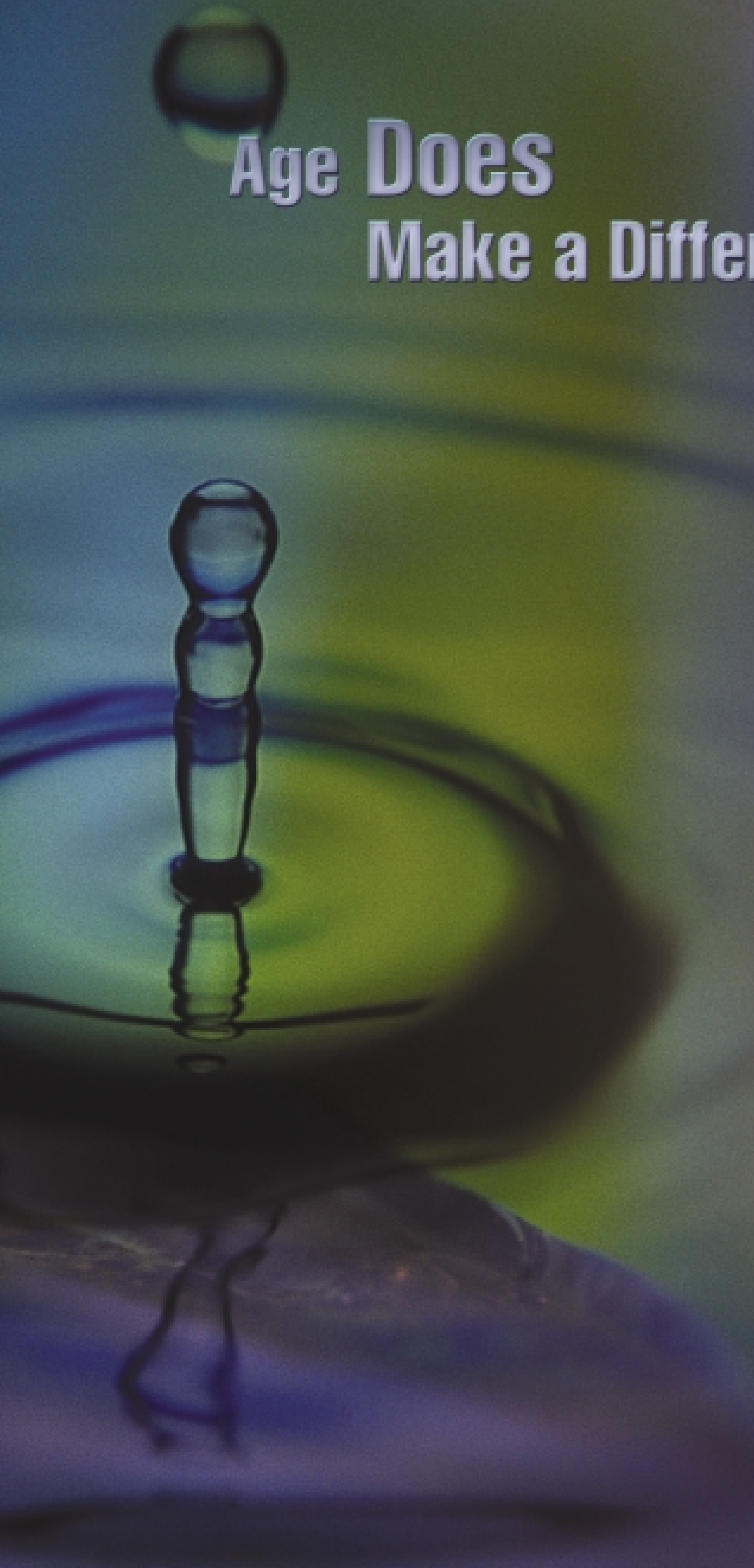


Age Does Make a Difference

WHEN you drink a glass of water, the first question that might come to mind is not "how old is this water?" but "what's in this water?" A study at Lawrence Livermore is demonstrating that, in many cases, answering the first question can help answer the second.

