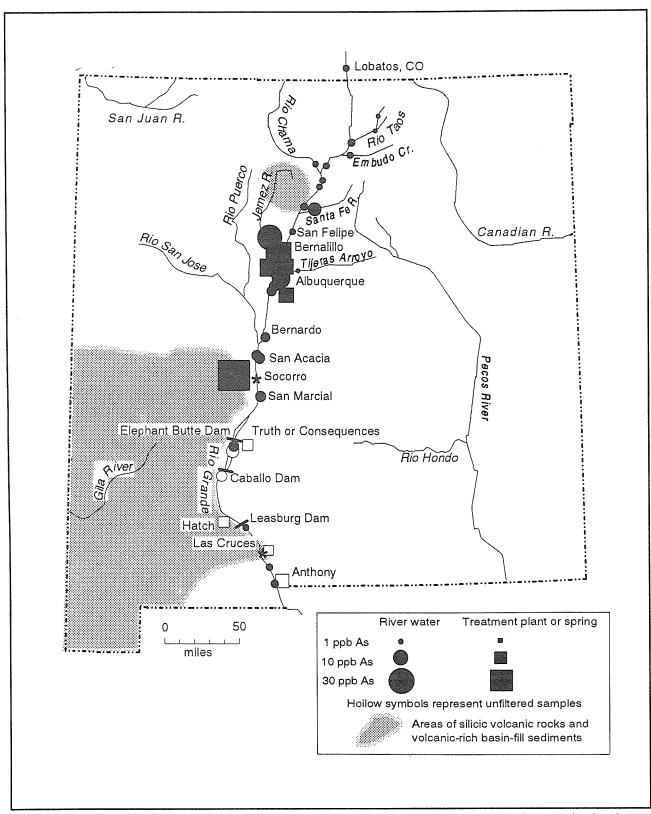


Figure 5. Map of the Rio Grande in New Mexico showing sample localities and representative arsenic abundances. Selected communities and sample localities are listed in Table 2.

rocks and potassium metasomatised rocks and basin-fill sediments. As noted earlier, the arsenic content of volcanic rocks and waters in volcanic terranes can be substantially elevated in arsenic, as are the waters in the Jemez volcanic field.

Arsenic is approximately 1000 times more abundant in sediments of the river bed than dissolved in water of the Rio Grande. Furthermore, total arsenic determined on unfiltered samples is usually 1.1 to 3.6 times higher than dissolved arsenic, and often even higher. The strong affinity between arsenic and iron, manganese, and aluminum hydroxides under oxidizing conditions and alkaline pH leads to self-regulation of dissolved arsenic in the river. From San Felipe Pueblo north, the Rio Grande and its tributaries (except for the lower Santa Fe River) are low in dissolved arsenic (average about 2 ppb). The As enrichment in the lower Santa Fe River may be related to local mineralization. Silicic volcanism and active geothermal systems in the Jemez Mountains contribute high levels of dissolved arsenic to the Jemez River and to groundwaters in the northern Albuquerque Basin. Discharges from the Bernalillo (38 ppb) and Rio Rancho (12-18 ppb) wastewater treatment plants reflect the Jemez influence on groundwaters in the northern Albuquerque Basin. However, in spite of these discharges and the contribution of the Jemez River, dissolved arsenic in the Rio Grande as it flows through Albuquerque is only 3.3 to 4.7 ppb, and from the confluence of the Jemez River to the confluence of the Rio Concho, near Big Bend, Texas, a distance of about 500 miles (800 km), there are no perennial tributaries, yet the dissolved arsenic content does not increase significantly in the downstream direction, despite input of high-As groundwaters. The reason appears to be the abovementioned self-purification effect of arsenic sorbing onto iron, manganese, and aluminum oxides and sediment grains in suspension and in the river bed. Total arsenic in bottom sediment (dry weight) along this reach ranges from 1500 to 3800 ppb in contrast to 4.1 to 5.3 ppb arsenic dissolved in the water flowing above. The arsenic levels of bottom sediments are highest in reservoirs, probably due to the greater content of finer sediment, and resulting increase of surface area available for sorption, as well as increased organic content.

