Hydrogeochemistry of Contaminated Springs at TA-16

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Deep drilling at Technical Area (TA) 16 at LANL recently revealed high explosives (HE) contamination at depths from 750 to 1500 ft, including in the regional aquifer. The levels of HE are over 40 times the Environmental Protection Agency lifetime health advisory for the HE RDX (cyclotrimethylenetrinitramine). This discovery has heightened concerns among members of the public, neighboring Indian pueblos, and other stakeholders about groundwater contamination from Laboratory operations. In addition to HE, barium and nitrate contamination are also of concern at TA-16. We are determining the extent of contamination and investigating the processes that control contaminant concentrations in the TA-16 mesa and canyon environments.

Based on extensive interviews with site personnel and widespread environmental sampling, we determined that the most significant source of HE contamination appears to be outfall from the HE-machining building, TA-16-260 (Figure 1). Total HE levels in soil at this site range to over 20 weight percent (wt%). To reduce the concentrations of HE available for transport, the contaminated soils have been excavated and staged for off-site disposal.

Because water is the most likely medium by which the HE constituents may affect human or ecological receptors, the crucial scientific question associated with the environmental investigations at TA-16

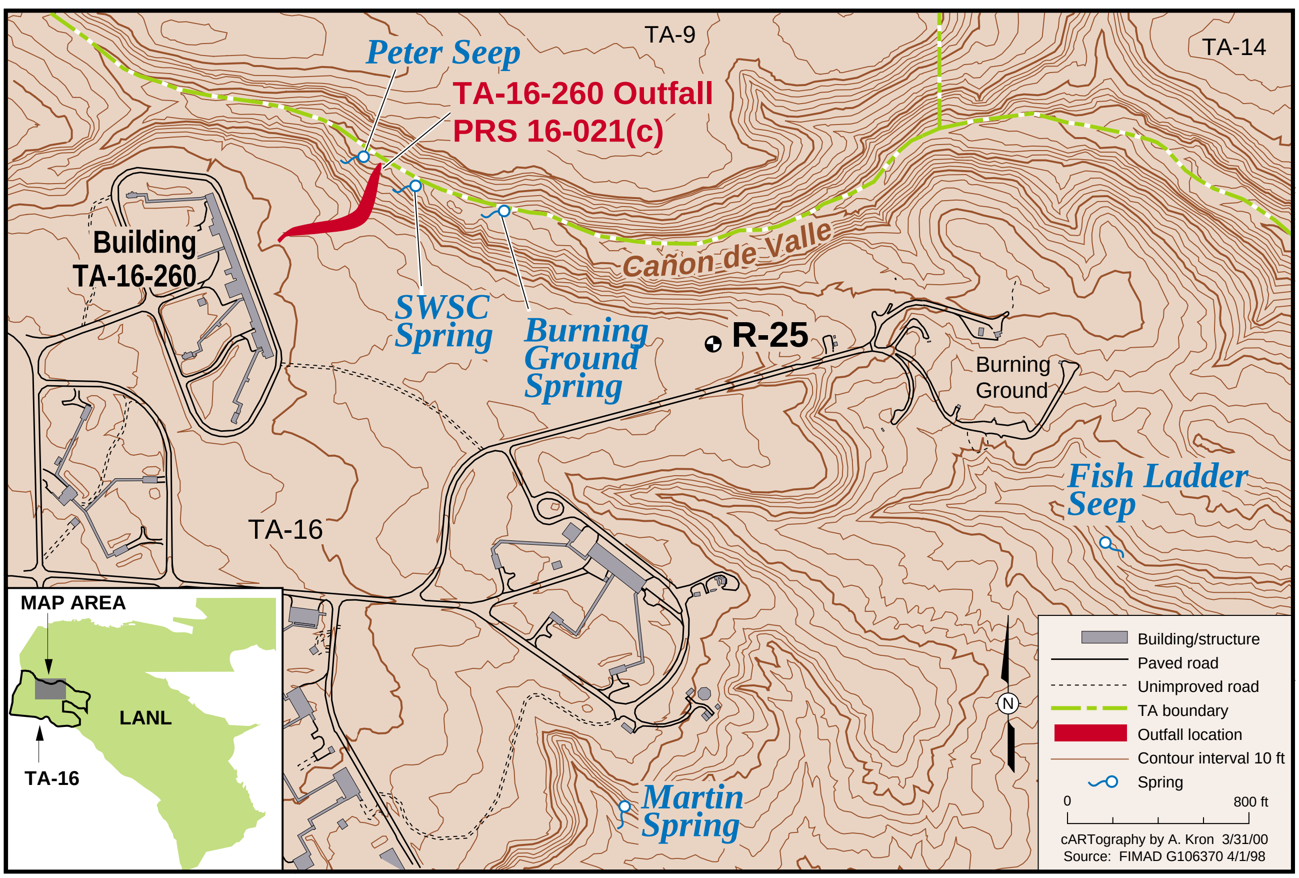

Figure 1. Technical Area 16.
Map showing the location of the TA-16-260 outfall and nearby features. Inset shows the location of TA-16 at LANL.

concerns how water and its associated contaminants move through the hydrogeologic system in this area. We have addressed this question in our study.

A conceptual model of likely fluid flow paths at TA-16 is shown in Figure 2. Water in three springs (sanitary wastewater system consolidation [SWSC], Burning Ground, and Martin), the Cañon de Valle alluvial system, and deeper groundwater in well R-25 is contaminated with HE.

At this time, we are focusing on understanding the shallow (less than 200-ft depth) hydrologic system as it manifests itself in the springs and seeps located in Cañon de Valle and Martin Canyon. We are using measurements of spring water chemistry, spring flow rates, and stable isotope compositions to determine (1) the principal recharge locations for the TA-16 springs (and by inference the recharge locations for the deeper hydrologic systems), (2) the nature of temporal variability in both natural and anthropogenic constituents in springs, and (3) whether contaminant concentrations are decreasing or increasing with the passage of time.

