Groundwater Age and Groundwater Age Dating

Craig M. Bethke and Thomas M. Johnson

Department of Geology, University of Illinois, Urbana, Illinois 61801;
email: bethke@uiuc.edu, tmjohnsn@uiuc.edu

Key Words

residence time, isotope age dating, reactive transport modeling

Abstract

A new way of thinking about groundwater age is changing the field
of groundwater age dating. Following a rigorous definition of age,
a groundwater sample is seen not as water that recharged the flow
regime at a point in the past, but as a mixture of waters that have
resided in the subsurface for varying lengths of time. This recogni-
tion resolves longstanding inconsistencies encountered in age dating
and suggests new ways to carry out age dating studies. Tomorrow's
studies will likely employ sets of marker isotopes and molecules span-
ning a broad spectrum of age and incorporate a wide range of chem-
ical and physical data collected from differing stratigraphic levels.
The observations will be inverted using reactive transport model-
ing, allowing flow to be characterized not in one direction along a
single aquifer, but in two or three dimensions over an entire flow
regime.

INTRODUCTION

Hydrologists in recent years have begun to think about groundwater age in a new way, and the new thinking is opening doors to understanding the nature of subsurface flow regimes. Interest in groundwater age, of course, is not new: The concept has long been central to a hydrologist's work (e.g., Kazemi et al. 2006). In considering the sustainability of groundwater production, to prevent a resource from being overexploited, for example, the first question asked is, How old is the water? An aquifer filled with modern precipitation is known to refill quickly, whereas one containing mostly ancient water may not recharge to a useful extent over human timescales. Furthermore, filled with modern water, an aquifer is vulnerable to contamination from the surface by wastes improperly disposed of or poor agriculture practices.

A groundwater's age is closely related to the rate it migrates. Considering simple migration in one dimension, flow velocity is the reciprocal of the age gradient, which is the rate that age changes with distance along the direction of flow. The more sharply age increases, the more slowly water migrates. In siting a repository to isolate nuclear waste from the biosphere, designing a deep injection well to minimize the risk of contaminating shallow water supplies, or figuring how long leachate from a landfill will take to reach a nearby well, a hydrologist will likely begin by examining the distribution of groundwater age at his site. From differences in age, he can estimate transit time, the interval required for water to move from one point to another.

The distribution of groundwater age reveals aspects of the nature of a flow regime. Where we can figure flow velocity in an aquifer from the age distribution, if we observe the head gradient and porosity, we can apply Darcy's law to obtain a measure of hydraulic conductivity. Conductivity determined in this way may constitute valuable information, because it can be calculated over large or even regional distances, at scales greater than those amenable to laboratory measurement or well testing. As well, unexpectedly old water in an aquifer may point to upwelling of ancient fluids from below, and notably young water may reflect active infiltration from the surface. In these cases, the age distribution along an aquifer can give the rate of cross-formational flow or surface recharge, both of which may be difficult to determine by other means.

Groundwater age, furthermore, provides a critical intellectual link between arms of hydrology. On one hand, when physical hydrologists use Darcy's law to calculate flow velocity, they predict the age gradient. The results of a groundwater flow model include, at least implicitly, the distribution of age across the flow regime. Chemical hydrologists specializing in age dating, on the other hand, determine groundwater age from the concentration of a radioactive or radiogenic isotope, or of an isotope or molecule that marks an anthropic event, such as nuclear weapons testing. They figure age from the rate the isotope decays or accumulates, or the time elapsed since the event, without need to consider Darcy's law or the physical factors that affect flow. The approaches, then, are broadly independent in their assumptions and data requirements.

We might reasonably expect age determined by the two approaches, physical and chemical, applied to the same flow regime, to agree well, at least within the uncertainty in estimating parameters such as hydraulic conductivity. Indeed, early dating studies such as those by Pearson & White (1967) were promising in this regard. It has become clear with time, however, that physical and chemical hydrologic studies of the same flow regime are likely to yield sharply contrasting interpretations of groundwater age, and hence of flow rate (e.g., Drimmie et al. 1991, Mazor & Nativ 1992, Pinti & Marty 1998). The disagreement is in many cases too broad to attribute to any plausible level of uncertainty in parameter estimation.

