# Isotope Tracers Help Manage Water Resources

Livermore is using isotope tracer techniques to investigate groundwater movement beneath the Nevada Test Site and the Livermore site and to provide public water managers with tools to manage valuable groundwater resources.

AVE you ever thought about how old your drinking water is or where it came from? How would you figure out the answers to those questions if you wanted to know? If you had access to Lawrence Livermore's isotope tracing techniques, those questions might not be too difficult to answer.

Since the inception of the Laboratory, Livermore scientists have been studying both radioactive and stable isotopes. Support to the nuclear test program has given Livermore unparalleled nuclear chemistry expertise. This experience found an unexpected application when, after a decade of underground testing at the Nevada Test Site (NTS), the Laboratory began studying the movement of radioactive elements from those tests in groundwater. Initially, conventional hydrogeologic characterization

methods were used to learn about the aquifer beneath NTS. These studies look at data from well pumping tests to learn about the porosity, permeability, and other properties of the aquifer. The drawback to these conventional methods is that the natural heterogeneities in an aquifer are difficult to characterize without detailed geologic information. Additional data can be gathered only by drilling more wells. Drilling costs are particularly high in an arid region such as NTS where the water table is sometimes more than 600 meters (2.000 feet) below the surface. Moreover, the test site is enormous, encompassing over 3,600 square kilometers, which could necessitate hundreds of drilling sites.

Livermore scientists knew that determining the nature and extent of

radionuclide contamination in groundwater at NTS was a complex project. To augment conventional hydrogeologic techniques for their groundwater studies, Livermore began using isotope tracers, which look directly at the groundwater itself rather than at the rock through which the water flows. These methods are described in the box on p. 15.

Today, Dave Smith manages Livermore's work on radionuclide migration at NTS. (See Figure 1.) To better predict the possible transport of contaminants in groundwater, his team measures both stable isotopes (ratios of deuterium to hydrogen, oxygen-18 to oxygen-16, carbon-13 to carbon-12, strontium-87 to strontium-86, and noble gases) and radioactive isotopes (tritium, carbon-14, chlorine-36, and uranium isotopes) at more than a hundred springs and wells throughout southern Nevada. Recently obtained oxygen and hydrogen isotope data suggest that the regional aquifer underlying the test site is recharged from north of NTS rather than from the east as originally concluded from conventional hydrogeologic evidence alone. Carbon-14 age measurements indicate that the flow system is very heterogeneous, with highly variable flow rates. Exact flow rates are currently under investigation. Some of the contaminants in the

NTS groundwater, such as tritium and

many products of nuclear fission, have short half-lives and may decay long before they leave the test site. But a few contaminants have longer halflives, posing a potential threat as the groundwater migrates far from its source. Knowing the future location of contaminated groundwater is important information for water managers. When they can accurately predict where this groundwater will be, they can avoid using it.

# **A Water Management Tool**

Having proved their mettle at the Nevada Test Site, isotope tracer methodologies have since been applied to a number of other water resource projects, which are under the direction of Laboratory scientists Bryant Hudson and Lee Davisson.

# **Orange County Water District**

For the Orange County Water District in southern California, Hudson and Davisson's team is investigating the flow of artificially recharged water, which is recharged to the subsurface from spreading ponds. (See Figure 2.) Orange County wants to supplement its water supplies with treated wastewater



**Figure 1.** Groundwater sampling at the Nevada Test Site.



**Figure 2.** Orange County Water District uses abandoned gravel pits as spreading ponds to artificially recharge water to its aquifer.



Figure 3. A look down an Orange County Water District monitoring well.

and must respond to regulations requiring that such waters remain in the aquifer for a year before being withdrawn for drinking. Using the tritium-helium-3 (<sup>3</sup>H–<sup>3</sup>He) dating method and isotopically labeled water, Livermore has shown how recharged water moves from Orange County's main spreading pond facility. A plume of very young water extends several miles to the west of the spreading ponds, suggesting very rapid groundwater flow in that direction.

Orange County also brings in water from the Santa Ana River and sometimes from the Colorado River and recharges it to the subsurface. Santa Ana River water shows significant seasonal variations in the ratio of oxygen-18 to oxygen-16  $(^{18}O/^{16}O)$ , and Colorado River water has a different stable isotope signature altogether. In the fall of 1996, a batch of Colorado River water was spiked with a xenon tracer when it was introduced into the spreading ponds. From water samples taken at monitor wells down-gradient of the ponds (Figure 3), the distinctive  $^{18}\text{O}/^{16}\text{O}$  signature and the noble gas tracer have allowed Livermore scientists to follow the migration of this water in the subsurface, with a time resolution of just a few days. These isotope data also provide a means of delineating groundwater mixing with an accuracy of  $\pm 10\%$  for oxygen-18 and  $\pm 1\%$  for xenon-124.

