Age Dating Groundwater

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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 ^{3}H 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 (^{3}He) Method

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

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

where:

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

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

Analysis

Tritium is typically measured by a liquid scintillation counter. Tritium and ^{3}He can be measured by mass spectrometry, but dissolved gases such as H_2O, CO_2, O_2, and N_2 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/^{3}He 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/^{3}He 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.

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