## GEOCHEMICAL STUDIES OF ARSENIC IN THE ALBUQUERQUE BASIN, NEW MEXICO

M. R. Stanton, R. F. Sanzolone, S. J. Sutley, D. J. Grimes, P. J. Lamothe, and R. A. Zielinski U.S. Geological Survey, Mail Stop 973, Denver, Colorado, USA 80225

**INTRODUCTION** As part of the bureau-wide USGS Middle Rio Grande Basin (MRGB) Project, we have examined the abundance, residence, and mobility of arsenic (As) in sediments, rocks, and groundwaters near Albuquerque, New Mexico. As most of the area's drinking water supply originates from groundwater, and because EPA was considering a reduction in the dissolved As standard at the time the project began, a study directed toward a better understanding of As geochemistry in the Albuquerque Basin was warranted. The EPA's recent decision to lower the aqueous As standard to 10 ug/L makes this data increasingly important in shaping future decisions by water suppliers, managers, and consumers in the basin.

**APPROACH** Subsurface geochemical data for the Albuquerque Basin is generally lacking because there are few available samples of geologic materials from deeper parts of the basin. In 1996, a cooperative core drilling project was undertaken to obtain samples of Santa Fe Group basin-fill sediments on the western side of the City of Albuquerque (98th St. drilling site, Figure 1). A primary goal of the coring project was to determine geochemical, mineralogical, and geophysical characteristics of Santa Fe Group sediments that host major aquifers in the Albuquerque area. In addition, the drill hole would provide sediment and groundwater from an area having locally-high (up to 50 ug/L) total dissolved As concentrations. Additional samples (outcrops, subsurface well cuttings, groundwaters) from other areas in and adjacent to the basin would be utilized, in conjunction with newly-acquired hydrologic and geophysical data, to develop a more complete geohydrologic model for the basin.

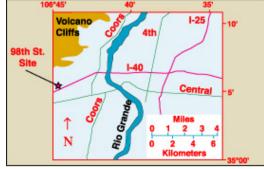


Figure 1. Location of 98th St. drilling site near Albuquerque, New Mexico.

Solid samples collected and analyzed include approximately 200 core samples from the 98th St. drill hole, 100 archived well cuttings samples from production (water) wells, 40 samples of well cuttings from sulfide-bearing volcanic rocks on the western basin margin, and 15 samples of volcanic rocks from surface outcrops. Our study focused on obtaining thorough geochemical and mineralogical analyses of the 98th St. core because it represents some of the most recent and complete samples available, and its 1560-foot length encompasses the depths of most aquifers in the basin. Long-interval composite samples (LIC; intervals >20 ft) representing the 22 lithologic units initially identified by Stone and others (1997) were first collected and analyzed to establish elemental distributions and abundances in the drilled section. Short-interval composite samples (SIC; intervals <1 ft) from 655-765 ft. were then analyzed to better-define As concentrations on a detailed scale. Grab samples were used for X-ray diffraction (XRD), scanning electron microscope (SEM), and fission track examination.

Using 98th St. core samples as a baseline, drill cuttings from water production wells from

other parts of the basin were characterized and compared to see if geochemical trends as in the 98th St. core (e.g., element concentrations, metal associations) were evident. Cuttings were available from 98th St., 5 westside wells, and one well near central Albuquerque. Recent exploration on the western basin margin permitted acquisition and study of cuttings and rock fragments from the Kachina well which penetrates a zone of sulfide-rich volcanic rocks at depth. Locally, volcanic flows cut or overly basin sediments, for example, Volcano Cliffs northwest of Albuquerque (Figure 1). Determination of background concentrations in these widespread rocks is a necessary component of the overall As geochemical study.

Water samples include 18 from the 4 monitoring wells completed in the 98th St. hole, 25 City production wells, and 2 thermal springs adjacent to the basin near Jemez Springs. Measurements of pH, conductivity (SpC), dissolved oxygen (DO), and temperature (°C) were made at the sample site. The 98th St. well waters were analyzed over a 2-year period to discern if there were any temporal trends in water chemistry.

