Technical Note
Use of deuterated water as a conservative artificial groundwater tracer

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Abstract Conservative tracers are necessary to obtain groundwater transport velocities at the field scale. Deuterated water is an effective tracer for this purpose due to its similarity to water, chemical stability, nonreactivity, ease of handling and sampling, relatively neutral buoyancy, and reasonable price. Reliable detection limits of 0.1 mg deuterium/L may be obtained in field tests. A field example is presented in which deuterated water, bromide, and pentafluorobenzoic acid are used as groundwater tracers. Deuterated water appeared to be transported conservatively, producing almost identical breakthrough curves as that of other soluble tracers.

Résumé Il faut utiliser des traceurs conservatifs pour connaître les vitesses de transport dans les nappes à l'échelle du terrain. Pour cette application, l'eau deutériée est un traceur efficace à cause de sa similarité avec l'eau, de sa stabilité chimique, de sa non réactivité, de la facilité de son utilisation et de son échantillonnage, de sa flottabilité relativement neutre et de son prix abordable. La limite de détection de 0.1 mg/L de deutérium peut être atteinte lors de tests sur le terrain. Une application de terrain est présentée, avec l'utilisation de l'eau deutériée, du bromure et de l'acide pentafluorobenzo comme traceurs d'eaux souterraines. L'eau deutériée est de toute évidence transportée de manière conservative, donnant des courbes de restitution pratiquement identiques à celles des autres traceurs.

Resumen Los trazadores conservativos son necesarios para estimar las velocidades de transporte de las aguas subterráneas a escala de campo. El agua deuterada es un trazador efectivo para este fin, debido a sus propiedades: similaridad con el agua, estabilidad química, no reactividad, facilidad de manejo y muestreo, escasa flotabilidad y precio razonable. Además, se puede obtener límites de detección fiables de 0,1 mg/L de deuterio en ensayos de campo. Se presenta un ejemplo en el que se utilizó como trazadores agua deuterada, bromuro y ácido pentafluorobencénico. Las aguas deuteradas se comportaron de forma conservativa, produciendo curvas de llegada prácticamente idénticas a las de otros trazadores solubles.

Keywords tracer tests · stable isotopes · solute transport · fractured rocks · groundwater density · deuterium

Introduction

Artificial tracers are routinely used to obtain important groundwater transport parameters at the field scale. When the effective transport velocity of the water is desired, a "conservative" tracer is used. By conservative, it is generally implied that the tracer is chemically and biologically inert so that it mimics the transport of water molecules. Water isotopes are attractive choices for conservative tracers in that they closely resemble water both physically and chemically. Waters enriched with the isotopes ^{18}O, ^{3}H, and ^{2}H have all been used as effective groundwater tracers (Gaspar 1987). Deuterated water has the advantage over ^{18}O-enriched or depleted water, however, in that it has a smaller natural abundance in nature (background concentration) and it is much more affordable. It has the obvious advantage over ^{3}H (tritiated) water in being non-radioactive (stable).

Deuterated water has been used as an artificial groundwater tracer by researchers throughout the world. García Gutiérrez et al. (1997) used deuterated water in a granite pluton in central Spain and found that it behaved as a conservative tracer, but exhibited a slightly different breakthrough than fluorescein and gadolinium-DTPA. The authors attributed the discrepancy in transport behavior among the tracers to differences in sorption and matrix diffusion. Himmelsbach et al. (1998) used deuterium with fluorescent dyes in a granite fault zone in Germany, and found that the deuterium transported generally with the dyes but exhibited an apparent influence of a contrast in diffusion rates. Deuterated water moved at the same approximate velocity as other solute and par-

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ticulate tracers in a granite pluton in northern California, but differences among breakthrough curves were significant (Becker et al. 1999; Karasaki et al. 2000). Becker et al. (1999) and Becker and Shapiro (2000) used deuterated water along with solute and particulate tracers in the granite/schist site at Mirror Lake in central New Hampshire, USA, and found that deuterated water was transported in a very similar manner as other solute tracers. Some of the data from Mirror Lake are presented here as an illustration of the use of deuterated water as an artificial groundwater tracer.

Tracer Characteristics of Deuterated Water

For a groundwater tracer to be conservative, it must be chemically non-reactive with the geologic medium, neutrally buoyant, and resistant to chemical and biological degradation. To be useful, a tracer must be detectable at low concentrations relative to the background concentration of the same species. To be safe, it must have minimal health effects both in its concentrated form at the injection point and in dilute form at the detection point. Finally, to be practical, a tracer must be affordable in large quantities. In this note the characteristics of deuterated water with respect to these desirable qualities of groundwater tracers will be discussed.