Arsenic Distribution in Groundwater

The means and ranges of arsenic in groundwater produced from wells in Albuquerque between 1973 and 1994 and in the Middle Rio Grande Basin between 1972 and 1989 are shown in Table 3. The mean arsenic content of 4,343 samples taken between 1989 and June 1994 from 139 City of Albuquerque production wells and reservoirs is 12.8 ppb. Individual analyses ranged from 2 to 79.1 ppb but only one well had a mean above 50 ppb (50.05 ppb). Wells producing water carrying more than 50 ppb arsenic have been shut in. The maximum contaminant level for arsenic in drinking water as established by the U.S. Environmental Protection Agency is currently 50 ppb, but is expected to be lowered in the near future. The distribution of mean arsenic concentrations among the other 138 sample points were: 30-50 ppb, 14 sample points; 20-30 ppb, 17 sample points; 10–20 ppb, 35 sample points; 5-10 ppb, 32 sample points; and 2-5 ppb, 40 sample points. Thus 77% of the sample sites had mean arsenic concentrations below 20 ppb while 11% had concentrations above 30 ppb.

TABLE 3. ARSENIC IN GROUNDWATER IN THE MIDDLE RIO GRANDE BASIN. FROM CITY OF ALBUQUERQUE UNPUBLISHED DATA AND CH2M HILL (1990). CONCENTRATIONS IN PPB; FILTERED SAMPLES (DISSOLVED ARSENIC)

BI WILL DEB (DISSOE VED TITCSETVE)							
Years	Mean	Min.	Max.	Number			
Albuquerque							
1973–1989	18.7	2.0	90	118			
1989–1994	12.8	2.0	79	4343			
Regional							
1972–1989	16.9	2.0	780	319			

Discharges from municipal wastewater treatment plants in the Middle Rio Grande Basin are high in dissolved arsenic and, except for Bernalillo (38 ppb) which is located adjacent to the Jemez River, range from 7 to 18 ppb. Since these communities derive all their municipal water from well fields, 7 to 18 ppb may be a good approximation for average dissolved arsenic in groundwaters of the

Middle Rio Grande Basin. Total arsenic in discharges of wastewater treatment plants in southern New Mexico (Table 2) is relatively low (5–10 ppb) indicating lower arsenic levels in groundwater in that region.

A number of geochemical factors are associated with increases or decreases in arsenic concentrations in the Middle Rio Grande Basin (CH2M HILL 1990). Arsenic correlates positively with temperature, depth, fluoride, sodium, chloride, silica, nitrate, alkalinity and pH of water. Inverse correlations are observed with total water hardness (Ca, Mg) and Eh. Especially significant factors in increased arsenic concentrations are depth, temperature, and fluoride content (CH2M HILL 1990). Table 4 shows that wells having a total depth less than 1200 ft in the Albuquerque well fields produce mainly Ca-Mg-HCO3 waters containing less than 20 ppb arsenic with a pH between 7 and 8 and an Eh of approximately 300 mV (CH2M HILL 1990). In contrast, groundwater in wells having a total depth greater than 1200 ft produce mainly alkaline Na-HCO3 waters containing more than 30 ppb arsenic with higher fluoride contents, higher pH, and considerably less oxidation potential.

TABLE 4. CHANGES IN WATER CHEMISTRY AND ARSENIC CONTENT ABOVE AND BELOW 1,200 FEET TOTAL DEPTH IN ALBUQUERQUE MUNICIPAL WELLS (CH2M HILL 1990)

Ca-Mg-HCO₃ Water < 20 ppb Arsenic
pH 7-8 Eh 300 mV
Average TD 1200 ft
alkaline Na-HCO₃ Water > 30 ppb Arsenic
Higher fluoride
pH 8-9 Eh 100 mV

In both the Albuquerque area and elsewhere in the Middle Rio Grande Basin there are two contrasting types of groundwater from which mixing produces intermediate values (Table 5). At shallow depths near the Rio Grande, groundwater tends to be moderately oxidized, low in temperature, fluoride, and arsenic but higher in sulfate and total hardness. This groundwater is recharged from the river and irrigation systems. In contrast, groundwaters deeper in the basin and further from the river

are characteristically higher in temperature, arsenic, fluoride, sodium, chloride, and pH, but only mildly oxidizing. These groundwaters may or may not have good hydraulic connections with the river.