**METHODS AND ANALYSES** Core samples were pulverized to <100 mesh for mineralogical analysis and for a 4-acid total digestion followed by 40-element analysis using inductively coupled plasma-mass spectrometry (ICP-MS; Briggs, 1990). A 5-step sequential partial extraction scheme (SPE; Chao and Sanzolone, 1989) followed by ICP-MS analysis was applied to selected samples to determine residences of solid phase As in five operationally-defined fractions. For XRD, aliquots of the <100 mesh or grab samples were prepared as packed powder mounts and scanned; unpulverized grab samples were used for SEM examination. Fission-track methods examined different minerals as potential hosts for As. The basis of the method is that As and U exhibit similar behavior under the conditions in 98th St. wells. Mineral grains that sorb U from solution produce a higher density of fission tracks than grains that do not sorb U.

Groundwater samples were immediately filtered thru a 0.45 um nitrocellulose filter. Arsenic species ( $As^{3+}$ ,  $As^{5+}$ ; Ficklin, 1983) samples were preserved with 1% (v/v) ultrapure HCl and kept in the dark; cation samples were preserved with 1% (v/v) ultrapure HNO<sub>3</sub>; both were subsequently analyzed using ICP-MS. Aliquots for anions and alkalinity (both unpreserved and kept at 4 °C) were later analyzed using ion chromatography (IC) and titration, respectively.

**RESULTS AND DISCUSSION** Arsenic is widespread but not highly-concentrated in Santa Fe Group sediments, ranging from below detection (<2 ppm) to 25 ppm with a mean abundance of 8.5 ppm in the SIC samples. Maximum values of many elements, including As, Fe, V, Co, Cu, and Zn, are found within the clay- and Fe-oxide-rich interval from 655-765 ft. Higher As levels (>10 ppm) are nearly always associated with finer-grained (clay and silt) fractions in this interval (Figure 2).

Some strong relationships among certain elements were observed 98th St. LIC's. For example, Fe is strongly correlated with As and Zn (r= 0.83). As and Zn increase from 6 and 25 ppm, respectively, at the top of the Atrisco Member ("Tma" unit) to 18 and 80 ppm at its base (Figure 3). Arsenic and Zn anomalies at base of the Atrisco may be a useful geochemical marker in stratigraphic studies of Santa Fe Group sediments. The r value (correlation coefficient) is high for Fe vs As in 98th St. 1-ft. composites (0.84), cuttings (0.93), and the westside city well Gonzales-1 cuttings (0.84). Thus, some cuttings samples retain the strong associations observed in 98th St. LIC samples. The upper 1900 ft of Kachina samples are Santa Fe Group sediments comparable to 98th St., with a mean As concentration of 18 ppm.

X-ray diffraction studies indicate specific As-bearing minerals (such as arsenopyrite, FeAsS) are not present at detectable levels or are absent. SEM studies do not indicate distinct As-bearing

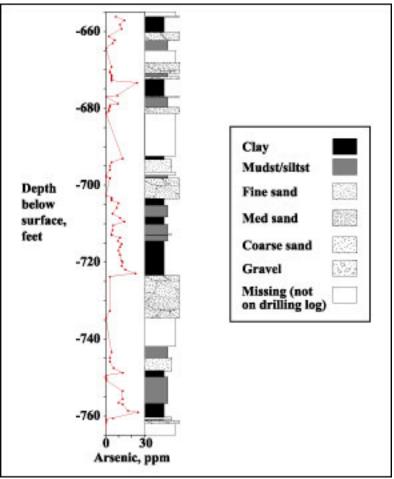


Figure 2. Detailed stratigraphy of 98th St. drill core samples from 655-765 ft. showing As concentrations and associations with solid phases.

