

Every Drop Tells a Story:

On the face of it, calculating the age of water seems like an exercise best suited to academia. After all, what difference does it make to us if the water we're using fell in last week's rainstorm or in a storm 500,000 years ago? As it happens, it can make a great deal of difference.

"For one thing," says Niel Plummer, a hydrologist at the U.S. Geological Survey (USGS), "it's important to know the age so you can assess the susceptibility of drinking water supplies to surface contamination. If you know that the groundwater in a particular area fell 10 years ago as surface rainfall, you can then decide how long it will take a surface contamination to reach the water supply." Plummer says that information on groundwater age, or the average time since the molecules were removed from the atmospheric cycle, provides a "fourth dimension" to hydrologic investigations, allowing scientists to observe spatial variations in water composition and relate these variations to the time of

recharge. By determining water age at specific points in a hydrologic system, Plummer says, it is possible to estimate how quickly an aquifer can replenish itself.

According to M. Lee Davisson, group leader of environmental chemistry and toxicology at the Lawrence Livermore National Laboratory Health and Ecological Assessment Division, water dating is also important because it can give a much clearer picture of how quickly a groundwater supply is replenished and thus how heavily the supply can be used. In practice, Davisson says, several ages would be generated over the aquifer area and calculated into a mean age for the entire water volume. If the water in a given aquifer

A New Technique for Dating Water

had a mean age of 1,000 years, for example, it would be fairly safe to assume that a system of wells would remove water faster than the aquifer could replace it. This overextraction is called water mining, and it's a big problem in many areas of the United States, where the demands of exploding populations are outstripping the ability of the hydrologic system to replenish the supply.

Recently, Robert Criss, a professor of earth and planetary sciences at Washington University in St. Louis, Missouri, developed what he feels is an entirely new method for determining the age of water. Criss has devised a mathematical equation that relies upon a time-tested ratio between oxygen-16 (^{16}O ; a common isotope, comprising 99.8% of the oxygen in water) and oxygen-18 (^{18}O ; a much scarcer isotope, comprising only about 1 in every 500 atoms). The equation, Criss says, gives an accurate interpretation of residence time in a groundwater system and incorporates the impact of more recent rainfall on the

isotopic balance. Says Criss, "The main unique feature about our model is that it provides a very accurate fit to the observed data for both a spring and a river that have been carefully monitored for many years, and accomplishes this with a simple model containing a minimum of parameters."

A New Use for an Old Ratio

Methods currently in use for determining water's age mostly revolve around determining the age of certain substances found in the water. For instance, the USGS sometimes uses a method based on chlorofluorocarbon (CFC) content. Although now being phased out on a global basis, CFCs were widely used in refrigerants, air-conditioning systems, aerosol propellants, and similar products until the mid-1990s. Because the amounts of CFCs in the atmosphere over the past 50 years have been reconstructed and the solubility of CFCs in water is well known, it's relatively simple to determine not the age of the water per se,



Robert Criss

The age of Aquarius. Frederickson and Criss use oxygen isotopes to estimate the age of water in the Meramec Spring (right), which feeds into the Meramec River (above), home to extremely diverse aquatic fauna. Understanding the age of water may help in tracking pollutants that can threaten such ecosystems.

but rather the point at which the contaminant was added. And carbon-14 dating, using dissolved inorganic carbon-14 in the water, is sometimes used to date water further into the past. (There is, however, some degree of controversy over how carbon-14 data should be interpreted because of interference by other sources of carbon.)

