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Special Section: Applications of Hydrologic Tracers

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Hydrologic tracers are chemical substances (liquid or gaseous) found in water and ice that shed light on processes related to the mechanism and rate of ground water recharge, the time of recharge of ground water, flow pathways, the sources of waters making up a water body, water quality, geochemical evolution, carbon and nutrient cycling, rock-water interactions, the origin of salinity, and contaminant fate and transport. Furthermore in association with climatic data, they are instrumental in paleoclimatic reconstructions of temperature and atmospheric composition (Clark and Fritz 1997).

Some tracers are naturally occurring, whereas others are artificially introduced into the environment as part of controlled experiments. One main class of hydrologic tracers comprises the isotopes, which are atoms of the same element that differ in the number of neutrons found in their respective nuclei. Thus oxygen-18 (denoted by ^{18}O) differs from oxygen-16 (O) in that the former features two more neutrons than the latter. Specifically, ^{18}O has 10 neutrons and 8 protons in its nucleus, whereas O exhibits 8 neutrons and 8 protons. Carbon-14 (^{14}C) exhibits two more neutrons than carbon-12 (C). There are 8 neutrons and 6 protons in the nucleus of ^{14}C , and 6 neutrons and 6 protons in the nucleus of C.

Besides the intrinsic chemical difference between oxygen and carbon, there is another key difference between the pair of isotopes ^{18}O -O and ^{14}C -C that has profound consequences for scientific discovery. Specifically, the ratio $^{18}\text{O}/\text{O}$ in a sample of mass (such as water) would remain constant over time if that sample were to be removed from further contact with exogenous sources of these two isotopes. In contrast, the ratio $^{14}\text{C}/\text{C}$ in a similar sample of mass would decline over time until eventually vanishing altogether.

It is said that ^{18}O is a stable isotope, while ^{14}C is said to be an unstable, or radioactive, isotope (i.e., a radioisotope) that loses mass spontaneously through the emission of a variety of subatomic particles (Faure 1986). The time it takes for an initial mass of an isotope like ^{14}C to be reduced by one-half is called the half-life, and it is a unique and fundamental characteristic of a radioisotope. Stable isotopes and radioisotopes are used for scientific inference, including hydrologic applications (Drever 1988; Clark and Fritz 1997), while some are found in water and ice in various degrees of abundance and are used to gain understanding of hydrologic processes that could not be forthcoming otherwise.

Examples of stable isotopes that have been used in hydrologic discovery are deuterium (D or ^2H), helium-3 (^3He), lithium-6 (^6Li), boron-11 (^{11}B), carbon-13 (^{13}C), sulfur-34 (^{34}S), nitrogen-15 (^{15}N), chloride-35 (^{35}Cl) and chloride-37 (^{37}Cl), bromide-81 (^{81}Br), and strontium-87 (^{87}Sr). Radioisotopes sometimes used in hydrologic applications are tritium (^3H), ^{14}C , chlorine-36 (^{36}Cl), argon-39 (^{39}Ar), krypton-85 (^{85}Kr), krypton-81 (^{81}Kr), iodine-129 (^{129}I), radon-222 (^{222}Rn), radium-

226 (^{226}Ra), thorium-230 (^{230}Th), uranium-234 (^{234}U), and uranium-238 (^{238}U).

Most of the stable isotopes and radioisotopes found naturally on earth originated during the formation of the solar system: they are of primordial origin. A prime example is ^{238}U , whose half-life is comparable to the age of the universe, and whose decay series produces daughter radioisotopes such as ^{222}Rn , ^{226}Ra , ^{230}Th , and ^{234}U (Faure 1986). Other isotopes are formed by cosmic radiation that transforms the nuclei of atoms in the atmosphere. Fission in nuclear reactors and the production and testing of nuclear weapons produces various radioisotopes (tritium, ^3H , is a case in point).