TABLE 5. CONTRASTING GROUNDWATER TYPES IN THE MIDDLE RIO GRANDE BASIN. DATA FROM CH2M HILL (1990) AND THIS STUDY				
Shallow along river	Low temperature (10–20°C) Low arsenic (<20 ppb) Low fluoride (<1000 ppb) pH 7–8 Eh + 300 mV or more Higher SO ₄ Higher total hardness (Ca, Mg)			
Away from river and deeper	Higher temperature (20–40°C) Higher arsenic (30-50 ppb) Higher fluoride (>1000 ppb) pH 8–9 Eh + 100 mV or less Higher chloride (1x10 ⁵ -2x10 ⁵ ppb) Higher sodium			

Two contrasting types of groundwater have been observed in the Socorro area (Table 6 and Figure 6). Precipitation which falls on the Magdalena Range west of Socorro (Figure 6) sinks into the La Jencia Basin as shown by anomalously low heat flow in that area (Barroll and Reiter 1990). Its path to the Rio Grande is blocked by a 1000-ft (305-m) thick deposit of playa clays which forces the water to flow through potassium metasomatised, arsenicrich volcanic rocks beneath the basin floor where the water becomes heated. Along the flow path, the waters change from Ca-HCO3 waters to Na-HCO3 waters and, as they become heated and less oxidizing, arsenate loosely held by iron and manganese oxides is partially reduced and mobilized. These waters issue as Na-HCO3 springs, whereas waters in the Magdalena Range and La Jencia Basin are Ca-HCO3 waters (Hall 1963; Anderholm 1983; Gross and Wilcox 1983). Hall (1963) attributed the change in composition to ion exchange as the groundwater flowed through the fractured volcanic rocks. Some of the water rises along the major fault zone separating the Socorro Mountain block from the Socorro Basin and issues forth as the warm (32°C) springs which were largely responsible for settlement of the community and are a major source of municipal water. The arsenic content of the spring waters is relatively constant at 46–47 ppb (Table 6).

TABLE 6. DISSOLVED ARSENIC CONTENT OF MUNICIPAL WELLS AND SPRINGS AT SOCORRO, NEW MEXICO. CONCENTRATIONS IN PPB. DATA FROM CITY OF SOCORRO WATER DEPARTMENT

FROM CITY OF SOCORRO WATER DEPARTMENT		
	May 1991 (ppm)	Oct. 1994 (ppm)
WARM SPRINGS Sedillo Spring Socorro Spring	47 47	47 46
MIXED WATERS Industrial Park Well Zimmerly City Well	28 24	27 27
SHALLOW, NEAR RIO GRANDE Olson City Well Eagle Picher City Well	7 8	7 9

In contrast to the thermal waters described above, two City of Socorro wells near the Rio Grande floodplain produce Ca-Na-SO₄-HCO₃ waters with arsenic values of only 7–9 ppb. These wells produce waters with compositions near that of average irrigation water (Anderholm 1983). The wells are probably in good hydraulic connectivity with the river and irrigation ditches. Two wells within the City of Socorro, between the thermal springs and the floodplain, produce waters with intermediate arsenic values (Table 6) which may reflect mixing of the end-member water types.

The Socorro example cited above helps explain increases in arsenic with depth elsewhere in the Middle Rio Grande Basin. In the Albuquerque area, wells deeper than about 1200 feet produce Na-HCO₃ waters with arsenic contents generally

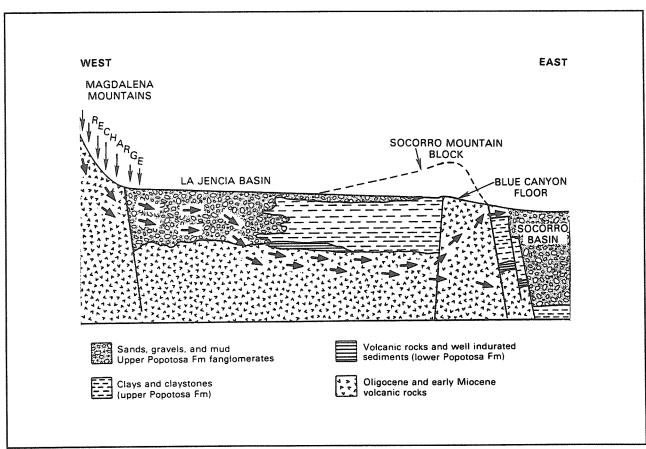


Figure 6. Generalized hydrogeologic cross section west to east through La Jencia Basin and the Socorro Mountain block. Arrows denote hydrologic recharge and postulated groundwater flow path. From Barroll and Reiter (1990) with permission of the American Geophysical Union.

