Dating Groundwater With Isotopes

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An effective integrator of hydrologic history, isotope hydrology is a key to understanding fundamental physical, chemical, biological, and climate forcing processes occurring in a watershed. The measurement of the concentrations of isotopes in groundwater and surface water can be incorporated into models to predict future responses of the watershed to trends in land-use change, water resource management decisions, and climate variability. Isotope methods are useful in regions where more traditional hydrologic tools — such as geologic mapping of aquifer material, piezometric data, pump tests, hydraulic conductivity measurements, major ion chemistry, and hydrologic models – give ambiguous results or insufficient information. Isotopes can be used to efficiently unravel water sources that have combined at the sampling location, and they can accurately determine residence time information, which has important implications for water resources management. If a major urban drinking water supply well from a Southwest basin pumps thousand-year-old water, for example, then it is mining the groundwater resource at a much faster rate than natural recharge. Likewise, a consultant might use isotope ages to prove that owner A, who bought property in 1965, is responsible for a contaminant leak rather than owner B who bought the property in 1980.

This article serves as an introduction to isotopes that are used to determine residence time, sources for age-dating isotopes, and guides for assessing which isotopes are appropriate with regard to their age-range, sample volume size, and analytical measurement. For more information on this subject, see Clark and Fritz (1997) and Cook and Herzeg (2000).

What is an Isotope?

Isotopes of a particular element have the same number of protons but a different number of neutrons in the nucleus, resulting in a different atomic mass. For example, the most common element in the universe, hydrogen, by definition contains one proton in its nucleus, but it can contain none, one, or two neutrons. Some isotopes are stable, meaning they do not decay to any other form over time, and others are unstable, or radioactive, meaning they spontaneously decay at a predictable rate to form a new element. For example, hydrogen with two neutrons is known as tritium, an unstable element. Tritium decays by emitting a radioactive beta particle and converting into a stable helium element.

Sources of Isotopes

Both anthropogenic and natural sources exist for many isotopes. Anthropogenic sources are a result of the nuclear age of weapons testing, nuclear power generation, fuel rod reprocessing, and nuclear medical waste. These activities have elevated many isotopes to concentrations well above their natural state. Most became elevated on a global scale, particularly in the northern hemisphere, after 1950. Natural isotopic sources are divided into three broad categories: 1) cosmogenic, 2) subsurface production, and 3) uranium decay series. Cosmogenic isotopes arise from high-energy cosmic rays known as electrons and photons and lower-energy cosmic rays such as protons and other light nuclei. These cosmic particles assail the earth’s atmosphere, creating secondary particles, such as neutrons, that subsequently bombard other atmospheric nuclei and transform into other isotopes.

Subsurface production occurs through the by-products of natural radioactive decay series. These isotopes often must be accounted for when interpreting cosmogenic isotopic transit times. They can also be directly used for age-dating groundwater.

The uranium decay series (238U) spawns many isotopes with long half-lives that have been used in hydrologic studies and are listed in Figure 1. Uranium-238 is referred to as a primordial isotope because it was incorporated into the Earth during its formation. The 238U half-life is 4.47 billion years.

Understanding the various sources for each isotope helps hydrologists determine which isotopes are most appropriate for hydrologic problems. If the focus is on recharge or vadose zone processes, then cosmogenic isotopes are a good choice because they are incorporated into rain, snow, or dry deposition. On the other hand, if a hydrologist plans to study processes that occurred after 1950, anthropogenic isotopes are useful. For long-term process studies within a groundwater system, cosmogenic, subsurface production, and uranium decay-series isotopes all may be appropriate.

Sources of Isotopes

Isotopes are classified into three broad categories: 1) cosmogenic, 2) subsurface production, and 3) uranium decay series. Each category has specific applications in hydrologic studies.

Cosmogenic isotopes arise from high-energy cosmic rays that bombard the Earth’s atmosphere and create secondary particles, such as neutrons. These neutrons react with atmospheric nuclei to produce new isotopes.

Subsurface production occurs through natural radioactive decay series. These isotopes often must be accounted for when interpreting cosmogenic isotopic transit times.

Uranium decay series are long-lived isotopes that have been used in hydrologic studies. Uranium-238 (238U) is the most common isotope in this series.

Figure 1. Sources of Isotopes

Figure 2. Age Dating Range for Isotopes

Figure 3. Sample Volume for Isotope Measurement Methods

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Age Dating Fundamentals

Before we delve into practical aspects of age-dating isotopes, it is worth mentioning a common misconception. The term “age” sometimes creates the impression that the number represents a simple piston flow transit time of a small water parcel. Despite the prevalent use of this term, isotope hydrologists understand that the water sample measured represents the integrated travel time information; “age” and “mean residence time” are used interchangeably.