In another project, the Orange County Water District is injecting reclaimed wastewater into an array of wells that parallel the Pacific coastline. This "wall" forms a barrier to seawater that had begun to intrude into groundwater supplies and provides a significant source of drinking water as well. Livermore used <sup>3</sup>H–<sup>3</sup>He ages of the injected water to demonstrate compliance with required regulations.

# Isotope Hydrology at Livermore

Lawrence Livermore scientists use both stable and radioactive isotopes to learn about groundwater sources, ages, travel times, and flow paths and to determine the path and extent of contaminant movement in the water. The combination of Livermore's unique nuclear chemistry experience, multidisciplinary staff, and highly sensitive mass spectrometry equipment, including use of the Center for Accelerator Mass Spectrometry, means that Livermore can take the measurements and interpret the results effectively. Livermore is unique among isotope hydrology centers in having all of the various tracing methods in one place. Researchers routinely use a variety of isotopes to evaluate a groundwater system and create the most accurate picture possible.

#### The Water's Origin

All waters have "fingerprints" of naturally occurring isotopes that provide information about their origin. Among the most powerful and cost-effective fingerprinting tools are the ratios of stable isotopes of hydrogen-deuterium to hydrogen (D/H)-and of oxygen-18 to oxygen-16 (18O/16O). For example, the D/H and <sup>18</sup>O/<sup>16</sup>O ratios in precipitation vary according to elevation and distance from the ocean. An altitude difference of 250 meters (820 feet) produces a clear and measurable change in the two ratios, which is preserved once the precipitation infiltrates to the aquifer. While some mixing of waters in the aquifer is inevitable, an aquifer is typically not homogeneous. Layers of heavy clay retard the movement of groundwater within the aquifer and often serve to keep waters from different sources distinct from one another. Thus, scientists can use D/H and <sup>18</sup>O/<sup>16</sup>O ratios to determine the recharge location for a groundwater and to discriminate among multiple water sources within an aquifer.

The concentrations of atmospherically derived noble gases (neon, argon, krypton, and xenon) in groundwater provide another excellent fingerprinting tracer because the noble gases do not react with surrounding materials and because their concentrations are preserved as they are recharged into the aquifer. The relative abundances of the noble gases provide information about the temperature and altitude at the time of recharge. Isotopically enriched noble gases, which are commercially available at low cost, can also be used as nonhazardous artificial tracers. They are detectable at very low concentrations, rendering them highly effective for delineating groundwater flow systems.

#### The Water's Age

Naturally occurring radioactive isotopes provide information about a groundwater's age, which refers to the last time the water was in contact with the atmosphere. Once the recharge area has been established using isotope fingerprinting methods, radioisotopes may be used to estimate how long it took for a parcel of groundwater to travel from its recharge area to the measurement point. For young groundwaters, the best dating method is one that measures the relative abundance of tritium (<sup>3</sup>H) and helium-3 (<sup>3</sup>He). Tritium is a radioactive isotope of hydrogen that decays to <sup>3</sup>He with a half-life of 12.4 years. The amount of <sup>3</sup>He from the decay of tritium is measured along with the amount of tritium remaining in the water. That sum is equal to the amount of tritium that was present at the time of recharge. The <sup>3</sup>H–<sup>3</sup>He dating method is remarkably accurate for groundwaters up to 40 years old with an age resolution of plus or minus one year.

The ages of older groundwaters can be measured in several ways. One is by measuring the carbon-14 ( $^{14}$ C) dissolved in the water. Carbon-14 decays at a known rate with a half-life of 5,730 years, providing a useful dating method for groundwaters less than 40,000 years old. Another method uses the isotope helium-4 ( $^{4}$ He), which is produced continuously deep within the earth by the radioactive decay of uranium and thorium. Relative age relationships determined from the amount of  $^{4}$ He in a groundwater are a valuable supplement to  $^{14}$ C age determinations. The long-lived radionuclides chlorine-36 and iodine-129 are also being used to study very old regional groundwater flow systems.

#### **Rock and Contaminants**

Other isotopic and elemental measurements provide useful information about the interaction of water and its host rock or sediment or about the migration of contaminants in the water. For example, the isotopic composition of strontium (Sr) in groundwater depends on the <sup>87</sup>Sr/<sup>86</sup>Sr ratios of the rocks with which it interacted. (Different rock types can have significantly different <sup>87</sup>Sr/<sup>86</sup>Sr ratios.) In basins containing several aquifers with differing rock characteristics, the dissolved <sup>87</sup>Sr/<sup>86</sup>Sr of a water sample may help distinguish where a particular groundwater resides.

Pollutants in groundwater can be studied in several ways. Measurements of nitrogen and oxygen isotope ratios (<sup>15</sup>N/<sup>14</sup>N and <sup>18</sup>O/<sup>16</sup>O) can supply information about the source of nitrates, which are prevalent in agricultural fertilizers and may contaminate groundwater. Similar information about manmade pollutants can be gathered by measuring lead isotopes and heavy metal concentrations.