greater than 30 ppb (Table 4). The Albuquerque Basin was a closed basin from about 26 m.y. ago until about 5 m.y. ago and most of its sedimentary fill accumulated under oxidizing, alkaline, saline conditions. The best aquifer consists of the poorly consolidated sands and gravels deposited by the ancestral Rio Grande after the drainage became integrated. Similar decreases in water quality with increasing depth can be expected elsewhere along basins of the Rio Grande rift, especially where volcanic rocks and volcaniclastic sediments are abundant.

COMPARISON OF ARSENIC CONCENTRATIONS ALONG THE RIO GRANDE, SNAKE, AND COLORADO RIVERS

To check our observations and conclusions derived from studying the Rio Grande and to place them in regional perspective we examined all the arsenic data in the STORET data base for the Snake and Colorado rivers (figures 7 and 8). Similar ranges in arsenic concentrations and relationships between the arsenic data and geologic and climatologic parameters are evident in all three drainages. Arsenic concentrations are summarized for key sample sites along the Snake and Colorado rivers, respectively (tables 7 and 8). Arsenic concentrations in surface waters are very low (1-3 ppb) where these major rivers drain the Southern Rocky Mountains. Here, the combination of high regional elevation, high topographic relief, and relatively high precipitation results in abundant clear-water perennial tributaries and dilution of arsenic derived from water-rock reactions.

An abrupt increase in arsenic occurs in the Snake River drainage in southwestern Idaho. The Rocky Mountain and eastern Snake River Plains reaches of the Snake River average 1 to 3.6 ppb dissolved arsenic but where the Snake enters silicic volcanic terrane near Twin Falls, Idaho, the arsenic content of tributary streams and wells increases dramatically (Table 7). Many domestic wells near Weiser, Idaho, and in Malheur County, Oregon, have arsenic concentrations from 50 to 150 ppb. Dissolved arsenic in the Snake River averages

4.5–5.5 ppb through this volcanic terrane which is similar to the 4.3–5.3 ppb average dissolved arsenic for the Rio Grande as it flows along the eastern edge of the Mogollon-Datil volcanic field (tables 2 and 7). Arsenic concentrations in both the Rio Grande and the Snake decrease to more normal values after they pass through the silicic volcanic terranes.

Dissolved arsenic in the Colorado Plateau reach of the Colorado River is very low (1–2 ppb), although some tributaries in the Piceance Basin average 3-4 ppb (Figure 8 and Table 8). But where the Colorado River enters the Basin and Range province at Lake Mead, arsenic concentrations increase abruptly in tributary streams, springs, and wells (Table 8). The Basin and Range province from Lake Mead to Yuma contains both abundant rhyolitic volcanic rocks and large areas of potassium metasomatism. However, dissolved arsenic in the Colorado River itself remains low instead of increasing 2 to 3-fold as it does in the Rio Grande and Snake rivers where they traverse silicic volcanic terranes. The reason is because the Colorado River loses water to the arid basins it passes through between Lake Mead and Yuma, Arizona. Comparison of hydrogen and oxygen isotopic composition of Colorado River water at Hoover Dam with the isotopic composition of well waters in arid basins between Hoover Dam and Yuma indicates that 29 to 44% of the groundwater in these wells infiltrated from the river (Robertson 1991, Table 21). The isotopic data indicate that significant amounts of river water are moving into piedmont areas bordering the floodplain (op. cit., p. C69).