The disconnect is not merely between physical and chemical perspectives, since even the different geochemical methods commonly give inconsistent results (e.g., Glynn & Plummer 2005). A dating technique based on a rapid decay reaction applicable to recently recharged groundwater might suggest a water sample is young, for example, whereas a technique based on a slow decay applied to the same sample may give an old age estimate.

It has become increasingly apparent in recent years that the failure of the different physical and chemical perspectives to portray groundwater age in a consistent way cannot be explained by any error specific to carrying out the individual methods, or to collecting the data that goes into them. Hydrologists, for this reason, have begun to reexamine the very concept of groundwater age. In this paper, we consider the new thinking and what it might mean to the field of groundwater age dating.

Sample age: age of a groundwater sample calculated according to a geochemical age dating technique, as commonly applied

Piston flow age: the time required to traverse a flow line from the recharge point to a location in the subsurface

EVOLVING CONCEPT OF GROUNDWATER AGE

In preparing this review, we consulted nearly a dozen groundwater hydrology texts about the meaning of groundwater age. A simple definition of age, or residence time,[1] is the interval of time that has elapsed since groundwater at a location in a flow regime entered the subsurface. This point must seem obvious, because none of the texts explicitly state it or describe how age might be calculated from the pattern of groundwater flow, preferring instead to begin with the calculation of sample ages from isotope or marker molecule concentrations, for the different dating techniques.

Implicit, if unstated, in deriving the dating techniques is the idea that at some point in the past a packet of groundwater recharged the subsurface and began to migrate along a flow path to its present day position, where it was sampled for isotopic or chemical analysis (**Figure 1**). This idea is known as the piston flow model because the packet is visualized as a piston of water migrating through the flow regime, and the interval of time required for the packet to reach its current position is therefore the piston flow age. An alternative name is the streamtube model, in which the packet is seen as migrating along a streamtube, the area in a two-dimensional diagram between two

[1]The term residence time has been used synonymously with age, and in reference to the age of groundwater exclusively at a point of discharge from a flow regime.
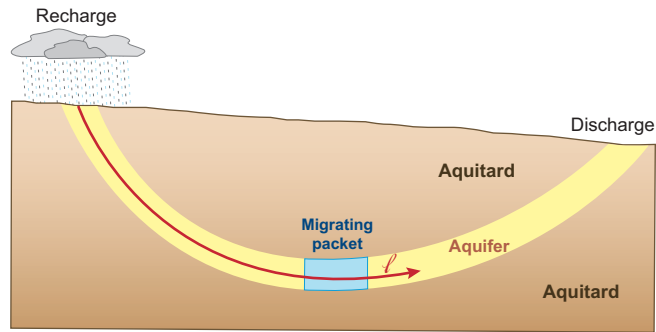
Figure 1

Piston flow model of groundwater age, as applied in groundwater age dating studies. An isolated packet of water moves along an aquifer, along flow path ℓ, from recharge to discharge point, without exchanging water molecules with neighboring aquitards or adjacent packets.

flow lines. Either way, the packet is taken to migrate as a closed system: water molecules neither enter nor leave.

If, in the piston flow model, ℓ represents distance along a flow line, groundwater age τ varies with position according to

$$\frac{d\tau}{d\ell} = \frac{1}{v_\ell},\tag{1}$$

where v_ℓ is flow velocity. Therefore, if water flows 10 m year^{-1}, a sample taken 1 km downstream from a given point would be expected to be 100 years older than at the upstream location. Age at a point $\ell = L$ along the flow line is

$$\tau(L) = \int_0^L \frac{d\ell}{v_\ell} = \frac{L}{\bar{v}_\ell},\tag{2}$$

where $\bar{v}_\ell$ is velocity averaged over time, as flow moves from 0, the recharge point, to the current position L.