Tracer and Sample Handling

Deuterated water can be purchased in the form of concentrated deuterium oxide (^2H_2O), at a price of roughly $500 per liter (for 99.9% pure) from many chemical suppliers. Preservation consists primarily of preventing atmospheric exchange which might allow deuterated hydrogen to exchange with the hydrogen of atmospheric water. The only health concern (according to the Material Safety Data Sheet in the USA) is that it is hydroscopic (Sigma Chemical Company 1997).

After injection, the ^2H (D) atoms will achieve equilibrium with the ^1H atoms in water molecules that compose the native groundwater. The occurrence of the tracer in groundwater is, therefore, HDO rather than D_2O. The most critical requirement of sample storage is to prevent isotopic exchange of deuterated hydrogen in the sample water with hydrogen of water in the atmosphere. Consequently, samples are best collected and stored in glass bottles with Polyseal caps or other bottles that prevent gas exchange with the atmosphere. Because atmospheric hydrogen gas does not readily exchange with hydrogen in water at ambient temperature, minimizing head space in the sample bottles is not necessary. In fact it is helpful to fill bottles only two-thirds full to prevent breakage in case the sample freezes during shipment to the analytical laboratory. Otherwise, no special sample preservation is necessary. Acid should not be added to the sample, as this will affect the hydrogen-isotope ratio.

Sample Analysis and Detection Limits

Although deuterated water is the actual tracer injected, only the relative abundance of ^1H and ^2H hydrogen is actually measured. Isotopic-hydrogen analysis requires an isotope-ratio mass spectrometer, which is an expensive device, but one that is widely available. The hydrogen-isotope analyses used for the field test discussed in this article were conducted by the US Geological Survey Isotope Fractionation Project, located in Reston, Virginia, USA. Since May 1990, hydrogen-isotope-ratio analyses in this laboratory have been performed using a hydrogen-equilibration technique (Coplen et al. 1991).

A brief summary of the analytical technique is as follows. Two milliliters of water is pipetted into a culture tube. Into each culture tube is placed a glass rod onto which is glued a platinum catalyst. Sixty culture tubes (with rods and catalyst) are loaded onto a vacuum line inside an air bath. The air is evacuated, gaseous hydrogen is added, and the temperature is elevated to 30 °C and maintained to within ±0.01°. Hydrogen-isotopic equilibration between the water sample and the gaseous hydrogen is achieved in a few minutes. Once temperature stabilization has been achieved, hydrogen gas is expanded under automated control into an isotope-ratio mass spectrometer for analysis. Each analysis is completed in about 15 min.

Results from the Isotope Fractionation Project are reported in parts per thousand (‰) relative to VSMOW (Vienna Standard Mean Ocean Water), and normalized on a scale such that the oxygen- and hydrogen-isotopic values of SLAP (Standard Light Antarctic Precipitation) reference water are each –428‰ (Coplen 1988). Concentrations in milligrams deuterium per liter in unknown, *x*, are found from the following relation:

$$D_{conc} = 34.82\left[\frac{1000 + \delta D_{VSMOW}}{1000}\right], \tag{1}$$

where

$$\delta D_{x-VSMOW} = \frac{\left(^2H/^1H\right)_x - \left(^2H/^1H\right)_{VSMOW}}{\left(^2H/^1H\right)_{VSMOW}} \cdot 1000. \tag{2}$$

The two-standard-deviation precision of hydrogen-isotope results using this method is 2‰ in normal terrestrial samples. The method, therefore, results in an uncertainty of ±0.07 mg deuterium/L. The minimum detectable concentration in practice is consequently about 0.1 mg/L above background.

Injectate Buoyancy

The density of an injected tracer fluid relative to the natural groundwater can be an important issue in transport studies. Istok and Humphrey (1995), for example, found that concentrations of bromide (injected as KBr) as small as 50 mg/L caused a breakthrough change in a laboratory physical-aquifer model. Ronen et al. (1995) saw density-driven transport in a laboratory test involving a column of standing water, with density contrasts equivalent to 30 mg/L total dissolved solids. These studies suggest

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that it is impractical to conduct field-tracer tests using ionic tracers without risking buoyancy effects. The detection limit of ionic tracers is about 0.1 mg/L, so that the injection concentration must be kept to less than 500 times the detection limit. If a two order-of-magnitude range in concentration is desired for the breakthrough curve, there must be less than an order-of-magnitude dilution between the injection and recovery wells for buoyancy effects to be minimized. As more than an order-of-magnitude of dilution is typical in field tests, buoyancy effects must be a consideration when ionic tracers are used as an artificial groundwater tracer.