CONCLUSIONS

Arsenic may be useful as a natural tracer in hydrologic systems. The main source of arsenic is water-rock reactions, both low and high temperature. Arsenic concentrations in groundwater vary with the type of rock in contact with the water, the temperatures, residence time, and geochemical parameters such as pH, Eh, salinity, complexing agents, etc. Arsenic concentrations in groundwater are highest in silicic volcanic terranes and lowest in regions underlain mainly by granitic and metamor-

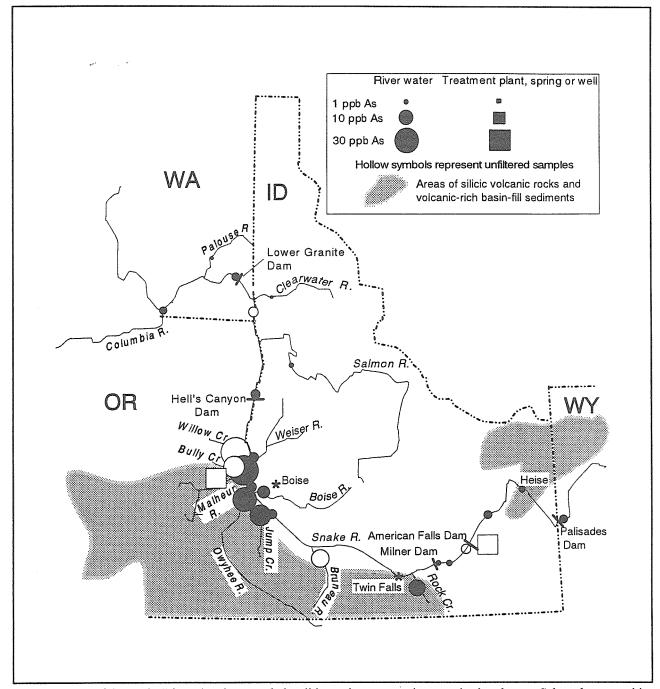


Figure 7. Map of the Snake River showing sample localities and representative arsenic abundances. Selected communities and sample localities are listed in Table 7.

phic rocks. The response, or lack of response, of arsenic levels in a river traversing a high-arsenic terrane may indicate whether it is a gaining or losing stream. Mixing of groundwaters with different arsenic contents can also provide useful hydrologic data as in the Socorro and Albuquerque

areas. The Middle Rio Grande Basin, stretching from Cochiti Reservoir to Elephant Butte Reservoir, encompasses a variety of rock types and interrelated surface and subsurface hydrologic systems. Detailed sampling and analysis of arsenic in both water and sediment should prove useful.

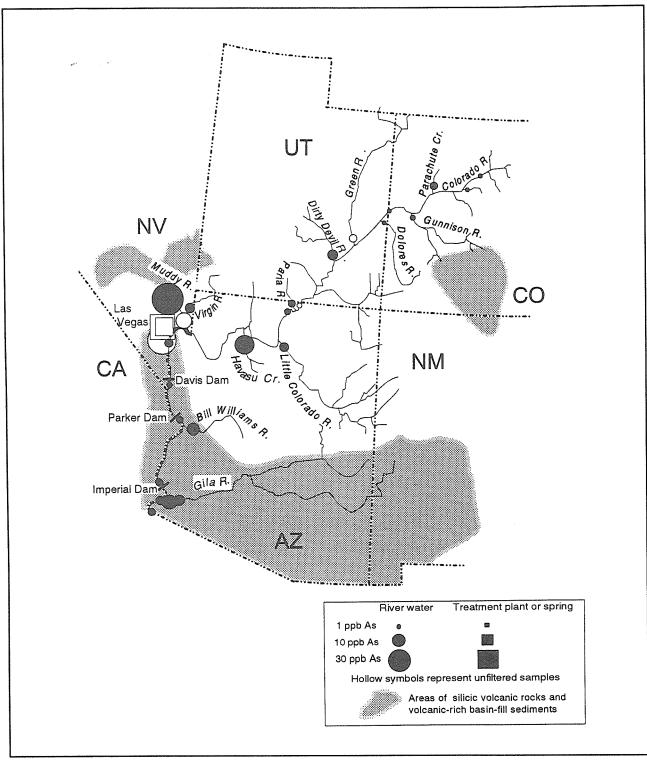


Figure 8. Map of the Colorado River showing sample localities and representative arsenic abundances. Selected communities and sample localities are listed in Table 8.