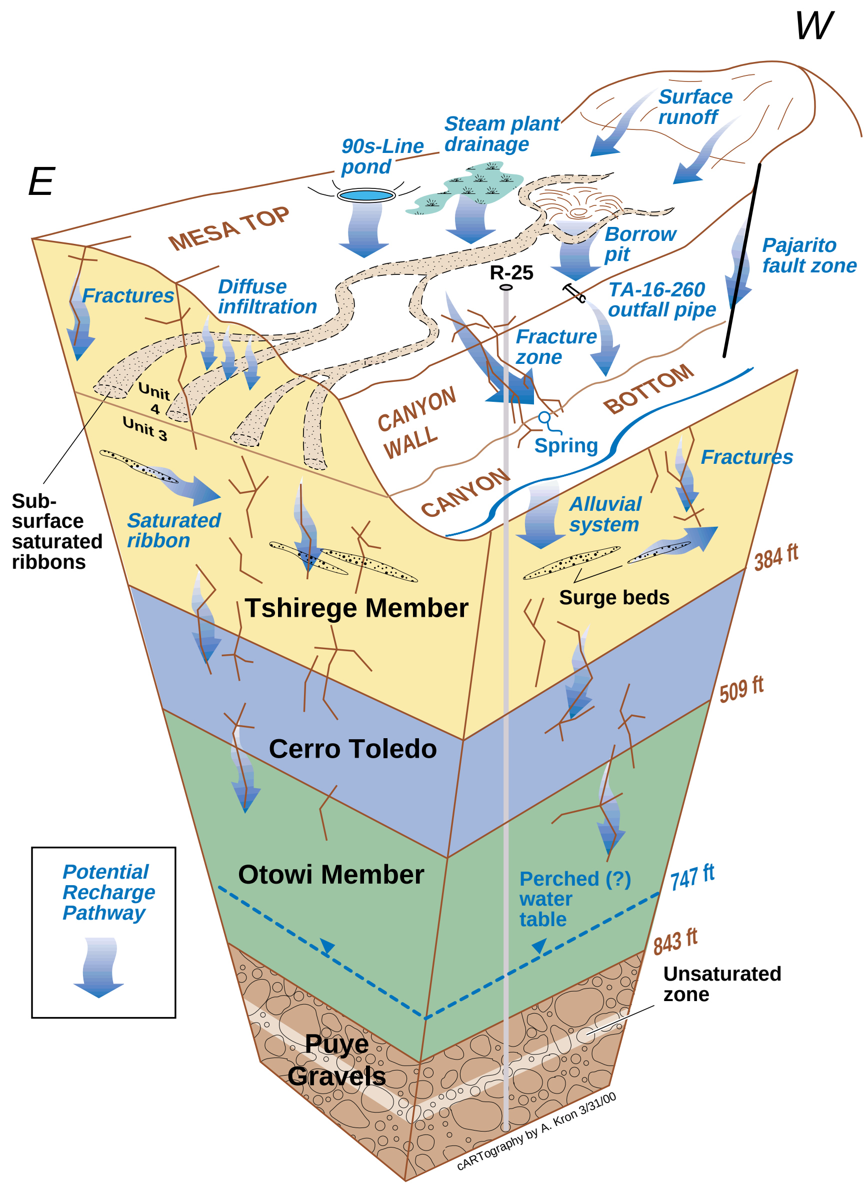

Figure 2. Water Transport.
Diagram showing a conceptual model for water transport at TA-16 (and by inference, associated HE and barium contamination).

Water Chemistry and Flow Rates

Data on spring flow rates and water chemistry provide information on the hydrologic systems and pathways that feed the springs. The water chemistry of a spring reflects local precipitation and interactions with soils and rocks along the flow paths that feed the spring. A spring system that shows little change in flow or chemistry over time is typically interpreted to represent a well-mixed system with little seasonal variation in recharge sources. A more dynamic spring system reflects differing proportions of water sources such as diffuse recharge, spring snowmelt, monsoonal water, and anthropogenic discharge.

Our observations suggest that the water chemistry of the TA-16 springs is typical of springs in the arid and semiarid Southwest, particularly those associated with evolved volcanic rocks such as those found in the Jemez Mountains. All the springs at TA-16 are low-ionic-strength calcium-bicarbonate, mainly because of the high pH in local soil, widespread occurrence of carbonate, and preponderance of Ca-K rich volcanic rocks and soils.

Temporal Variations. Both flow rates (Figure 3) and concentrations (Figure 4) of naturally occurring and anthropogenic compounds in the TA-16 springs vary with the seasons and with high-precipitation events. Not surprisingly, flows are highest following spring snowmelt and the summer monsoonal rains. Burning Ground Spring has the highest annual

