Isotopic Tracers in Groundwater Hydrology

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This article presents a brief overview of isotopic methods available for tracing and age-dating groundwater, introducing the reader to the methods, typical applications, and assessments of the usability of these techniques. Most of these analyses can be completed within one month, with more rapid turnaround times available upon request and with appropriate surcharges.

The analytical techniques associated with these methods are not typically found among standard U.S. Environmental Protection Agency, American Society for Testing and Materials, and/or regulatory agency protocols. However, the quality assurance/quality control procedures for isotope analyses are rigorous products of decades of collaboration between research institutions and the National Institute for Standards and Technology. These standards insure the quality of standard samples for interlaboratory comparisons of data and a mechanism by which the precision and accuracy of isotope analyses could be improved over time, to reach current uncertainties of about 0.1 to 0.002 percent.

Groundwater Geochronology

Commercially available methods for age-dating groundwater rely on either tritium (^{3}H) for qualitative ages or radiocarbon dating (^{14}C) if numerical ages are required. Both are cosmogenic – produced by nuclear interactions in the atmosphere – and each has its place in age-dating of groundwater.

Tritium, with a half-life of 12.43 years, decays to Helium-3 (^{3}He). Pre-atomic-bomb background levels of tritium ranged from about 5 to 10 tritium units (1 tritium unit = 1 TU =1 atom of ^{3}H per 10^{18} atoms of ^{1}H). Following atmospheric testing of nuclear weapons, levels of tritium rose to 500 to more than1000 TU by the mid-1960s but have been decreasing due to radioactive decay, the cessation of atmospheric detonations of thermonuclear devices, and removal through rainfall.

General interpretations of groundwater age based on TU levels are as follows:

- Pre-1952, less than 0.8 TU.
- 1960s, greater than 50 TU.
- Young, less than 10 years old, about 5 to 10 TU.
- Commingled old plus young groundwater, 10 to 50 TU.

Although the decay of tritium to ^{3}He has been used to provide radiometric ages of young groundwater (less than 30 years old), the analytical cost is high, the method is only available through a few research/government labs, and the turnaround times are lengthy since the sample must sit in order to accumulate enough ^{3}He for analysis.

Radiocarbon, with a half-life of 5730 years, is used to date groundwater up to 50,000 years old. Recent advances, such as accelerator mass spectrometry (AMS) have substantially reduced the amount of sample required but not the uncertainty in ages, which is a function of the amount of carbon analyzed. Applications of radiocarbon dating are well known in the hydrologic community. (See accompanying articles on pages 22-27.)

Other techniques used for dating groundwater are not yet commercially available. Examples include chlorofluorocarbon compounds (for groundwater 0-60 years old) and chlorine-36, which can date groundwater up to 2 million years old.

Light Stable Isotopes

The light stable isotopes (LSIs) of carbon, hydrogen, oxygen, nitrogen, and sulfur (CHONS) are undoubtedly the best known and most utilized isotopes in groundwater hydrology. Their mass numbers are low and

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Who Does the Analyses ?

The following laboratories are listed for information purposes only and represent an incomplete list. Southwest Hydrology intends no overt or implied endorsement of their services.

Commercial Labs

Geochron Laboratories
Cambridge, MA
(617) 876-3691
www.geochronlabs.com
^{14}C, tritium, stable isotopes, and others

ISO Analytical
Cheshire, UK
44 1 270 766771
www.iso-analytical.com
stable isotopes

ZymaX
San Luis Obispo, CA
(805) 544-4696
www.ZymaXusa.com
stable isotopes, ^{14}C preparation

University Labs

University of Arizona
Laboratory of Isotope Geochemistry
(520) 621-1638
www.geo.arizona.edu/researchers/mbaker/AustinLong/98prices.html
stable isotopes, tritium, ^{14}C, and others

University of Colorado INSTAAR
Stable Isotope Laboratory
Boulder, CO
(303) 492-7985
mysticplum.colorado.edu/groups/sil/
stable isotopes of oxygen, hydrogen, carbon

University of Waterloo
Environmental Isotope Lab
Waterloo, Ontario, Canada
Sciborg.waterloo.ca/research_groups/eilab/
Stable isotopes, tritium, and others

For a listing of isotope laboratories in North America and worldwide, visit the University of Vermont's Web site at geology.uvm.edu/geowww/isogeochem.html#anchor559545

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all are stable – being neither radioactive nor daughter products of a radioactive parent (radiogenic). Large mass differences between isotopes in each system, such as ^{18}O versus ^{16}O, allow separation (fractionation) of isotopes by biogeochemical processes and exchange reactions associated with water-rock interactions.