California residents have been asking a lot of questions about their drinking water, in particular about their groundwater—the source for 50 percent of the state's drinking water. The closing of several public drinking wells because of contamination has concerned citizens so much that in 1999, the state mandated the Groundwater Ambient Monitoring and Assessment (GAMA) Program to investigate to what degree groundwater is susceptible to contamination.

The GAMA Program calls for testing every one of the approximately 16,000 public drinking wells scattered throughout the state. It is a daunting task, to be sure, but Livermore is a natural choice for tackling the challenge. "Livermore has a history of working with the state on groundwater issues and providing solutions," according to environmental scientist Dave Rice. In 1999, for example, the Laboratory was part of an investigation that looked at leaking underground fuel tanks (LUFTs) and their effects on the state's groundwater. (See *S&TR*, April 1999, pp. 21–23.) The Laboratory developed GeoTracker, a geographic information system that provides online access to data such as LUFT sites and all public well sites in California. Maintained by the state, GeoTracker is providing a repository for data generated by the GAMA Program.

According to physicist Bryant Hudson, Livermore scientists have partnered with the California State Water Resources Control Board and the U.S. Geological Survey to test 1,200 wells so far. Two years into the project, the scientists have analyzed wells in the Los Angeles–Orange County basin, the Santa Clara Valley, the Livermore–Niles area, and the counties of Sacramento, Butte, Fresno, and San Joaquin. During this testing, they have also been educating the public and students in schools about groundwater.

Young and Vulnerable

With a suite of analytical tools at their disposal, Laboratory scientists are developing a comprehensive picture of the state's groundwater resources. They are determining where contamination has occurred, what the groundwater flow pattern is, and from where the groundwater originates. The work begins with age-dating water from municipal drinking water wells. For groundwater geologists, the age of water is a good indicator of its probability of contamination.

Geochemist Jean Moran says using age to assess the vulnerability of groundwater to contamination is based on a simple concept: younger water has been in the aquifer for a shorter time, so it has more recent contact with ground surfaces where contaminants are present. Older water that has been in the subsurface for hundreds or thousands of years will have stayed relatively isolated and protected from any pollutants on the surface.

To determine how long the water has been out of contact with the atmosphere, Livermore scientists use the tritium–helium-3 method, a capability available only in a handful of laboratories worldwide. Tritium, a radioactive hydrogen isotope, occurs naturally at very low levels in Earth's upper atmosphere, but it was produced in much greater amounts during atmospheric nuclear testing in the 1950s and 1960s. Thus, it is an excellent tool for age-dating water that has entered an aquifer in the past 50 years. Tritium has a half-life of 12.3 years; it decays into helium-3, a stable noble gas.

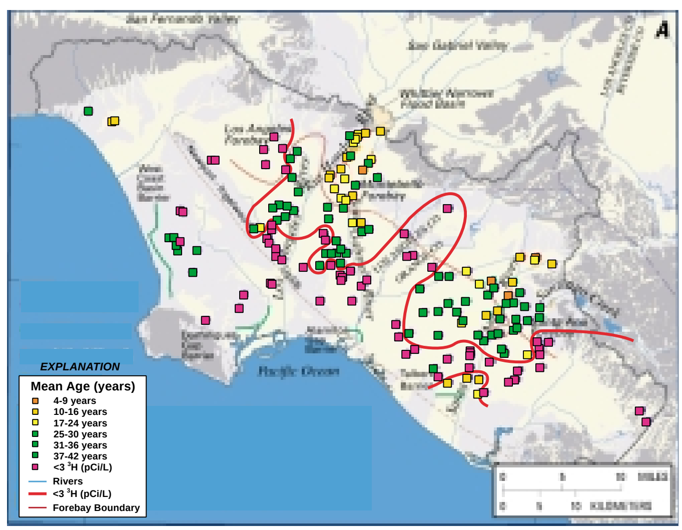
That helium-3 remains in solution once water containing tritium enters an aquifer. As tritium continues its decay over time, the amount of helium-3 in the water grows and the amount of tritium declines; the sum of both stays constant. By measuring both the remaining tritium and the decay product helium-3, scientists can determine the time at which the water entered the aquifer.