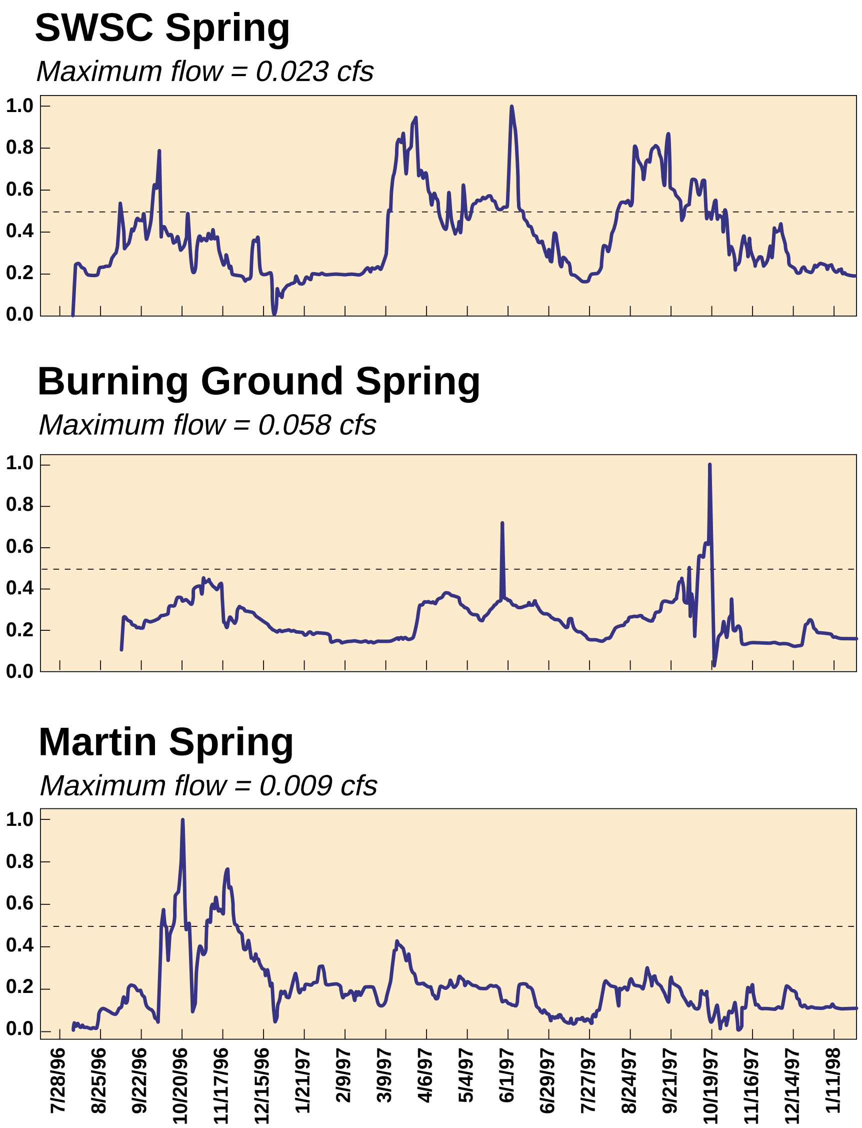

Figure 3. Water Flow.
Flow rates in cubic feet per second (cfs) at SWSC, Burning Ground, and Martin Springs between 1997 and 1999.

flow of the three; however, our analysis of the frequency distribution of average daily flow at Burning Ground indicates that it has a narrow range of flow rates, and the normalized standard deviation of flow rates is the lowest of the three. In contrast, the SWSC Spring and the highest normalized standard deviation of flow rates. Our data indicate that SWSC Spring has a more variable flow behavior than Burning Ground Spring. Martin Spring has the lowest flow rates of the three. Our data for Martin Spring show a continuous range of flow rates and an intermediate normalized standard deviation.

The flow variations (or more specifically, changes in recharge that cause flow of water to vary) affect the chemistry of the spring waters as well. The water chemistry varies with the extent of dilution during high-flow periods and the pathways taken by recharge. This variation takes place because different parts of the vadose zone are sampled as saturated zones grow and shrink during recharge (Figures 3 and 4). For example, recharge can increase dissolved oxygen in the spring waters, thus altering redox conditions. The variability of the redox conditions is likely responsible for some of the observed concentration variations in redox-sensitive species such as iron, and it also has implications for the breakdown of nitrate and HE.

Spring-Water Chemistry Comparisons. To examine the overall chemical behavior of the springs and evaluate differences between them, we developed correlation matrices for 39 chemical parameters (including pH and temperature). Our results show generally similar correlations of chemical parameters between the springs, although there are some important differences in actual concentrations of the chemical parameters between the springs. The correlations between the major anions and HE species are statistically significant, which is evidence that the HE species are behaving conservatively (i.e., they are highly mobile). All the springs have elevated nitrate concentrations, and nitrate correlates significantly with HE and barium, the two main anthropogenic sources of nitrate at TA-16. Barium concentrations are also elevated, and barium is correlated with the other major cations.

Burning Ground and SWSC Springs have relatively small differences in chemistry, which reflects their close proximity and implies that they are part of the same flow system. As noted above, there are some differences in their flow behavior that reflect different degrees of connectivity to the saturated zone and the different fast recharge pathways from which the two springs receive water. There are significant differences between the chemistry of Martin Spring versus Burning Ground and SWSC Springs. Martin Spring has greater boron, HE, nitrate, and sulfate concentrations (as well as other chemical constituents) than both Burning Ground and SWSC Springs. In addition, Martin Spring has higher