Light stable isotope data are reported using the delta notation; the sample's isotope ratio is measured relative to the lighter, lower mass number isotope in the LSI system of interest and compared to a standard. For example, in the case of oxygen isotopes:

$$\delta^{18}O = \frac{\{(^{18}O/^{16}O)_{SAMPLE} - (^{18}O/^{16}O)_{STANDARD}\} x 1000}{(^{18}O/^{16}O)_{STANDARD}}$$

The resultant δ value, measured in parts per thousand (per mil), is termed *heavy* if positive (enriched in the heavier isotope), and *light* if negative; however, these terms are relative since a $\delta^{18}O$ value of -3 is heavier than a value of -10. The Meteoric Water Line (MWL), which depicts observed global relationships between H and O isotopes in precipitation (δD - $\delta^{18}O$; Figure 1), is a classic means of demonstrating how stable isotope ratios are affected by biogeochemical and physical processes.

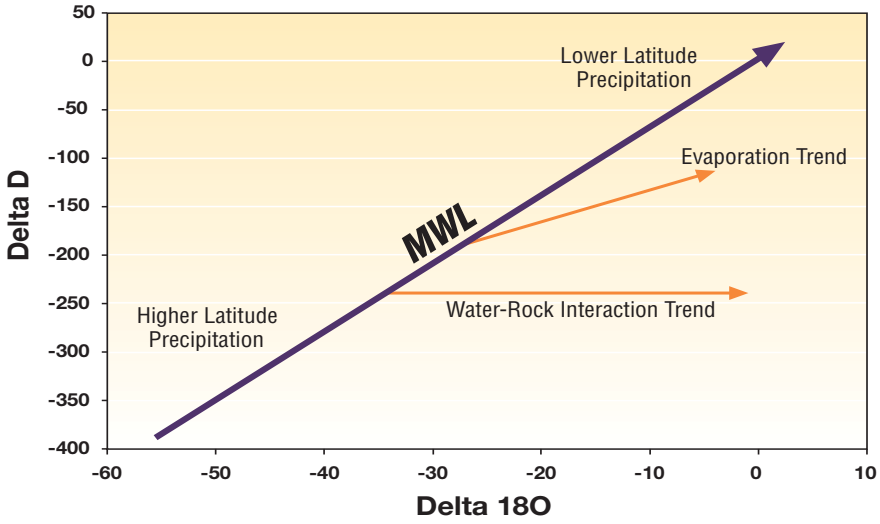

Figure 1. The Meteoric Water Line (MWL) of Craig (1961): Fractionation of D (deuterium) and ^{18}O, heavier isotopes, due to evaporation and condensation varies as a function of latitude; both H and O isotopes become lighter at higher latitudes. Hypothetical evaporation and water-rock interaction trends are shown for reference.

What Does It Cost?

(Information supplied by Richard W. Hurst – Hurst & Associates, Inc., and the University of Arizona's SAHRA Isotopes and Hydrology Web Site (http://www.sahra.arizona.edu/programs/isotopes/))

Tritium: *$80 to $300 per sample, depending on requested detection limit and method used*
Helium: *upwards of $1,000 per sample, available only through a few research/government labs*
Radiocarbon *(^{14}C): conventional dating--$300 per sample; AMS methods– $600 per sample*
Light stable isotopes *(carbon, hydrogen, oxygen, nitrogen, sulphur): $20-$235 per sample*
Stable radiogeneic isotopes *(such as Sr and Pb): $325 per sample*

Stable Radiogenic Isotopes

Stable radiogenic isotopes employed in groundwater investigations include strontium and lead. Although delta notations are sometimes employed, it is more common to see actual isotope ratios (e.g. $^{87}Sr/^{86}Sr$, $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$) reported. With the exception of ^{210}Pb, the isotopes of strontium and lead are stable, however ^{87}Sr and $^{206}Pb/^{207}Pb/^{208}Pb$ are also radiogenic, their abundances increasing over geologic time due to radioactive decay of rubidium and uranium/thorium isotopes, respectively. Unlike the LSIs, strontium and lead isotopes are not fractionated by natural processes to any appreciable degree, because mass differences between their isotopes are small.

Strontium and lead isotopic analyses of groundwater are commercially available, but have not been as widely used as the LSIs because groundwater hydrologists are not generally as familiar with these isotopic systems, analytical costs are higher, and most lead minerals are relatively insoluble.

Strontium isotopes, however, can be used to answer the same questions posed in groundwater investigations as the LSIs. Integrated Sr-LSI analyses have been effective in assessing the effects of saline intrusion and fingerprinting sources of chlorinated solvents. Lead isotopes are also a powerful tool in age-dating and identifying sources of hydrocarbon releases into groundwater.