Groundwater, of course, does not move through the subsurface in closed packets (e.g., Fontes 1983), as suggested by the piston flow model. Water molecules passing through an aquifer diffuse into the fine-grained sediments of neighboring aquitards, and those in the aquitards diffuse into the aquifer. Molecules enter and leave aquifers by cross-formational flow, the migration of groundwater across the confining layers. Even within an aquifer, water does not move in closed packets because a water molecule can follow any of a large number of tortuous pathways through the sediment. A given mass of water, as a result, exchanges molecules with water masses ahead of and behind it, and to its sides. This process of physical mixing is known as hydrodynamic dispersion; mixing along the direction of flow is longitudinal dispersion, and transverse dispersion is mixing across the flow.

Hydrologists are paying increased attention to the incorrectness of the closed system assumption. As discussed below, they (e.g., Sudicky & Frind 1981, Maloszewski & Zuber 1991, Sanford 1997, Shapiro 2001, LaBolle et al. 2006) have explored ways to correct age determinations to account for various ways in which solute is transferred

into and out of flowing water. More radically, hydrologists (e.g., Goode 1996, 1998; Varni & Carrera 1998; Etcheverry & Perrochet 2000) are considering the implications of abandoning altogether the simple definition of groundwater age in common use.

The reason for abandoning the simple definition is clear: If groundwater does not migrate in closed packets, there is no macroscopic entity onto which to assign an age value. Instead of being drawn from a packet of a certain age, a groundwater sample is seen rigorously as a collection of water molecules, each of which has its own age. A certain interval of time has passed since each water molecule in the sample recharged the subsurface, and there is no reason to believe a priori that the interval is the same for all of them.

Following this reasoning, the age of a groundwater sample is defined as the average over all the water molecules in the sample of the length of time each molecule has spent in the subsurface. The difference between this statement and the common definition may seem minor at first, until we consider its implications. A groundwater sample composed of molecules of a given average age, τ_{ave}, for example, can arise in many ways, as shown in **Figure 2**. The sample might contain water molecules that recharged the aquifer during a short interval of time (*plot a*). The age distribution, while having the same mean, alternatively, may contain a long tail reflecting old molecules that diffused from neighboring aquitards into the flow (*plot b*), or a bimodal mixture of young and old waters from different source areas (*plots c and d*). We argue in this review that conceptualizing groundwater age as the composite age of the water molecules in a sample, rather than as a single value, is an inherently richer avenue of thinking that will allow more information to be derived from age dating studies than possible by current practice.

GROUNDWATER AGE DATING

Groundwater age dating takes advantage of the known decay rates of radioactive isotopes, the timing of the introduction into the atmosphere of isotopes from nuclear testing or reactors, or the history of the release of manufactured gases to estimate the age of a groundwater sample. The water molecules in the sample carry no age information themselves, so concentration of a marker—a parent or daughter isotope, or a manufactured gas—serves in the methods as a proxy for age.

In common practice, each dating method is formulated assuming the sample has behaved since recharge as a closed system, that is, according to the piston flow model. Each method, then, gives a single value for sample age; it cannot treat samples as mixtures or define age distributions, such as those shown in **Figure 2**. As discussed below, the sample age does not in most cases represent the average age of the water molecules in a mixture.

Here, we review briefly three classes of age tracers and discuss how each can serve as a proxy for groundwater age. More exhaustive reviews of groundwater age dating are available in Clark & Fritz (1997), Phillips & Castro (2003), and Kazemi et al. (2006).