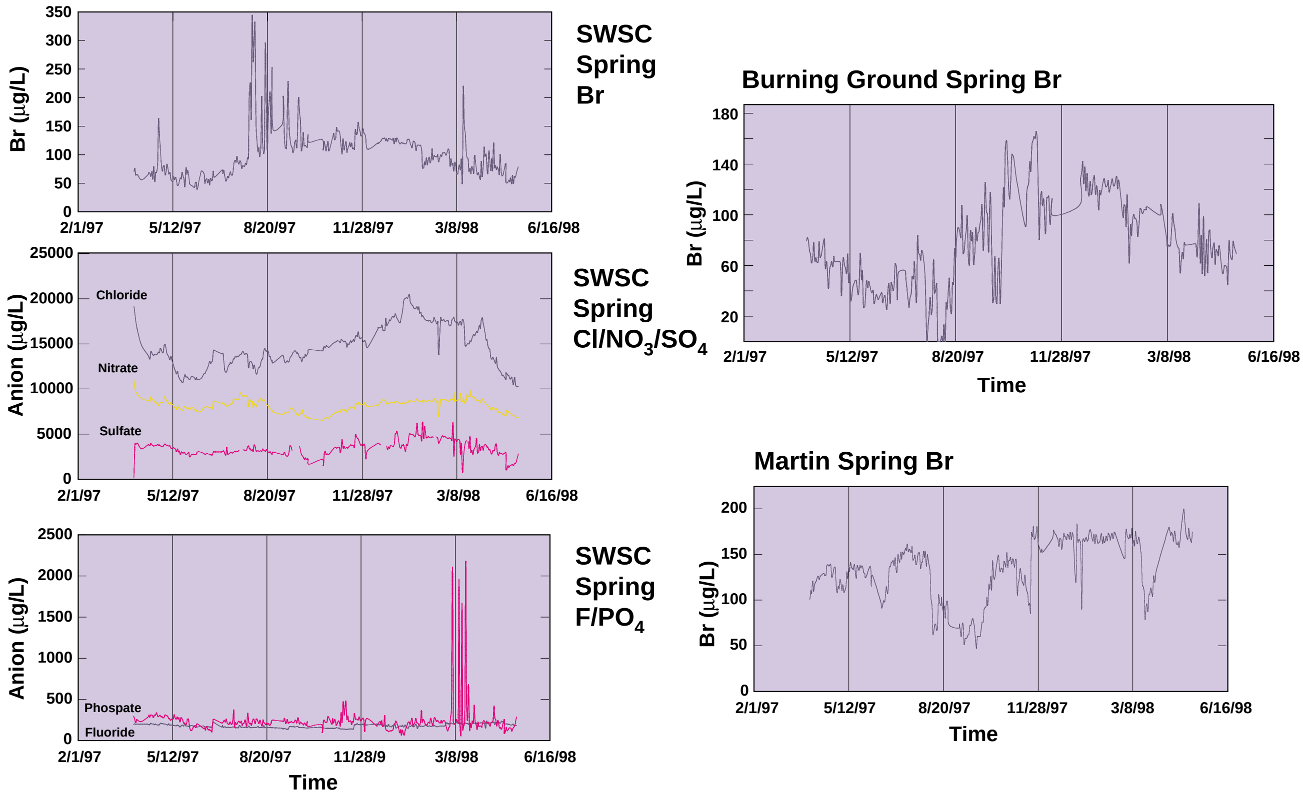

Figure 4. Bromide and Other Anion Concentrations.
The plots show constituent concentration (unfiltered data) versus time for the three springs.

stable isotope ($\delta^{18}O$ and δD) values than the other springs. The different flow behavior and chemistry in Martin Spring suggests that Martin may be part of a different flow system than SWSC and Burning Ground Springs or that it has an additional recharge source that is large enough to shift the spring chemistry away from that of the other springs.

Barium Colloids. A systematic bias occurs in barium concentrations for all three springs, where unfiltered barium concentrations are higher than filtered (0.45-mm filtration). This bias suggests that some of the barium inventory is being transported as either barite colloids or as sorbed barium on other colloidal minerals. Our geochemical modeling results using the code PHREEQC (Parkhurst 1995) suggest that barite ($BaSO_4$) colloids may be precipitating in the spring waters. The geochemical modeling results and filtered versus unfiltered analyses also suggest that iron and/or alumino-silcate mineral colloids may be precipitating in the springs. These minerals may act as a substrate for barium adsorption.

Tracer Study Results. We applied a potassium bromide tracer in the TA-16-260 outfall (Figure 1) during April 1997 and observed bromide break-through in SWSC Spring during August 1997 (Figure 4). This observation confirms the connection of the contaminated soils in the TA-16-260 outfall and the contamination in the springs.

The bromide tracer results suggest that fluid flow and contaminant transport are influenced by fractures. The nature of the bromide break-through suggests fluid flow through a porous media with a bimodal perme-ability distribution. The intermittent nature of the bromide peaks suggests a heterogeneous system and may reflect hydrologic dispersive effects. The rapid breakthrough (less than 6 months) is incompatible with flow through a homogeneous porous media with unsaturated hydraulic conductivities similar to those measured in the Bandelier tuff at TA-16 and suggests that fracture flow is an important recharge process.