TABLE 7. AVERAGE ARSENIC CONCENTRATIONS IN WATER AND SEDIMENT OF THE SNAKE RIVER AND SELECTED TRIBUTARIES (INCLUDING SOME WELLS AND SPRINGS). ALL ANALYSES FROM STORET DATA BASE AS OF 11/30/94. NUMBER OF SAMPLES GIVEN IN PARENTHESES. SNAKE RIVER SAMPLES ARE CAPITALIZED; TRIBUTARIES ARE NAMED

		VER SAMPLES ARE	<u> </u>	Sediment	
Location	Geologic setting	When sampled	Dissolved arsenic (ppb)	Total arsenic (ppb)	Dry wt. arsenic (ppb)
NEAR ALPINE, WY (above					. * * *
Palisades Reservoir)	Rocky Mtn	1/74–10/77	3.6 (11)	4.4 (11)	
NEAR HEISE, ID	Snake R. Plains	3/74–9/90	2.7 (58)	3.1 (41)	
AT BLACKFOOT, ID	Snake R. Plains	6/76–12/90	3 (8)	4.3 (4)	
Batiste Springs near Pocatello, ID	Snake R. Plains	3/75–7/87	27.5 (15)		
American Falls Reservoir	Snake R. Plains	8/737/92		5.1 (29)	4300 (27)
BELOW AMERICAN FALLS DAM	Snake R. Plains	7/73–8/77		4.4 (15)	1150
HOWELLS FERRY NEAR RUPERT, ID	Snake R. Plains	7/74–5/90	1.7 (3)	2.8 (12)	
MILNER RESERVOIR AT DAM	Snake R. Plains	4/68–6/81	1.2 (6)	3.1 (81)	
Rock Creek near mouth near Twin Falls, ID	rhyolite volcanics	10/78–7/89	14 (1)	12.8 (105)	2800 (1)
Bruneau River near Bruneau, ID	rhyolite volcanics	10/789/83		16.1 (12)	11,200
AT MARSING, ID UPSTREAM OF CALDWELL, ID	Snake R. Plains	10/70-8/89	4.6 (10)	3.4 (83)	
Jump Creek near Caldwell, ID	rhyolite volcanics	5/90-12/93	35 (2)	45.3 (9) 24 (14)	
Owyhee River at Owyhee, OR	rhyolite volcanics	6/797/94	30.4 (33)	41 (15) 31.4 (81)	6900 (5)
Boise River near Parma, ID	Snake R. Plains	7/69–3/92	7.0 (27) 31.4 (15)	8.2 (49) 30.5 (82)	
At Nyssa, OR	Snake R. Plains	6/75–9/90	5.5 (12)	5.6 (8)	
Malheur River	rhyolite volcanics	11/79–11/86	47 (1)	40.2 (9) 39.3 (77)	3500 (4)
Malheur River	rhyolite volcanics	10/85-7/94		35.7 (80)	8,600-10,000
Bully Creek (Malheur River)	rhyolite volcanics	10/85–5/94		24.5 (82)	
Willow Creek near Vale, OR (Malheur River)	rhyolite volcanics	10/85-5/94		48.3 (82)	
Wells in Malheur Co., OR and near Weiser, ID	rhyolite volcanics		high arsenic in	wells (up to 148 ppb)	
Weiser River at Weiser, ID	rhyolite volcanics	7/77			28,000 7,800
At Weiser, ID	rhyolite volcanics	6/71–10/90	4.5 (48)	5.9 (73)	
AT HELLS CANYON DAM	metamorphic rocks	7/71–5/86	4.5 (51)	5.5 (32)	7,800
Salmon River at White Bird, ID	granitic rocks	12/74-3/92	1.7 (50)	3.4 (20)	
NEAR ANATONE, WA	rhyolite volcanics	7/73-11/90		4.8 (57)	16,800
Clearwater River at Spalding, ID	Precambrian rocks	3/73-3/92	0.5 (13)	1.1 (17)	5,000
BELOW LOWER GRANITE DAM	Columbia Plateau basalts	9/75–7/78	3.3 (6)	2.6 (11)	12,400 (1)
Palouse River at Hooper, WA	Columbia Plateau basalts	12/59–9/84	0.63 (16)	0.6 (1)	1200 (1)
NEAR CONFLUENCE WITH COLUMBIA RIVER AT BURBANK, WA	Columbia Plateau basalts	2/73-9/91	2.8 (67)	3.0 (36)	7000