Figure 2

Various ways in which a groundwater sample of a given groundwater age might be composed. Groundwater age, τ_{ave}, is the average over the ages, τ_w, of water molecules in sample. (*a*) Water molecules recharged at about the same time and moved along the aquifer as a piston (*dashed line*), or a piston subject to longitudinal dispersion; (*b*) water flowing along aquifer is influenced by longitudinal dispersion and exchange by diffusion of water molecules with neighboring aquitards; (*c*) water age is influenced by upwelling of older groundwater; and (*d*) young water recharges the aquifer from above.
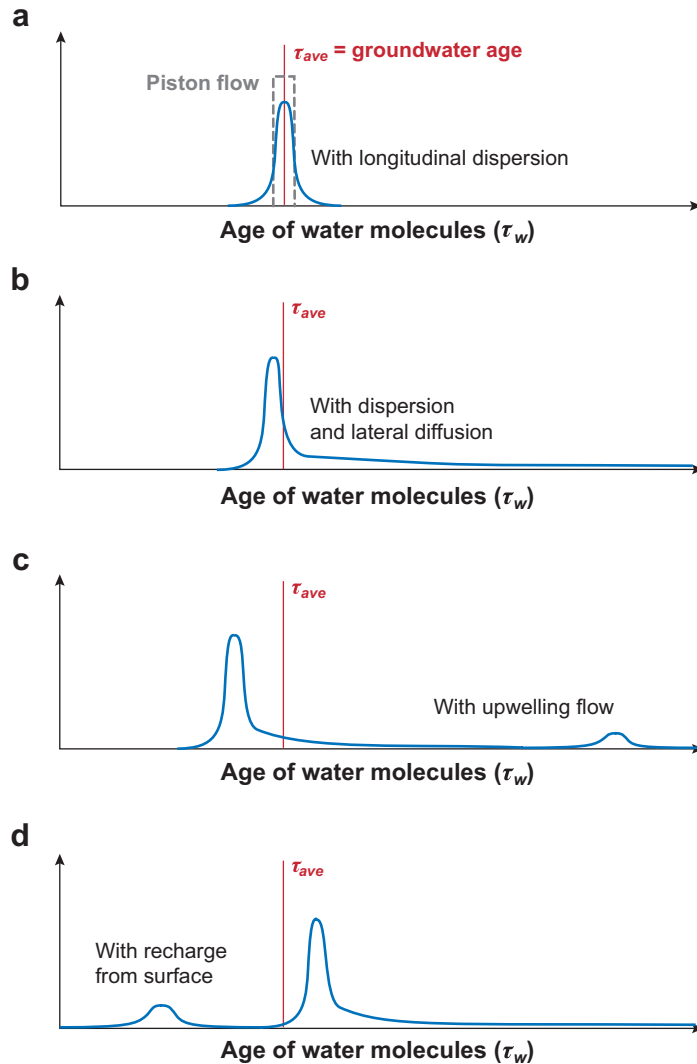
Asymptotic Decay Methods

Recharging groundwater contains radionuclides from the atmosphere that, once the water infiltrates the subsurface, decay asymptotically to zero concentration. Of the methods based on asymptotic decay, the radiocarbon, or ^{14}C, method, useful for dating groundwater less than approximately 50,000 years old, is best known. Cosmic rays produce ^{14}C naturally in the atmosphere and the isotope, which has a half-life $t_{1/2}$ of 5730 years, dissolves as CO_2 in rainfall and in moisture in the root zone.

In a closed system, ^{14}C concentration decreases with time according to

$$C = C_{\circ} e^{-\lambda \tau_s}. \tag{3}$$

Here, C is the concentration in the measured sample (formally in mol m^{-3}, but other units are possible, as we discuss below); $C_\circ$ is the initial concentration at recharge; λ (year^{-1}) is the decay constant for the radionuclide, where $\lambda = \ln 2/t_{1/2}$ varies with the reciprocal of half-life; and τ_s is sample age (year), the time elapsed since recharge. Rearranging gives

$$\tau_s = -\frac{1}{\lambda} \ln \left(\frac{C}{C_\circ} \right), \tag{4}$$

which allows sample age to be calculated from a water's ^{14}C concentration.