Stable Isotopes and Tritium. Hydrogen (including tritium) and oxygen isotopes are excellent tracers of hydrologic processes. Hydrogen and oxygen stable isotope ratios and tritium activities can be measured accurately using modern spectromet-ric techniques. In low-temperature environments, the isotope ratios of hydrogen and oxygen are not strongly influenced by interactions with soil or rock matrix. Hence, stable-isotope ratios are extremely sensitive indicators of recharge source and of fluid-mixing processes. Stable isotope data are typically expressed in delta (δ) notation in permil (‰) units.

Our measurements of oxygen stable isotope compositions in local precipitation show both seasonal and shorter-term variations. Summer monsoonal storms generally have higher $\delta^{18}O$ values than winter storms or snow. In addition, $\delta^{18}O$ can vary significantly (by up to 10‰) between individual precipitation events. This variability reflects the multiple precipitation sources that affect the Jemez Mountain region.

In contrast, the oxygen isotope compositions of the three springs vary less than local precipitation. SWSC and Burning Ground Springs vary by at most 3‰ in $\delta^{18}O$ and Martin Spring varies by at most 5‰. This damping of the oxygen isotopic signature reflects the mixing and dispersion that occur between recharge and discharge in the springs. However, most well-mixed springs show even less annual variability in $\delta^{18}O$, suggesting that the time frame of flow for the springs is short (less than a few years). Our preliminary mixing model calculations suggest that a large proportion (>30%) of the increased flow in response to some precipitation events is new water. In other words, significant amounts of water recharge the spring systems and are discharged within 24 hours of a given precipitation event. These data reinforce the concept of fast pathways and suggest that spring residence times are relatively short. Work is currently underway to examine the spring residence times more thoroughly.

The stable oxygen isotopic data also show strong similarities between the SWSC and Burning Ground Springs and suggest that Martin Spring has different recharge sources. As well as having a damped annual signal relative to Martin Spring, SWSC and Burning Ground Springs also are consistently lower in $\delta^{18}O$ than Martin Spring. A particularly important feature of the hydrogen and oxygen isotope compositions of precipitation is that they vary linearly with elevation. Higher-elevation precipitation has lower average isotopic values than lower-elevation precipitation. Because of this linear relation with elevation, spring stable-isotope compositions can be used to estimate recharge elevations. Using a simple (non-mass flux weighted) average, these data suggest that the recharge zone for the mass of water seen at Martin Spring may be about 900 ft lower in elevation than that for the other two springs. It is also possible that Martin Spring has received recharge from an evaporated source such as ponds on the mesa top. This type of input will result in an estimated recharge elevation that is too low. In any case, the difference in stable isotopes between Martin and SWSC/Burning Ground Springs is consistent with the major ion and contaminant data discussed above and supports a difference in recharge sources.

Tritium (^3H) can be used to trace young groundwater signatures because it has a short half-life (12.4 yr) and because it was produced during atmospheric nuclear testing during the 1950s and 1960s. All three springs contain elevated tritium (29–43 tritium units), suggesting young recharge sources. Assuming a piston-flow regime (Blake et al., 1995), the tritium model ages are less than 30 yr. However, this is a maximum age estimate, and ages are likely to be less than 5 yr.

Conclusions

Stable isotope, tracer, and water chemical data all suggest that the TA-16 springs are fed by complex hydrologic systems that tap a base-flow component, a young-recharge component, and a contaminated, anthropogenic component. Recharge for all three springs appears to be local, and the residence times for this precipitation in the hydrologic system discharged at the springs is probably short (less than a few years). SWSC and Burning Ground Springs have similar isotopic signatures, chemistries, and flow characteristics. Martin Spring appears to be distinct.

This hydrologic information is significant for the ongoing studies of HE contamination at TA-16 for three reasons. First, the short residence times for spring discharge suggest that the spring HE concentrations will decrease following removal of the principal HE sources on the TA-16 mesa top. Second, the contaminant flux information that is being derived in these studies will be vital to support both human health and ecological risk assessments for the site. Finally, the studies provide fundamental hydrologic information on the flow and transport of water in a semiarid, fractured hydrologic system. Fractured systems are among the most difficult to develop adequate conceptual models and, hence, simulate numerically. The empirical data collected in these studies will represent an excellent test of complex hydrologic codes used to simulate vadose zone flow in fractured systems. ■

Further Reading

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