Two classical hydrologic applications of isotopes are (1) dating of groundwater, that is, determining the time that a groundwater sample has spent in an aquifer since its recharge (this is called the groundwater age), and (2) determining the sources of water making up a water body (i.e., groundwater provenance). The determination of the age of groundwater is elegantly illustrated by the decay of ^{14}C , which has a half-life $\tau=5,730$ years. The equation of conservation of mass of ^{14}C dissolved in groundwater is (where λ is the decay constant of ^{14}C , in 1/year)

$$\frac{d^{14}\text{C}}{dt} = -\lambda^{14}\text{C} \quad (1)$$

Assuming that the concentration of ^{14}C at the time of recharge in groundwater was $^{14}\text{C}_0$ and that rock-groundwater interactions do not affect the decay of ^{14}C in groundwater, the previous equation can be integrated between time 0 (the time of recharge) and present time t (when the concentration is $^{14}\text{C}_t$), representing the age of groundwater in years

$$t = \frac{1}{\lambda} \ln\left(\frac{^{14}\text{C}_0}{^{14}\text{C}_t}\right) \quad (2)$$

Notice also that the following relation holds for multiples of the half-life of ^{14}C , $t=\tau, 2\tau, 3\tau, \dots$

$$\frac{^{14}\text{C}_t}{^{14}\text{C}_0} = \left(\frac{1}{2}\right)^{t/\tau} \quad (3)$$

In fact, the last equation holds for any time t , so that solving for t yields

$$t = \frac{\tau}{\ln 2} \ln\left(\frac{^{14}\text{C}_0}{^{14}\text{C}_t}\right) \quad (4)$$

Eqs. (2) and (4) estimate the same age, t , therefore, by equating the values of t one obtains the relationship between the half life and the decay constant (in 1/year)

$$\lambda = \frac{\ln 2}{\tau} \quad (5)$$

Groundwater samples collected at present can be analyzed for their $^{14}\text{C}_t$; and provided that the initial $^{14}\text{C}_0$ can be inferred, either Eq. (2) or Eq. (4) can be used to approximate the age of ground-

water. If the age of groundwater, however, exceeds many half-lives, the extant concentration of the radioisotope may fall below the instrumental detection limit. In this instance, a longer-lived radioisotope must be searched for the purpose of dating groundwater.

Slightly more complicated equations for determining the age of groundwater or of any other radioisotope-containing material arise when a parent radioisotope decays into a different daughter atom. Consider, for example, the decay of rubidium-87 (^{87}Rb) to stable strontium-87 (^{87}Sr). Let $^{87}\text{Sr}_0$ denote the mass of ^{87}Sr at the start of the decay of ^{87}Rb , λ be the decay constant of ^{87}Rb (about $1.39 \times 10^{-10} \text{ year}^{-1}$), and ^{86}Sr denote stable strontium-86 (^{86}Sr), which is used, for convenience, to normalize the masses of ^{87}Sr and ^{87}Rb . The (normalized) parent-daughter decay equation is easily shown to be (Krauskopf 1979)

$$\frac{^{87}\text{Sr}_t}{^{86}\text{Sr}} = \frac{^{87}\text{Sr}_0}{^{86}\text{Sr}} + \frac{^{87}\text{Rb}_t}{^{86}\text{Sr}}(e^{\lambda t} - 1) \quad (6)$$

from which the age of the mass containing ^{87}Rb , ^{87}Sr , and ^{86}Sr is solved for

$$t = \frac{1}{\lambda} \ln \left[\frac{\frac{^{87}\text{Sr}_t}{^{86}\text{Sr}} - \frac{^{87}\text{Sr}_0}{^{86}\text{Sr}}}{\frac{^{87}\text{Rb}_t}{^{86}\text{Sr}}} + 1 \right] \quad (7)$$

The (dating) Eqs. (2) and (7) are of scientific significance. They allow the estimation of how long a sample of any parent material—water and ice included—has existed, which by itself is sometimes of interest. When correlated with other geologic, chemical, and biologic data, the ages so determined can shed important clues about processes that formed and transformed the materials now being examined.

Establishing the sources of water to a water body (i.e., establishing the provenance of a water body) is a key application of stable isotopes in hydrology. It has been established [first by Craig 1961] that the ^{18}O and ^2H content of freshwaters worldwide follow consistently about an average regression line (called the global meteoric water line, or GMWL):

$$\delta^2\text{H} = 8.13\delta^{18}\text{O} + 10.8 \quad (8)$$

where the δ value in parts per thousand (‰) for, say, ^{18}O , in a water sample is defined as follows:

$$\delta^{18}\text{O} = \left(\frac{\frac{^{18}\text{O}}{^{16}\text{O}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{VSMOW}}} - 1 \right) \cdot 1,000 \quad (9)$$

where the ratio $(^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}}$ is a reference value, the Vienna Standard Mean Ocean Water. A similar definition holds for the δ value of ^2H , which has its own VSMOW reference value. By comparing the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ content of a water sample with the GMWL, it is sometimes possible to establish whether that water originated from precipitation, snowmelt, groundwater, or whether it is a hybrid from multiple sources.