In most ^{14}C studies, the isotope's concentration is expressed relative to the total mass of dissolved carbon, for example, as specific activity A, the number of disintegrations detected per second, per gram C. Sample age, in this case, is given as

$$\tau_s = -\frac{1}{\lambda} \ln \left(\frac{A}{A_\circ} \right), \tag{5}$$

where $A_\circ$ is the natural background activity of carbon in equilibrium with the atmosphere. Figured this way, the results are not affected by changes over time in the concentration $C_\circ$ of CO_2 in the recharging water (Clark & Fritz 1997).

Care must be taken in using this approach, however, because oxidation of ancient organic matter or dissolution of carbonate minerals in the subsurface can contribute "dead" (i.e., ^{14}C depleted) carbon to groundwater. Dead carbon dilutes ^{14}C as a fraction of total carbon, reducing ^{14}C activity and leading to erroneously old age estimates. The dead carbon, then, needs to be subtracted from the pool of total carbon before applying Equation 5. Correction techniques based on the sample's ^{13}C/^{12}C ratio, and on mass balance modeling can be applied to this end (e.g., Wigley et al. 1978, Fontes & Garnier 1979).

The ^{36}Cl method is in many ways similar to the radiocarbon technique, although the isotope's half-life of approximately 301,000 years is considerably longer than for ^{14}C, and hence the method is appropriate for dating much older groundwater. Cosmic rays produce small amounts of ^{36}Cl in the atmosphere, which dissolve in rainfall as chloride and decay slowly in water flowing through the subsurface. Sample age is calculated using Equation 4, where C and $C_\circ$ refer now to ^{36}Cl concentration, or to the ^{36}Cl/Cl ratio, the abundance relative to total dissolved chloride.

The latter choice, in contrast to the radiocarbon method, is seldom clearly superior. The ^{36}Cl/Cl ratio in recharge is less likely than the initial ^{14}C activity to be constant over time. And there are significant potential sources of dead Cl that can affect the ratio, including dissolution of halide minerals, diffusion of salt from depth, and mixing with saline groundwater. It is not an uncommon practice to report age dates figured from ^{36}Cl concentration alongside those from ^{36}Cl/Cl ratios (Bentley et al. 1986, Phillips et al. 1986, Torgersen et al. 1991).

Unlike ^{14}C, there is an important subsurface source of ^{36}Cl because the isotope can be produced as a result of neutron capture by stable ^{35}Cl (Lehmann et al. 1993). The production rate depends on the uranium and thorium content of the sediments, which controls the neutron flux, and on groundwater chlorinity. Where sediments

are rich in U and Th, or groundwater is saline, the ^{36}Cl produced in the subsurface can overwhelm the meteoric signature.

Tritium, ^{3}H, which has a half life of 12.3 years and hence is suitable for dating very young groundwater, was released to the atmosphere in large quantities by nuclear weapon testing, mostly from 1954 to 1964 (Gat 1980). We cannot use Equation 4 to estimate age from ^{3}H decay directly because the isotope's atmospheric concentration varied over several orders of magnitude, depending on time and location (Clark & Fritz 1997), so the value of $C_\circ$ for a sample is not generally known. If we measure the daughter product ^{3}He, however, we can estimate groundwater age because

$$\frac{C_{^{3}\text{He}} - C_{atm}}{C_{^{3}\text{H}}} = e^{\lambda \tau_s} - 1, \qquad (6)$$

where C_{atm} is the concentration of ^{3}He derived from the atmosphere, rather than from ^{3}H decay (Schlosser et al. 1988). Rearranging Equation 6,

$$\tau_s = \frac{1}{\lambda} \ln \left(\frac{C_{^{3}\text{He}} - C_{atm}}{C_{^{3}\text{H}}} + 1 \right), \qquad (7)$$

gives sample age.

Several other radionuclides have been used as age tracers. ^{39}Ar ($t_{1/2} = 269$ years) and ^{81}Kr ($t_{1/2} = 229{,}000$ years) are nonreactive noble gas isotopes with good theoretical potential, but they present considerable analytical challenges (Loosli et al. 2000). ^{32}Si ($t_{1/2} = 152$ years) is more easily measured, but sorbs strongly to soils and aquifer solids. To date, the isotope has not provided reliable results (Morgenstern 2000).