Fluorescent dyes can be reliably measured at concentrations as low as 0.01 µg/L. As a result, the density of the injection fluid is rarely a concern when fluorescent dyes are used as groundwater tracers. Unfortunately, these dyes react readily with subsurface materials, particularly in groundwaters of neutral and lower pH values, so their transport is often retarded with respect to water movement (Kasnavia et al. 1999). Organic acids such as fluorinated benzoic acids are relatively neutrally buoyant, and have been used successfully in the field (Reimus et al. 1997; Becker and Shapiro 2000). Unfortunately, the pH of the tracer-injection solution usually must be neutralized by the addition of NaOH or another base, which raises the density of the injectate relative to the groundwater. There is a need for groundwater tracers of relatively neutral buoyancy for purposes of conservative groundwater tracing.

Deuterated water offers a considerable advantage over ionic tracers with respect to injectate buoyancy. As an illustration, about 100 g of both bromide (as 129 g of granular NaBr) and deuterium (as 99.9% pure D_2O) were injected during a tracer test at Mirror Lake, New Hampshire, USA, described later in this article (test D). The volume occupied by sodium bromide when it is added to water is 0.27 cm^3/g at 20 °C, based upon our laboratory measurements made for this study. That is, adding 1 g of sodium bromide to a volume of water, increases the volume of the solution by 0.27 mL. The volume occupied by D_2O when added to water is 0.901 cm^3/g at 20 °C (based upon a density of deuterated water of 1.11 g/cm^3). The density of the injected solution can be calculated by:

$$\rho_{\mathrm{sol}} = \frac{M_{\mathrm{t}} + M_{\mathrm{w}}}{V_{\mathrm{t}} + V_{\mathrm{w}}} \tag{3}$$

where M_t and M_w are the masses of tracer and water added to the solution, respectively, and V_t and V_w are the volumes associated with the tracer and water, respectively. The total volume of water in the injection solution was 41 L. Adding 129 g of sodium bromide increased the volume of the injection solution by 35 mL, whereas adding 100 g D_2O increases the volume of the injection solution by 91 mL. The density of the injectate for bromide and deuterium was therefore 1.002 and 1.0002 g/cm^3, respectively, resulting in a $\Delta\rho/\rho$ for bromide and deuterium of 0.002 and 0.0002, respectively. Consequently, the increase in density over that of groundwater for a bromide tracer test will be about 10 times that of a deuterium test for roughly the same analytical accuracy at the monitoring point.

Reactions with Geologic Media

Deuterated water is expected to be transported with groundwater because it is identical to water, with the exception of an additional neutron. Because hydrogen is exchanged freely among water molecules, however, isotopic exchange can cause an apparent retardation of deuterated water with respect to other tracers. Minerals that hold a comparatively large amount of water near their surface are particularly susceptible to isotopic exchange with deuterated hydrogen. Retardation has been noted in tritiated-water-transport experiments in clay, presumably due to reversible isotopic exchange of water surrounding clay particles (Gaspar 1987, p. 57). Similar behavior might be expected for deuterated water in subsurface environments. Little is known, however, about isotope exchange in time scales of relevance to artificial tracer tests. Further research is needed to determine the circumstances in which deuterated water can be retarded relative to groundwater transport at the field scale.

Additional differences between natural and deuterated water may be realized under certain conditions. Deuterated water has a slightly lower vapor pressure than water, and therefore may be transported differently from water in the vadose zone. Hydration reactions also may fractionate water of different isotopic content. The molecular diffusion rate of HDO in water is 2.3×10^{-5} cm^2/s (Wang et al. 1953), which is rapid compared with other conservative solute tracers. In geologic media with large dead-end pore space, tracers of different diffusivity may produce significantly different breakthrough curves. As with any other tracer, if one wishes to assure that a tracer is conservative, it is best to use more than one non-reactive tracer in field tests.