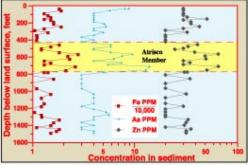


Figure 3. Fe, As, and Zn values in 98th St. samples, showing elevated values of these elements within the Atrisco Member. Note the high As concentration near the base of this unit.

solids. Fission track studies indicate mobile U (and by analogous chemistry, As) is housed primarily in secondary Fe-oxides, and that primary silicates (quartz, feldspars) are relatively depleted in U. The results also demonstrate the existence of distinct, separate Fe-oxide grains in Santa Fe Group sediments, and that these grains house the bulk of uranium in most samples. SPE results show that a large proportion of As in the 98th St. SIC sediments (655-765 ft) is associated with secondary iron-oxides (Figure 4) which may exist as distinct grains, or coatings on mineral surfaces including clays.

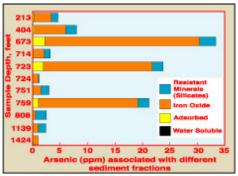


Figure 4. Arsenic associations with different sediment fractions based on SPE scheme. (In this diagram, the final 2 extractions are combined into one fraction designated as "resistant minerals").

In contrast to sediments, As concentrations are relatively high in outcrop rocks and subsurface volcanic rocks. In outcrops such as Cerro Colorado (9 miles west of 98th St.), the maximum As abundance is 140 ppm. Below approximately 1900 ft in the Kachina hole, volcanic rocks are dominant and As is as high as 1340 ppm with a mean of 290 ppm. Thus, As from volcanic rocks is about 10-100 times that of basin-fill sediments. Mineralogy in lower Kachina samples is dominated by feldspars and pyrite, with lower abundances ( $\leq 10$  vol %) of mixed-metal oxides. The lower Kachina samples, while not part of the Santa Fe Group sediment section, represent a potential source of As elsewhere in the basin. Although the volcanic rock fragments appear oxidatively weathered at depth, the hydrologic connection of the basin margin with basin-fill sediments is not known, so the volcanic rocks might be only local sources of As. Travertine and fresh iron oxide precipitates at Jemez Springs contain high As (420 ppm and 3.3 wt. % As, respectively).

98th St. waters generally show little variation in As concentrations over a 2-year period (Table 1). Aqueous As concentrations from other basin ground waters (e.g., production wells) range from 10 to 30 ug/L. Thermal waters near the Jemez Mountains have As concentrations of 1500 ug/L.

Sample No./	1997	1998	1997	1998	1997	1998	1997	1998
Depth [ft]	pН	pН	Fe(tot)	Fe(tot)	As3+	As3+	As5+	As5+
98-4/438	9.94	9.24	.044	.022	<.003	<.002	.015	.019
98-3/749	8.61	8.26	.029	.01	.006	.008	<.003	<.002
98-2/1112	9.08	9.03	.013	.01	.028	.031	.014	.004
98-1/1544	8.40	8.33	<.01	<.01	.003	<.002	.027	.030

Table 1. Groundwater pH, total Fe, and As species (in ppm) in 98th St. samples, 1997 and 1998.

The SPE, mineralogical, and fission track results suggest Fe- oxides are sources and sinks of As in Santa Fe Group sediments. Water data indicate As in the sediments may be mobilized by interaction of As-bearing iron oxides with higher-pH groundwater.

## REFERENCES

Briggs, P. H. 1990, Elemental analysis of geologic materials by inductively coupled plasma-atomic emission spectrometry, <u>in</u> Quality assurance manual for the Branch of Geochemistry, U.S. Geological Survey, ed. B.F. Arbogast, 83-91. USGS Open-File Report 90-668.

Ficklin, W.H., 1983, Separation of As(III) and As(V) in ground waters by ion-exchange. Talanta, v. 30, p. 371-373.

Chao, T.T., and Sanzolone, R.F., 1989, Fractionation of soil selenium by sequential partial dissolution. Soil Science Society of America Journal, v. 53, p. 385-392.

Stone, B. D., Allen, B. D., Mikolas, M., Hawley, J. W., Johnson, P., and Thorn, C. R., 1997, Preliminary lithostratigraphy, interpreted geophysical logs, and hydrogeologic characteristics of the 98th St. core hole, Albuquerque, New Mexico. USGS Open-File Report 98-210, 82 p.