Linear Accumulation Methods

A second class of age tracers consists of stable nuclides that are produced in the subsurface and accumulate in flowing groundwater. The isotopes are produced by decay of naturally occurring nuclides with very long half-lives. The decay is slow enough that the parents' abundance, and hence the rate they produce daughter products, is nearly constant. The accumulation with time, then, is essentially linear, and the methods are suitable for age dating very old groundwater.

The best example of these is ^{4}He, which is produced within the aquifer solids by alpha decay. Production proceeds at a predictable rate that depends on the uranium and thorium content of the sediments (Kipfer et al. 2002). ^{4}He diffusion through the solids is relatively rapid, and in stable aquifers bearing old groundwater, the isotope is thought to reach a steady state in which it escapes into the groundwater at the rate it is produced (Torgersen 1980, Torgersen & Clarke 1985). Once dissolved, the ^{4}He does not react or sorb strongly, and therefore is carried unimpeded with the flowing groundwater.

^{4}He accumulates in groundwater flowing through an aquifer owing to release not only from the aquifer solids but also from fine-grained interlayers and the bounding aquitards. The aquitards, in fact, may represent the dominant source, if they are thicker than the aquifer, or richer in U and Th. The isotope, furthermore, is produced

throughout Earth's crust and must ultimately escape upward. Significant amounts of ^{4}He seem to pass into groundwater flow regimes from beneath (e.g., Torgersen & Clarke 1985, Castro et al. 1998a, Bethke et al. 1999), so the flux across a regime's basal boundary represents a large, poorly constrained source.

Where the overall source rate in an aquifer can be taken to be uniformly distributed, ^{4}He accumulates according to the piston flow model in a linear fashion with time, according to

$$C = C_\circ + \frac{R_\alpha \tau_s}{\phi}.\tag{8}$$

Here, C is ^{4}He concentration measured in the sample (mol m^{-3}), $C_\circ$ is the concentration inherited from the atmosphere at recharge, R_α is the source rate (mol m^{-3} year^{-1}), and ϕ is aquifer porosity. Rearranging Equation 8, the ratio

$$\tau_s = \frac{\phi(C - C_\circ)}{R_\alpha}\tag{9}$$

gives sample age.

^{40}Ar is similar to ^{4}He, as it is produced within aquifer solids in the subsurface, in this case by decay of naturally occurring ^{40}K, but differs in that it diffuses less readily. Perhaps for this reason, its release from the aquifer solids seems less predictable than ^{4}He release. In one field study (Torgersen et al. 1989), the ^{40}Ar distribution proved considerably more difficult to interpret than ^{4}He, perhaps because the ^{40}Ar was being released from the aquifer solids locally in discrete events, rather than at a steady rate across the regime. To date, the method has not achieved widespread application.

History Matching Methods

Radionuclides and anthropogenic chemical compounds that were rare or nonexistent in preindustrial times have been released recently to the atmosphere, where they circulate, dissolve in rainfall, and infiltrate the subsurface. A number of the isotopes and compounds are sufficiently unreactive and trace the transport of water well enough to serve as proxies for age (Ekwurzel et al. 1994, Plummer & Friedman 1999). The markers have appeared within about the past 50 years and therefore are applied to dating groundwater that has recharged quite recently.

The concentration of each of the markers has a unique history in the atmosphere, and in meteoric precipitation. Some markers appeared in pulses marking specific events, others have accumulated steadily with time. Using the piston flow model, interpreting groundwater age from marker concentration is straightforward: The concentration is compared to the known history to find one or more recharge dates that match.

Nuclear weapons testing in the 1950s to mid 1960s released to the atmosphere certain radionuclides notable because they form a "bomb pulse," a period during which groundwater recharge was rich in the isotopes. After atmospheric testing was banned, the isotopes diminished in concentration as they mixed into the oceans and subsurface, and, if short-lived, decayed. ^{3}H, in fact, has been depleted from the

atmosphere to the point that groundwaters recharged in the past 25 years can be hard to distinguish from each other.