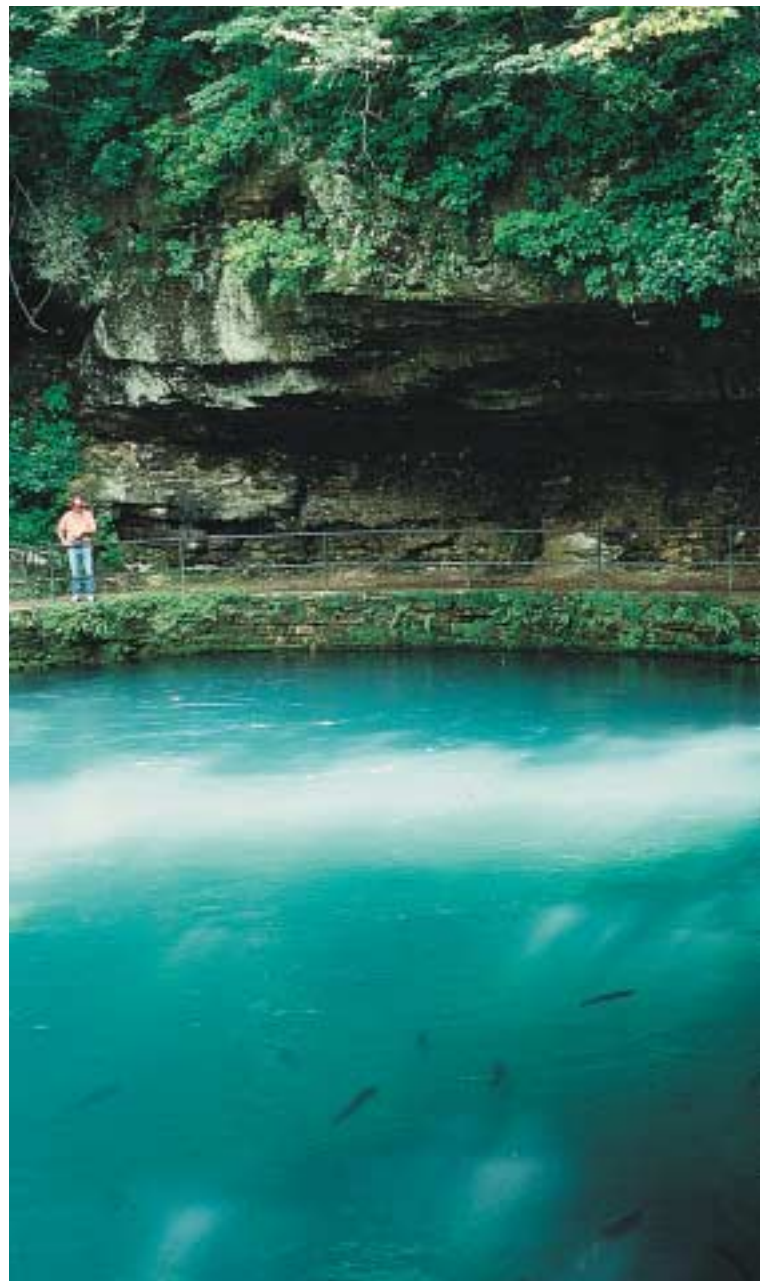
Such methods determine the age of something in the water, not the water itself. As Criss elaborates, “You then have to be really careful that you don’t just assume that’s an accurate reflection of the water’s age. . . . I mean, if you pull up a sample of 10,000-year-old water from an aquifer that happened to have a tiny amount of some trace chemical that has only been in use for 30 years, are you then going to decide that water is only 30 years old?”

Alternately, Criss’s equation looks to the ratio of ^{16}O to ^{18}O in the water. Scientists currently use this ratio to track ancient rainfall and temperature as part of the study of prehistoric climates. Concentrations of ^{18}O tend to be lower when the air is cooler, for instance during a rainfall or snowfall—the isotope is heavier, and thus condenses more readily and evaporates less freely than ^{16}O . Winter ice can be 5–20 per mil lower in ^{18}O than summer precipitation, says Criss, and during periods of significant glaciation, the ^{18}O content of Antarctic ice was 5–10 per mil lower than modern ice at corresponding locations. Ocean water, meanwhile, became significantly heavier during glacial periods because of the removal and storage of low- ^{18}O ice on the continents,

and the shells of marine organisms that formed during those times contain greater concentrations of ^{18}O than those formed during interglacial periods.

The ratio of ^{16}O to ^{18}O is also used to date more current water supplies, says USGS isotope geochemist Gary Landis. “They’re stable isotopes, so they don’t decay,” he says, “but you need to have some idea of a reason from the past for why the ratio might have changed—precipitation under different temperatures, for example. There are a variety of other factors to consider, but in general, if you test a water supply that’s isolated from surface changes and find it to be more depleted in ^{18}O , it would imply that this is water that originated during a much colder climatic period. If you then knew that the last glacial period in that area ended 15,000 years ago, then you could infer that this water was that old or older. But it doesn’t give you anything in the absolute sense of time.”

Criss has taken the use of this ratio a step further. His equation, published in the 24 May 1999 issue of *Chemical Geology*, allows the incorporation of this ratio information to determine not only the age of very recent



water supplies, but also the age of groundwater that has already migrated into a river and mixed with the surface runoff.

The equation is

$$\delta^{18}\text{O}_{\text{flow}} = \frac{\sum \delta_i P_i e^{-t_i/\tau}}{\sum P_i e^{-t_i/\tau}}$$

where δ_i and P_i are the $\delta^{18}\text{O}$ value and rainfall amount for a given rain event, t_i is the time interval between the storm date and the sampling date of the spring or river, and τ is the residence time of the water in the system. The $\delta^{18}\text{O}$ value is defined as a measure of the ^{18}O content of a sample, but is reported not as a concentration, but rather

as a normalized difference from the natural abundance of ^{18}O in seawater.

Criss explains, “As is well known, the isotopic concentration of ^{18}O and ^{16}O varies with climate and temperature. And it changes as you move away from the moisture source.” So, he says, moisture that comes directly off the ocean will produce coastal rain with more ^{18}O than would be found in Missouri rain, which in turn would have more ^{18}O than Montana rain. “ ^{18}O is heavier,” says Criss, “so it precipitates out sooner. We also get variations in single storms.”