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TABLE 8. AVERAGE ARSENIC CONCENTRATIONS IN WATER AND SEDIMENT OF THE COLORADO RIVER AND SELECTED TRIBUTARIES (INCLUDING SOME SPRINGS AND WASTEWATER TREATMENT PLANT DISCHARGES). ALL ANALYSES FROM STORET DATA BASE AS OF 12/1/94. NUMBER OF SAMPLES ARE GIVEN IN PARENTHESES. COLORADO RIVER SAMPLES CAPITALIZED; TRIBUTARIES AS NAMED

CATTALIZED, TRIBETAR			<u>Water</u>		Sediment
Location	Geologic setting	When sampled	Dissolved arsenic (ppb)	Total arsenic (ppb)	Dry wt. arsenic (ppb)
AT HOT SULPHUR SPRINGS, CO	Rocky Mtn	10/79–5/94	1.0 (58)	1.0 (58)	
Eagle River at Gypsum, CO	Rocky Mtn	1/80-3/94	1.0 (56)	1.1 (56)	
Parachute Creek near Parachute, CO	Piceance Basin	4/75–9/81	3.7 (30)	4.4 (12)	
Gunnison River near Grand Junction, CO	Colorado Plateau	10/75–9/91	1.5 (58)	2.2 (22)	
Near Colorado– Utah border	Colorado Plateau	10/79–9/91	1.1 (49)	1.8 (11)	
Dolores River near Cisco, UT	Colorado Plateau	5/79–6/91	1.0 (44)	2.3 (6)	
Green River above confluence	Colorado Plateau	5/83-8/88		2.8 (20)	
Dirty Devil River above confluence	Colorado Plateau	1/77–10/86	4.3 (3)	4.7 (133)	
Below Glen Canyon Dam	Colorado Plateau	5/78–11/86		1.3 (39)	
Paria River near Page, AZ	Colorado Plateau	9/77–11/79	2.0 (26)		
At Lees Ferry, AZ	Colorado Plateau	5/74-7/94	1.5 (88)	1.7 (78)	10,400
Little Colorado River	Colorado Plateau	7/79	3 (1)	3 (1)	
Havasu Creek near Supai, AZ	Colorado Plateau	3/82	19 (1)	16 (1)	
Virgin River near Riverside, NV	Basin and Range	3/78-9/86	4.9 (30)	9.6 (14)	
Muddy River near Overton, NV	Basin and Range	4/798/91	51.8 (35)	54.9 (9)	
Lake Mead	Basin and Range	5/70–9/80		14.4 (15)	4250 (2)
BELOW HOOVER DAM	Basin and Range	12/74-6/93	2.6 (58)	3.7 (21)	
Springs in Las Vegas Valley	Basin and Range	2/70–5/70		44.0 (6)	
Las Vegas and Clark County STP effluent	Basin and Range	5/70		22.0 (2)	
Las Vegas Wash near Boulder City	Basin and Range	1/759/80		40.5 (71)	
BELOW DAVIS DAM	Basin and Range	8/86–7/92	2(1)	3 (2)	13,600
Below Parker Dam	Basin and Range	1/76–6/94	2.5 (90)	2.6 (147)	
Bill Williams R. near Planet, AZ	Basin and Range	11/74–6/94	6.6 (84)	7.6 (20)	
ABOVE IMPERIAL DAM, CA	Basin and Range	5/74–7/91	2.1 (56)	2.8 (24)	
Gila R. near Dome, AZ	Basin and Range	11/83–6/94	4.7 (33)	4.9 (29)	
Gila R. near Yuma, AZ	Basin and Range	11/74-4/83	9.3 (25)	11.2 (22)	
ABOVE MORELOS DAM near Andrade, CA	Colorado R. delta	5/73-5/94	3.1 (120)	3.8 (119)	4000 (1)
Main Drain at International Boundary	Colorado R. delta		2 (1)	3.1 (55)	3800 (1)

Acknowledgements

We thank Jim Piatt for providing us with the STORET data base information on the As content of river waters and sediments, and Matt Falkenstein for help with data compilation. Thanks also to Scott Anderholm, Fraser Goff, Jim Piatt and Mike Whitworth for reviewing the manuscript. Thanks to the City of Albuquerque Public Works Department for providing access to geochemical data, as did Rich Sanchez of the City of Socorro Utilities Department.

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