Of these isotopes, ^3H, ^{36}Cl, and ^{14}C track water movement and are well suited as age tracers (Bentley et al. 1982, Clark & Fritz 1997, Gat 1980). Groundwater enriched in the isotopes could have recharged only during the bomb pulse and hence is known to have an age falling within a bracketed range. Assigning a more specific age to a sample can be complicated, however, because an observed concentration matches two points in time, one on the rising and one on the falling limb of the pulse.

^{85}Kr ($t_{1/2} = 10.76$ years) is released during the operation of nuclear reactors and its concentration in the atmosphere has increased in a nearly linear fashion over the past several decades (Smethie et al. 1992). Accordingly, a ^{85}Kr concentration measured in groundwater matches a unique age, when radioactive decay is taken into account.

Among the manufactured gases, chlorofluorocarbon compounds, or CFCs, and sulfur hexafluoride, SF_6, have proved useful for age dating. The various CFC compounds have different histories: Some increased in concentration early and then leveled off as they were banned from use, others have accumulated more recently (Cook et al. 1995). The atmospheric concentration of SF_6, used primarily in electrical equipment and manufacturing semiconductors, has increased steadily since about 1965 (Busenberg & Plummer 2000). The concentration in groundwater of one of the manufactured compounds, then, generally maps to a unique sample age.

Effects of Mixing

The dating methods, we have noted, predict a single value for the age of a sample, or perhaps two alternative ages, assuming the sample has behaved as a closed system since recharge, according to the piston flow model. Actual groundwater, we have also noted, is a mixture of waters of various, possibly broadly differing, ages. We need to consider, then, how mixing affects the sample age predicted by the dating methods. The effect, it turns out, depends on the type of dating method used.

For the asymptotic decay methods, sample ages calculated for mixtures are biased, in many cases quite strongly, toward youth. This effect is shown in **Figure 3a**. Marker concentration in an unmixed water decays with age along an exponential curve, according to Equation 4. A similar trend (not shown) is predicted by Equation 6 for the isotope ratio in the ^3H-^3He method. When fluids mix, marker concentration plotted against age falls along a straight line. The mixing line falls to the right of the decay curve, so a mixture's apparent age, the age predicted by the dating technique, is invariably younger than the actual age of the mixed sample. The error may be small when the waters are of similar age, as might be the case for longitudinal dispersion (Johnson & DePaolo 1996). But if one of the waters in the mixture is young and the other very old, the bias toward youth is extreme.

For the linear accumulation methods, such as ^4He, the mixing line overlies the marker curve, which is of course also linear (**Figure 3b**). Where the source rate R_α is uniformly distributed, then, the methods accurately predict sample ages for not only unmixed samples but also mixtures of waters. For a heterogeneous source, such as where the marker isotope is produced more rapidly in aquitards than the aquifer, the
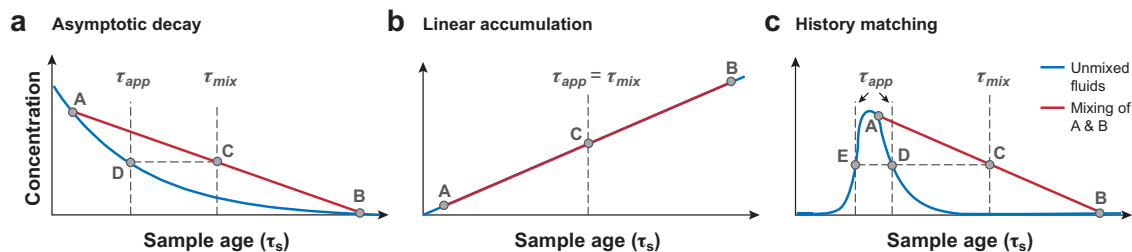
a **Asymptotic decay** **b** **Linear accumulation** **c** **History matching**