To measure tritium, the scientists remove all of the helium from a large water sample so they can see the decay of tritium into helium-3 over a two-week period. "The beauty of all of this is in the sensitivity of the measurements," Moran notes. Noble gas mass spectrometry allows measurements sensitive to just a few thousand helium-3 atoms. With such precision, the scientists can determine the age of a water sample to within about one year. These age determinations allow them to directly infer the direction and rate that the groundwater in the aquifer is flowing.

Tracking the Contamination

To test the principle that younger water is more likely to be contaminated, Livermore scientists perform several types of

An important part of the Groundwater Ambient Monitoring and Assessment Program is public education. Here, at the 2002 Edward Teller Science and Technology Education Symposium, Bryant Hudson uses a groundwater model to show students how water moves in a simulated aquifer.



A map of tritium–helium-3 ages measured in drinking water wells from Los Angeles and Orange counties. A general pattern of increasing age away from the artificial recharge areas (where water entering the aquifer reaches saturation) is observed. The red line shows the boundary between younger groundwater and groundwater more than 50 years old. The measured age shows the direction and rate the groundwater in the aquifer is flowing.

analyses to get a larger picture about groundwater resources in the state. One analysis detects actual contamination at ultratrace levels, using gas chromatography in combination with mass spectrometry to track volatile organic compounds (VOCs) such as the gasoline compound methyl tertiary-butyl ether (MTBE) and the dry cleaning solvent perchloroethylene (PCE). Such VOCs are ubiquitous and can be detected at very low concentrations nearly anywhere on Earth's surface. The analyses require that the mass spectrometer used to detect VOCs in groundwater be stringently clean; the responsibility for keeping it that way falls to Livermore scientist Roald Leif, who makes it possible to detect VOCs to parts-per-trillion sensitivity. The detection results indicate where groundwater has been contaminated and also verify the age-dating results.

In another analysis to round out their information about the state's groundwater, the scientists measure two stable oxygen isotopes (oxygen-16 and oxygen-18) to determine the origin and flow patterns of contaminated water. The ratio of oxygen-16 to oxygen-18 in the water varies, depending on where the water precipitated, the elevation at which it was found, and its distance from the ocean. For example, water from the Sierra Nevada has a different ratio of these oxygen isotopes than that found in precipitation in the San Francisco Bay Area. Using a mass spectrometer, the team can measure the isotope ratio and determine the source of the water.

Older May Be Better

Some of the data analysis shows that older water can remain relatively contaminant-free, despite its location. For example, the Silicon Valley, with its large number of contaminated waste disposal sites and more Superfund sites than anywhere else in the nation, has remarkably uncontaminated drinking water wells. Because most of the Silicon Valley water has been resident in underground aquifers for longer than the contaminants have been present, the water has been relatively protected, and very few VOCs have been detected. A similar example is in the Los Angeles and Orange County basins. Despite their urban location, 59 of 176 wells tested were devoid of tritium, and those same wells were free of VOCs. The pathway of water into the aquifer is blocked by thick layers of clay, and that has kept most of the water underneath the basin protected from surface contaminants over the past 50 years.

The vulnerability of younger water to contamination can be seen in the Livermore Valley. The east side of the water basin (under the city of Livermore) has widespread PCE occurrence and younger groundwater ages than the west side. Water located on the west side of the basin, under the city of Pleasanton, approximately 10 kilometers away, is protected by a confining layer that prevents the direct transport of water from the surface to the aquifer.

Being Prepared

Next year, the group hopes to take the age data accumulated so far and study nitrate contamination, which is the most frequent cause for shutting down a drinking water well in California. In the meantime, Livermore's data showing that newer isn't better will help the state make informed decisions to protect wells and plan future development. Moran says California intends to increase its use of groundwater for drinking purposes, and these data could keep the state from making costly mistakes.

"If you know the age of the groundwater in a basin, it can tell you how fast water is moving, where it is being replenished in the ground, how much storage you have, how fast water turns over—a complete picture," Moran says. "Water is a huge issue in California, so the more data you have, the better."

—Laurie Powers

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