

Age Dating Groundwater

by

William E. Motzer, Ph.D., P.G.

Todd Engineers

2200 Powell Street, Suite 225

Emeryville, CA 94608

bmotzer@toddengineers

Numerous methods exist for age dating groundwater, including carbon-14, krypton-85, chlorine-36, and chlorofluorocarbon analyses. Many of these methods require either large quantities of sampled water, have complex chemical analysis, or require instrumentation found in only a few laboratories. However, the simplest, most frequently used, and currently most popular method involves analyzing water for isotopes of hydrogen and helium; this technique is discussed below.

Tritium Fundamentals

Tritium (T) or ^3H is a radioactive isotope of hydrogen (having two neutrons and one proton) with a half-life of 12.4 years. Tritium concentrations are measured in tritium units (TU) where 1 TU is defined as the presence of one tritium in 10^{18} atoms of hydrogen (H).

In the earth, small amounts of natural tritium are produced by alpha decay of lithium-7. Natural atmospheric tritium is also generated by secondary neutron cosmic ray bombardment of nitrogen, which then decays to carbon-12 and tritium. Tritium atoms then combine with oxygen, forming water that subsequently falls as precipitation.

Prior to atmospheric nuclear bomb testing in the 1950s, tritium's natural average concentrations ranged from approximately 2 to 8 TU. Approximately 1.13×10^9 TU were added in the northern hemisphere from atmospheric nuclear bomb testing with the largest tritium concentrations peaking in 1963. Since cessation of atmospheric nuclear tests, tritium concentrations have dropped to between 12 and 15 TU, although small contributions from nuclear power plants occur. Because most tritium is disseminated in the environment as water, it enters the hydrologic cycle as precipitation and eventually becomes concentrated in levels detectable in groundwater.

Tritium Method

Because groundwater tritium concentrations reflect atmospheric tritium levels when the water was last in contact with the atmosphere, tritium can be used to date groundwater recharge. Given that TU values vary both spatially and temporally, it is important to establish the closest precipitation measurement point to provide a reference to estimate groundwater recharge and travel times. Groundwater age estimation using tritium only provides semi-quantitative, "ball park" values:

- <0.8 TU indicates submodern water (prior to 1950s)
- 0.8 to 4 TU indicates a mix of submodern and modern water
- 5 to 15 TU indicates modern water (<5 to 10 years)
- 15 to 30 TU indicates some bomb tritium
- >30 TU: recharge occurred in the 1960s to 1970s

In the period of three half-lives (1963 to 2000), tritium concentrations have been reduced by a factor of 8. With no further atmospheric nuclear weapons testing, tritium will continue to drop to near natural background levels. Therefore, usage of tritium for age dating groundwater recharge is approaching an expiration date.

Tritium-Helium-3 (³He) Method

Tritium decays to ³He by beta particle emission, and knowing this decay rate allows for a more accurate shallow groundwater recharge age. T/³He ratios are useful for groundwater ages ranging from several months to about 30 years (but no further out than about 50 years). T/³He ratios have an accuracy of one to three years. Groundwater ages can be estimated using the following equation:

$$\text{Groundwater Age (in years)} = -17.8 \ln (1 + {}^3\text{He}_{\text{trit}}/{}^3\text{H})$$

where:

- ³He_{trit} = component of ³He from the decay of tritium corrected for other ³He sources such as the Earth's atmosphere, small contributions from spontaneous fission of lithium-6, and from uranium and thorium decay.
- ³H = tritium concentration in TU.

Because ³He is also present within the mantle, in the ratio of 200 to 300 parts of ³He to a million parts of ⁴He, ratios of ³He/⁴He in excess of atmospheric concentrations are indicative of a contribution of ³He from the mantle. This commonly occurs in geothermal areas and crystalline crustal sources dominated by ⁴He, which is produced by the decay of radioactive elements in the crust and mantle. Therefore, in other than alluvial terrain, terrigenous-produced helium may give anomalous results.

Analysis

Tritium is typically measured by a liquid scintillation counter. Tritium and ³He can be measured by mass spectrometry, but dissolved gases such as H₂O, CO₂, O₂, and N₂ must be first removed, generally by exposure to heated titanium.

Sampling and Cost

For tritium alone, water samples can be collected in plastic bottles. However, for T/³He samples, water must be collected in crimped ("cold welded") copper tubes because helium will diffuse through glass and plastic containers. Sample costs vary from about \$300 per sample for tritium alone to \$1,000 per sample for T/³He depending on the laboratory.

Further Information

A more complete discussion of age dating groundwater was given by Dr. Jean Moran (with Dr. Carol Kendall) in the March 2007 GRA course: *Isotope Methods for Groundwater Investigation*. This course will be repeated at a southern California location; so, stay tuned to a future GRA web page and HydroVison's announcement.