Unstable isotopes periodically but predictably emit a particle or break into two smaller nuclei. The time period between emissions is known as the half-life for radioactive decay, and forms the basis for most age-dating methods. An ideal age-dating isotope should behave conservatively by not experiencing any losses or additions during the transit time of the water. This is rarely the case, but we will discuss the ideal case to illustrate the straightforward age-dating technique.

We can calculate the time since groundwater recharged (left the atmosphere) if we know the original recharge concentration of a radioactive isotope (N₀), its associated half-life (T₁/₂), and measure the number of atoms remaining in our groundwater sample at the time of collection (N). T₁/₂ is related to the decay constant (λ) by λ = ln2/T₁/₂.

Assuming a single flowpath without mixing, losses, or additions of the isotope, we can calculate the approximate time since recharge as t = -(1/λ)ln(N/N₀).

For practical reasons, we might have to make assumptions regarding the initial parent atom concentration, which creates larger uncertainties. Therefore, it is more direct to measure the parent atom remaining (N) and daughter produced (D) at the sample collection time. This approach is appropriate if the radioactive parent isotope decays to a stable daughter product that remains with the water parcel containing the parent isotope. In this case, the age calculation is t = -(1/λ)ln1+D/N₀.

Another method to determine residence time is to compare measured concentrations with the time-varying concentrations known as input source functions. Careful historical measurements or reconstructions of the time-varying global fluxes of anthropogenic isotopes can be exploited to derive fairly informative age determinations over the past several decades. Precipitation measurements between 1950 and present day record peak-shaped curves (such as for ‘H, ¹⁴C – see page 22 – and ‘Cl) while others related to nuclear power facilities or fuel rod reprocessing have either increased steadily (such as ‘Kr) or remain elevated (such as ‘I). If only one anthropogenic isotope is measured, then the interpretation may be limited to the determination that the water was recharged within the last 50 years.

Due to their varying concentrations through time, if more than one anthropogenic isotope is measured, then more precise age determinations may be possible. Often the ratios of two isotopes (such as ‘Kr/’H and ‘Cl/‘I) can be combined with each separate isotope concentration to create a unique time when all three factors match the historical signals. Tritium (‘H), an anthropogenic isotope, has an advantage because it decays to a stable daughter product (‘He), and both can be measured in the water sample collected in the field. In this case, one can use the second age equation mentioned above as long as enough tritium and ‘He remains in the sample to be measured in the lab. Also since ‘H is part of the H₂O molecule it directly tracks the movement of the water.

Consideration of Age Ranges

The practical limit on the hydrology residence time age range is a function of the half-life, the laboratory detection limit, and the practical constraints regarding local evidence for the different source generation processes for each isotope. Figure 2 depicts both the natural and anthropogenic tracers and their respective practical age-dating ranges. The y-axis on Figure 2 is logarithmic due to the immense range between several days for the ²²⁴Rn isotope to the potential 80 million-year maximum age for ‘I.

Practical Limits of Field Sample Volume

The required sample volume must also be considered when choosing an isotopic system. Figure 3 lists both the isotopes and their associated general lab measurement category, which significantly impacts the required field sample volume. The y-axis on Figure 3 is also logarithmic due to sample volumes that range between a few milliliters to 3,000 liters. Few hydrologists are willing to extract ‘Kr gas out of 3,000 liters of water as was done for Cyclotron measurements of ancient Great Artesian Basin water in Australia. In general, required sample volumes have decreased with mass spectrometer labs and especially accelerator mass spectrometer (AMS) labs. However, the sample costs are higher for AMS measurements. Thus, many larger volume samples are collected to be measured in low-level counting labs in order to lower the cost.

Lately, there is a trend toward more routine use of isotope tools by hydrologists. The cost of analyses is quite reasonable for many isotopes (see page 20), and a variety of commercial and research labs are available to perform the analyses (see page 19). One could possibly spend a few thousand dollars on isotopic analyses of water collected from existing wells to produce a first order answer to a question that alternatively could require several labor-intensive pump tests, additional borehole installations, and/or a groundwater model that relies upon extensive water level data. As more hydrologists see the power of the isotope techniques and learn to use them effectively, we will ultimately gain an improved understanding of our water resources and be better equipped to manage them effectively.

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References