#### Figure 4. A contour map of groundwater in the Brentwood area of Contra Costa County, California, based on measurement of the ratio of oxygen-18 to oxygen-16. Two distinctive types of groundwater are evident from this map: local rainfall and irrigation water. Precipitation accounts for only 6% of total annual recharge in the area.

Figure 5. The safe yield is the amount of water that can be withdrawn from an aquifer without exceeding recharge. The relationship between the safe yield and population growth in the Brentwood, California, region shown here indicates that the future water demands of Brentwood will be difficult to meet using only local groundwater resources.



#### **Contra Costa County**

Livermore was also asked to study groundwater resources in the Brentwood region of Contra Costa County, California, which is undergoing rapid urbanization after decades of agricultural use. Declining water quality, particularly that caused by high nitrate concentrations, is the result of fertilizer application and extensive agricultural irrigation. Water samples from 80 different wells in the area were used to construct a contour map of groundwater  $^{18}O/^{16}O$  ratios, shown in Figure 4. Two distinctive types of groundwater were observed, one corresponding to local rainfall and the other to irrigation water imported from the San Joaquin River. Most of the local groundwater recharge is from irrigation. In fact, Livermore's study revealed that only 6% of total annual recharge is from precipitation.

As urbanization in the Brentwood area increases, agricultural recharge will decrease, reducing total recharge to the aquifer. Figure 5 shows the relationship between population growth and the amount of groundwater that can be pumped out without exceeding recharge. It is clear from the graph that it will be difficult to meet future water demands in Brentwood using only local groundwater resources.

# **Groundwater Remediation**

Isotope tracers are also playing a role in a groundwater remediation project at the Lawrence Livermore site. Hudson and Davisson's team is working with the Environmental Restoration Division and the Earth and Environmental Sciences Directorate, which are cleaning up fuel hydrocarbons that several decades ago had leaked from fuel storage tanks into the subsurface.

Recently, steam was injected into the subsurface to stimulate recovery of the hydrocarbons.

Groundwater samples collected from monitoring wells farthest from the spill show relatively high carbon-14  $(^{14}C)$  and carbon-13 to carbon-12 ( $^{13}C/^{12}C$ ) values, which are consistent with normal dissolved inorganic carbon levels in Livermore Valley groundwaters. In contrast, samples taken from within the spill have low <sup>14</sup>C and <sup>13</sup>C/<sup>12</sup>C values, as would be expected from the breakdown of petroleum products. These results indicate that fuel hydrocarbons are breaking down and provide a measure of how much breakdown has taken place.

### **Meeting the Demand**

Isotope scientists use isotope tracing methods to determine the origin, age, and flow paths of groundwater in hydrogeologic systems. At the same time, geologists input data from conventional hydrogeologic studies to computerized groundwater models to predict where and how fast groundwater is flowing. Until recently, the two technologies had not been combined to solve groundwater resource issues. But steps are being taken at Livermore to "marry" them because each has much to offer the other. For example, isotope tracer data are proving valuable for verifying and validating the predictions of the numerical models for the Nevada Test Site. Together these technologies can give water resource managers a powerful forecasting tool.

As the demand for fresh water grows with increasing population, so will the demand for creative ways to predict the availability and sustainability of our underground and surface water resources. Some isotope tracing methods are beginning to be applied to surface

water, which is a source of water for millions of people. These techniques offer solutions, on both a local and regional scale, to such critical problems as water resource management, water quality, and contaminant transport. -Katie Walter

Key Words: groundwater, groundwater contamination, groundwater remediation, hydrology, Nevada Test Site, nuclear chemistry, radioisotopes, stable isotopes, water resource management.

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# **About the Team**



responsible for isotopic sciences programs in nuclear safeguards, nonproliferation, stockpile stewardship, environmental monitoring and technologies, waste repositories, and hydrology. Isotope hydrology is currently a principal area of scientific interest in the division. The division's isotope hydrology program applies the broadest range of isotopic techniques to characterize groundwater systems. The program seeks to develop isotope hydrology as a new tool for water resource management.

Members of the Isotope Sciences Division whose work is reported in this article are (left to right): LEE DAVISSON, JACKIE KENNEALLY, BRYANT HUDSON. DAVID SMITH, JEAN MORAN, TIMOTHY ROSE, WAYNE CULHAM, SIDNEY NIEMEYER. ANNIE KERSTING. and JOAN BEIRIGER.

The Isotope Sciences Division is a multidisciplinary organization

Niemeyer is the division leader, and Hudson, Davisson, and Smith are principal investigators for the various isotope hydrology projects being done by the division. Rose, Kersting, and Moran are research staff for the program; Kenneally, Beiriger, and Culham provide research support.