Evaluating the Whole Story

As a caution about the misinterpretation of tritium data, consider this case of a landslide at the base of a 400-foot high cliff. The slope instability was attributed to over-watering of crops by a farm on the cliff's plateau. Plaintiffs' experts in the ensuing lawsuit argued that high nitrate concentrations in local springs originated from fertilizer, so liability for property damage resided with farm owners. Tritium data from pore water sampled at depths of 10 to 30 feet below ground surface at the top of the cliff ranged from 3-4 TU; these results were used by plaintiffs' experts as evidence that young, 5- to 10-year old irrigation water caused the landslide.

However, in addition to tritium analyses, groundwater $^{87}Sr/^{86}Sr$ and $\delta^{15}N$ of nitrate were also measured to evaluate nitrate sources and supplement the hydrologic modeling. The integrated $^{87}Sr/^{86}Sr$, $\delta^{15}N$, and tritium results suggested an alternative interpretation, which was consistent with hydrologic modeling. The Sr and N isotope characteristics of the irrigation water containing fertilizer differ dramatically from those of local spring, surface, and pore water, indicating the irrigation water is not a likely source of nitrate (Figure 2). Furthermore, Sr-N ratios of high nitrate springs and surface water are identical to those of organic-rich marine sediments – the bedrock in the region. So, in reality, sources of nitrate are more likely the result of groundwater-organic rich marine sediment exchange reactions, not overwatering.

In the absence of isotopic evidence for commingling of irrigation with any surface or groundwater, combined with the fact that Sr-N-tritium data indicated pore water tritium was controlled by rainwater-marine sediment exchange reactions, not infiltration of irrigation water over the last decade (Figure 2), the Court ruled to dismiss the suit against the farm.

Conclusions and Recommendations

Proceed cautiously when interpreting isotopic data. Experienced groundwater professionals are competent and capable of performing most of their own interpretations of isotope data from the methods discussed. However, do your homework and do not step too far outside of your comfort zone. Unfortunately, isotopic data are often treated independently of other geochemical and hydrogeological data, which limits the effectiveness of these very powerful tools, and can lead to erroneous interpretations. Remember too, that well-defined sampling plans should always be an integral part of your investigation, and can make or break the interpretations that follow.

Richard Hurst has 34 years experience in isotope geochemistry, focusing on applications of isotope geochemistry to environmental problems. Contact Hurst at www.hurstforensics.com

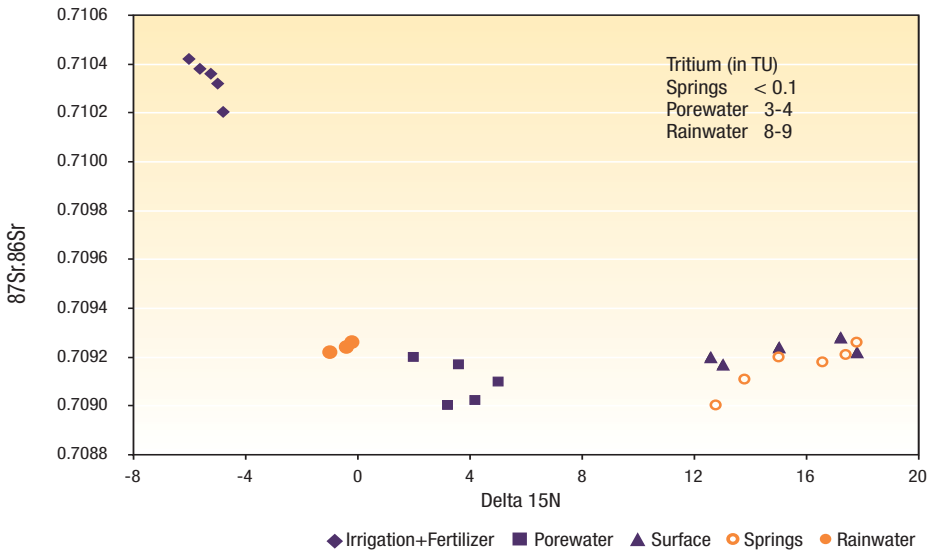

Figure 2. Covariation of Sr and N isotopes of waters in the vicinity of a landslide. The large gap observed between the respective $^{87}Sr/^{86}Sr$ – $\delta^{15}N$ results of the irrigation water plus fertilizer and those of local waters indicate separate, distinct sources of nitrate for the two. Tritium results of the pore water, when viewed in light of the Sr-N data, are derived by rainwater-bedrock exchange reactions; local bedrock is comprised of organic rich marine sediments whose Sr-N isotopic characteristics are reflected in those of surface and spring waters.