Example of Deuterated Water as an Artificial Groundwater Tracer

Deuterated water was used as a tracer in a series of experiments conducted in the fractured crystalline bedrock (granite and schist) near Mirror Lake, in Grafton County, New Hampshire (readers are referred to Becker and Shapiro 2000 for details of the experiments). In addition to deuterated water, bromide and pentafluorobenzoic acid (PFBA) were used as tracers. Prior to tracer injection, an approximately steady-state forced hydraulic gradient was implemented between an injection and recovery well, situated 36 m apart. The flow field was induced as a weak-dipole, with 5% of the withdrawn water being reinjected throughout the test. Tracer was introduced to the formation in a method similar to that described by Shapiro and Hsieh (1996). A single-fracture set was isolated in the well bore using two inflatable packers. A third, center packer with a flow-through port was then used to seal the fracture set itself, while tracer was mixed

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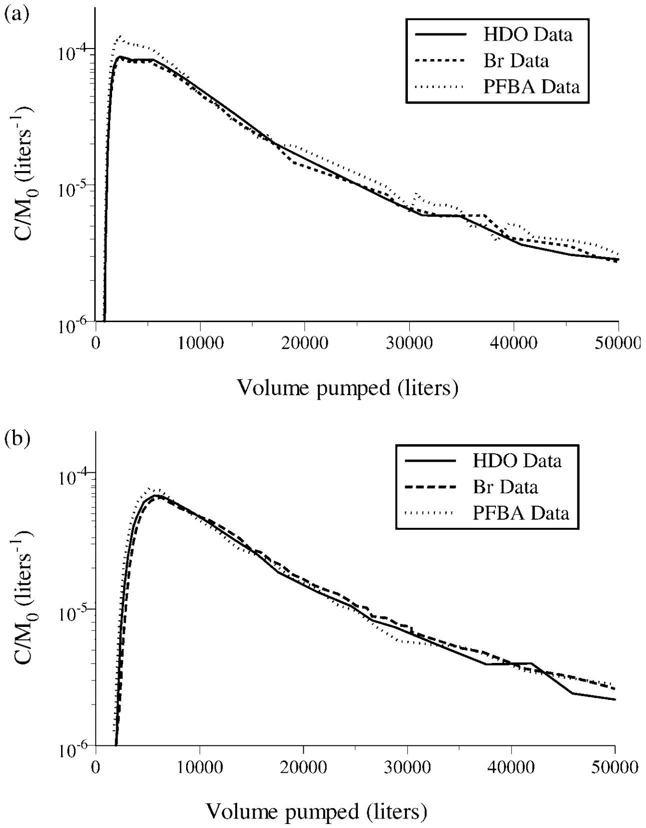

Fig. 1 Breakthrough of deuterated water (*HDO*), bromide (*Br*), and pentafluorobenzoic acid (*PFBA*) from tracer tests D and C, conducted at Mirror Lake, New Hampshire, in 1997. Note that all tracers transported in a very similar manner in this fractured crystalline bedrock. Pumping rates were approximately 9.8 L/min for test D (**a**) and 2.9 L/min for test C (**b**)

in the well bore by circulating tracer fluid to the surface with a downhole pump. Injection commenced when the center packer was deflated, and reinjection was routed from the pumping well to the injection well. This method assured that tracer was completely mixed in the well bore, and that tracer did not enter the formation prior to the intended initiation of the experiment. Four tracer tests were conducted, with pumping rates ranging from 2.9–9.8 L/min.

Figure 1 displays the tracer breakthrough from these tests, plotted as log concentration (*C*) normalized to injected mass (*M$_0$*), against volume of water pumped from the withdrawal well. Figure 1a shows the result from the test conducted at the greatest pumping rate (test D, 9.8 L/min) and Fig. 1b shows the result from the test conducted at the slowest pumping rate (test C, 2.9 L/min). In both cases, the deuterated water transported in a manner similar to the bromide and PFBA tracer. There is some difference between PFBA and the other two solute tracers in test D, possibly due to the greater molecular size of PFBA and its relatively lower rate of molecular diffusion. Because there is no offset in time observed in breakthrough, it does not appear that there is a significant difference in chemical reactivity among the tracers.

Conclusions

Deuterated water is an effective artificial tracer in most groundwater environments. Some of its advantages as a tracer are that it is non-toxic, requires no sample preservation other than properly sealing the sample bottle, is more neutrally buoyant than ionic tracers, and is relatively inexpensive. Some of its disadvantages as a tracer are that samples cannot be analyzed on site, and analysis requires expensive and specialized equipment. The published literature indicates that deuterated water behaves in a similar manner to other non-reactive tracers, except when the comparative tracers have a significantly slower molecular diffusion rate. Problems with using deuterated water as a conservative tracer may be encountered in clay aquitards, due to isotopic exchange. Further research is required to better understand how isotopic exchange affects the behavior of deuterated water over the time scale of an artificial tracer test.

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