Selected References

Clark, I. D. and P. Fritz, 1997, *Environmental Isotopes in Hydrogeology*: Lewis Publishers, Boca Raton, Florida, 328 p.

Clark, I. and Aravena, R., 2005, *Environmental Isotopes in Groundwater Resource and Contaminant Hydrogeology #394*: National Ground Water Association Short Course, San Diego, CA, January 25-26, 2005

Eisenbud, M. 1987, *Environmental Radioactivity*: Academic Press, New York, NY, 475 p.

Gat, J.R., Mook, W.G., and Meijer, H.A.J., 2000, *Atmospheric Water*, in W.G. Mook (editor), *Environmental Isotopes in the Hydrological Cycle – Principals and Application, Volume II*: International Atomic Energy Agency (IAEA), Vienna, Austria, 117 p.

Geyh, M., Amore, F.D., Darling, G., Paces, T., Pang, Z., and Silar, J., 2001, *Groundwater Saturated and Unsaturated Zone*, in W.G. Mook *Environmental Isotopes in the Hydrological Cycle – Principals and Application, Volume IV*: International Atomic Energy Agency, Vienna, Austria, 117 p.

Heemskerck, A.R., 1998, *Techniques: Tritium (Direct and Enriched [TP 01])*: Environmental Isotope Laboratory University of Waterloo, Waterloo, Ontario, Canada:
<http://www.science.uwaterloo.ca/research/elab/Methodology/inContent/tp01.html>, 2 p.

Kazemi, G.A., Lehr, J.H., Perrochet, P., 2006, *Groundwater Age*: Wiley Interscience, Hoboken, NJ, 325 p.

Kendall, C., Sklash, M.G., and Bullen, T.B., 1995, *Isotope Tracers of Water and Solute Sources in Catchments*, in T.E. Trudgill (editor), *Solute Modeling I: Catchment Systems*: John Wiley & Sons, Ltd. New York, NY, pp. 261-303.

Mazor, E., 1991, *Applied Chemical and Isotopic Groundwater Hydrology*: Halsted Press New York, NY, 274 p.

Mook, W.G., 2006, *Introduction to Isotope Hydrology: Stable and Radioactive isotopes of Hydrogen, Oxygen and Carbon*: Taylor & Francis Group, London, Great Britain, 226 p.

Mook, W.G. and de Vries, J.J., 2001, *Environmental Isotopes in the Hydrological Cycle: Principles and Application, Volume I: Introduction, Theory, Methods, Review* (W.G. Mook, editor), UNESCO/IAEA, Vienna, Austria and Paris France, 280 p.

Moran, J.E., 2007, *Introduction to Groundwater Age Dating*, in C. Kendall and J.E. Moran, *Isotope Methods of Groundwater Investigation Course*: Groundwater Resources Association of California, March 28, 2007, Hilton Hotel, Concord, CA.

Moran, J.E., Hudson, B.G., Eaton, G.F., and Leif, R., 2002, *California Aquifer Susceptibility: A Contamination Vulnerability Assessment for the Santa Clara and San Mateo County Groundwater Basin*: Lawrence Livermore National Laboratory (LLNL) Report, Contract No. W-7405-ENG-48, LLNL, Livermore, CA, 49 p.

Schlosser, P., Stute, M., Sonntag, C., and Munnich, K.O., 1988, *Tritogenic ^3He in Shallow Groundwater*. Earth and Planetary Science Letters, v. 89, pp. 353-362.

Solomon, D.K., Poreda, R.J., Cook, P.G., and Hunt, A., 1995, *Site Characterization Using $^3\text{H}/^3\text{He}$ Ground-water Ages, Cape Cod, MA*: Ground Water, v 33, n. 6, pp. 988-996.

University of Miami/RSMAS, 2003, *Tritium Laboratory: Environmental Level Measurements of Tritium, Helium and Chlorofluorocarbons (CFC's)*:
<http://www.rsmas.miami.edu/groups/tritium/>, 3 p.

University of Miami/RSMAS, 2005, *Advice on Sampling*: <http://www.rmas.miami.edu/groups/tritium/prices.html>.

U.S. Geological Survey (USGS), 2004, *Stable Isotopes and Radiochemicals*, in *National Field Manual for the Collection of Water-Quality Data, Chapter A5 – Processing of Water Samples, Version 2.2*: USGS Techniques of Water-Resources Investigation, Book 9:
<http://pubs.water.usgs.twri9A>.

U.S. Geological Survey (USGS), 2005, *Tips on How to Collect Samples*: USGS Reston Stable Isotope Laboratory, Reston, VA, <http://www.isotopes.usgs.gov/Instructions.htm>.

U.S. Geological Survey (USGS), 2006, *The Reston Chlorofluorocarbon Laboratory: $^3\text{H}/^3\text{He}$ Dating Background*: <http://water.usgs.gov/lab/3h3he/background/>, 6 p.