To Build an Equation

Criss and his students have spent the last five years studying rainfall and groundwater in the Meramec River basin, a 10,300-square-kilometer area of east-central Missouri. Criss has collected rain and snow and analyzed it for ^{18}O variations (which show, he says, that midwinter snows in St. Louis could be as depleted of ^{18}O as most snow falling over Antarctica). Criss collected data tracking variations in ^{18}O in the rainfall in the region, and performed similar samplings of the rivers and springs in the area. These samplings showed that the rivers and springs in the basin have patterns and timing of isotopic variation similar to those seen in the precipitation, but that the variations are “damped out,” or much smaller in amplitude.

According to Criss, plugging rainfall and other data in to his equation yields calculated curves that very closely match the general variation that can be measured in springs and rivers. This “fingerprint,” Criss says, is characteristic of the water being sampled.

The equation Criss has developed may appear esoteric on the face of it, but he points out that it reveals some significant information. Previous isotopic studies, he says, have used simple mass balance equations to separate components of river or spring discharge, and have assumed that the value of $\delta^{18}\text{O}$ in the baseflow, or groundwater-feeding river flow resulting from precipitation, remains constant. That’s reasonable for deep groundwaters, he wrote in the *Chemical Geology* paper, but not for systems

supplied by shallow groundwaters, which are clearly influenced by the amount and isotopic character of previous rainfall events.

“In view of these difficulties,” he wrote, “we have developed a new model that relates the isotopic values of the springs and rivers to the weighted average of previous precipitation events.” The weighting factor is an exponential function that, when multiplied by the amount of precipitation, in effect damps out the precipitation in such a way that the more recent rainfall events factor in to the average more than older rainfall events.

“What [Criss] has done,” says Davisson, “is to exploit the fact that, in the Meramec River system, ground and surface water signatures both distinguish themselves by their ^{18}O signatures. Different events have different ^{18}O levels, and if you knew what the ^{18}O composition was of the rain and of the river, you could determine the proportion of each, and from that, how long it took the rainfall to reach the groundwater.”

Surface water isn’t generally dated, says Davisson, because most dating techniques measure elements or compounds that are susceptible to atmospheric loss or exchange, but a significant part of the surface water flow in streams and rivers actually comes from groundwater. He also says that, although hydrologists do not routinely measure ^{18}O in precipitation, the measurement is not a hypothetical advantage but a real one that has been proven useful in many academic research exercises.

Liquid Asset

It’s a fairly consistent phenomenon: when heavy rains fall, creeks and rivers rise. It’s a popular misconception, Davisson says, that this rise in river level and flow is caused solely by runoff from the storm. “There’s strong evidence that these storms are actually raising the groundwater level, which in turn contributes to the river flow,” he says.

Davisson adds, “[Criss] has developed a method to date groundwater that has migrated into a river and mixed with surface runoff. To my knowledge, no one has ever attempted this before. Furthermore,” he says, “all the

dating methods typically [used for] dating water in an aquifer can’t easily be applied to river water because of the mixture of surface and groundwater, or [because] the chemical of interest is volatile. It’s hard enough just trying to get reliable ages collected directly from water residing in aquifers.”

Landis notes that Criss’s equation may be less useful in some systems than in others. “The longer it takes groundwater to go from the site of precipitation into the baseflow, the more diluted the variation will be, and likewise, the faster the water flow between those points, the more intense the individual signals,” he says. “And things like subsurface heat, like you find in the Yellowstone region, can also affect the isotopic signature.” He continues, “Implicit in Bob’s approach is the belief that you can understand surface water variability. I’ll be interested to see if this works out west.” He explains that while St. Louis, for example, might have intermittent rain over three months, a location such as southern Utah might have a single downpour lasting five minutes; such downpours lead, through evaporation, to intense isotope fractionation, or unequal partitioning of the different isotopes.

Criss plans to expand his study into an ambitious survey of the Missouri River system, where he envisions ultimately being able to isolate the source of different waters, and thus the sources of different pollutants that plague the river system. “For example,” he says, “if you take a sample from a gauging station in South Dakota, it will be isotopically depleted [of ^{18}O] compared to Missouri contributions. If it’s dry in the Missouri area, you’ll see more western water, while if there have been big floods in Missouri, you’ll see more of our water. I believe this technology will allow us to isolate pollutants to their sources.”

Criss says he recognizes that some of his approaches go against what he labels current orthodoxy, but he remains optimistic. “If you live in a world where you’re concerned about pollution, you need to understand the environment,” he says. “Hydrology is a tricky business—you don’t have fossil records, only atomic fingerprints, and if you divorce hydrology from geochemistry, relying instead on traditional technologies like volume and flow rate, you see a very static thing that gives no accurate picture of the system with which you’re trying to deal.”

“The thing is,” says Criss, “once you understand the system, and what makes it work the way it does, water is no longer an amorphous thing, but something with real shape and depth, and that’s vital in a world whose survival depends upon water.”

Lance Frazer

Suggested Reading

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