This differentiation of water sources is made possible by the fractionation of isotopes, which may be caused by evaporation and condensation. For example, the lighter isotope (say, ^{16}O) is preferentially removed from water undergoing evaporation, which is then left enriched with the heavier isotope (^{18}O , in this example). Conversely, when water vapor in the atmosphere con-

denses, the heavier isotope (^{18}O) is preferentially removed by precipitation. The repeated fractionation of isotopes imprints distinct $\delta^2\text{H}$, $\delta^{18}\text{O}$ signatures on waters, that, when compared with the GWML, provide clues about their provenance. Fractionation of isotopes also occurs during chemical reactions, which provides insight on the provenance of the parent material and of elemental cycling in natural processes.

The utility of tracers transcends the isotopic realm. Several other substances and gases are used as tracers, and so is temperature, a key physical, biological, and chemical characteristic of all waters. In particular, ideal or nonreactive tracers, i.e., those that do not decay, do not fractionate, or react minimally with other substances or materials while dissolved in water, are useful in water balancing. Consider, for instance, a catchment that receives water from precipitation (P), loses water by evapotranspiration (E), and is drained by stream flow (Q). Assume that P is measured whereas E and Q are not and are unknown. Assume, further, that the (tracer) chloride (Cl^-) concentration in P (denoted by C_P) and Q (or C_Q) are measured (evaporated water does not remove chloride with it). The catchment is assumed in steady state so that two equations of conservation of mass hold [A is the area of the catchment (in m^2), P and E are fluxes (in m^3/year), and Q is the flow rate (in m^3/year):

$$P \cdot A - E \cdot A - Q = 0 \quad (\text{conservation of water volume}) \quad (10)$$

$$P \cdot AC_P = QC_Q \quad (\text{conservation of chloride mass}) \quad (11)$$

From Eq. (11), it follows that the streamflow Q equals

$$Q = \frac{P \cdot AC_P}{C_Q} \quad (12)$$

Eq. (12) is used in Eq. (11), and E is solved for

$$E = P \left(1 - \frac{C_P}{C_Q} \right) \quad (13)$$

If $C_Q \geq C_P$, Eq. (13) indicates that E is positive, that is, a loss of water. Otherwise, E is negative, in which case it would be interpreted as condensation or a gain of water to the catchment. The merging of hydraulic (e.g., flow measurement) and chemical data as shown in Eqs. (10)–(13) is one active area of application of tracers in hydrology.

Dating, water provenance, and water balancing are three prominent applications among the gamut of possible applications of hydrologic tracers. There are many other applications in which tracers may undergo adsorption/desorption, cation exchange, diffusion, advection, dispersion, biodegradation, and other biogeochemical processes. Through carefully designed experiments, tracers are useful in calibrating numerical and analytical process-oriented hydrologic models and in estimating model parameters. To illustrate the richness of hydrologic tracers' applications, the titanium content of marine sediments in the southern Caribbean basin was used to discern the variations of river flow to the sea over the last two millennia. Titanium is transported from the land to the sea bed by river flow. River flow depends on precipitation, so that low titanium content in marine sediments reflects periods of droughts. This association of titanium output and precipitation established that there was a relatively dry century spanning from 810 to 910 A.D., which was then postulated as a primary cause of the demise of the Mayan civilization in the lowlands of the Yucatan Peninsula in Mexico (Haug et al. 2003).

This special issue on hydrologic tracers contains six papers with a rich variety of tracer applications in hydrology. The papers

by Ivey et al. dwell on the matter of groundwater dating and location of leakage areas, The paper by McDermott et al. deals with pathway determination and travel-time estimation. Meillier et al. present a broad-based application of stable isotopes and radioisotopes to characterize recharge in one of the largest aquifer storage and recharge operations in the United States. Troldborg et al. shed light on how tracers can help decipher groundwater flow characteristics in heterogeneous aquifers. Plummer et al. exemplify the application of tracers in groundwater contamination problems.

If the past and present are clues to the future, one can only expect an expanding role for hydrologic tracers in hydrologic applications. Tracers allow insights to hydrologic processes that would be difficult, if not impossible, to obtain by other means. Improvements in measurement instrumentation continue to widen the range of application of hydrologic tracers, especially for radioisotopes and tracers found at very low concentration in water. This special issue on the application of hydrologic tracers pro-

vides a summary of their usefulness in examining a variety of common practical problems.

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