Figure 3

Apparent ages of mixed waters for age dating methods based on (*a*) asymptotic decay (Park et al. 2002), (*b*) linear accumulation, and (*c*) history matching. In the absence of mixing, marker concentration varies with sample age along the trends shown, and concentration in mixtures of waters A and B falls along the straight segments; τ_{mix} is the mean age of a mixture *C*. For an asymptotic decay method, the apparent age τ_{app} (*point D*) of the mixture is invariably younger than the actual age. For linear accumulation, the actual and apparent ages coincide (*C*), and for history matching, apparent ages *D* and *E* are most commonly younger than the actual age, and may be younger than either end-member.

age of a single mixed sample cannot be determined unless the source rate and mass fraction of each water in the mixture are known.

History matching methods, like those based on asymptotic decay, tend to be biased toward youth. If one of the waters in a mixture is much older than approximately 50 years, the mixing line lies to the right of the curve tracing marker history (**Figure 3c**), leading to a sample age younger than the mixture's actual age. Like the case of asymptotic decay, the bias can be significant (e.g., Weissmann et al. 2002). Where both waters in a mixture recharged recently, within about the past 50 years, sample age is younger than actual age if the marker curve between end-member ages is concave upward, and older if the curve is convex.

DISTRIBUTION OF GROUNDWATER AGE

Concept of Age Mass

Groundwater age by the new definition is a property acquired by water molecules with time and carried with them as they move through a flow regime. To describe the distribution of age, we need to understand how it is carried with the water, and to do that, we must identify the precise quantity that is transported. The quantity cannot be age itself, because age is an intensive property and hence not additive. We could not, in other words, figure the age of a mixture of waters 20 years and 40 years old by adding the ages: Combining the waters would not give a fluid 60 years old.

The quantity that we seek can be found by analogy with the transport of a solute. Concentration C (mol kg^{-1}), an intensive quantity, is used to represent the solute's distribution in the flow regime, but concentration is not the quantity transported. Instead, it is the number of moles of solute that is the additive, extensive property, the quantity conserved during transport. The mole number is given by the product

ρVC of concentration and fluid mass, which is fluid density ρ multiplied by sample volume V. The analogous quantity needed to describe age distribution is the product of groundwater age τ and fluid mass ρV; it is referred to as "age mass" (kg s) and given as $\rho V \tau$ (Goode 1996, 1998).

Because age mass is an extensive quantity, and additive, we can figure the age of a mixture of two fluids according to the age mass each contributes to the mixture following the linear mixing relation

$$\tau = \frac{(\rho V \tau)_1 + (\rho V \tau)_2}{(\rho V)_1 + (\rho V)_2} \tag{10}$$

(Goode 1996). Returning to our example of mixing 20-year-old and 40-year-old waters in equal parts, this equation correctly predicts the average water molecule in the mixture will be 30 years old.

Transport Equation

Because age mass is an extensive, additive property of the fluid, its movement is described by the same transport laws we would use to describe any other such property, such as moles of a solute, or joules of enthalpy. The advective flux of age mass $\mathbf{J}^{\text{adv}} = J_x^{\text{adv}}, J_y^{\text{adv}}$ (kg m^{-2}), the amount of age mass carried across a plane of unit area, per unit time, is given by

$$\mathbf{J}^{\text{adv}} = \rho \mathbf{q} \tau = \rho \phi \mathbf{v} \tau. \tag{11}$$

Here, $\mathbf{q} = q_x, q_y$ is the specific discharge vector (m^3 m^{-2} s^{-1}); ϕ is porosity of the medium; and vector $\mathbf{v} = v_x, v_y$ is the groundwater velocity (m s^{-1}), where $\mathbf{v} = \mathbf{q}/\phi$.

Similarly, the flux owing to dispersion and diffusion, $\mathbf{J}^{\text{disp}} = J_x^{\text{disp}}, J_y^{\text{disp}}$ (kg m^{-2}), can be represented by Fick's law,

$$\mathbf{J}^{\text{disp}} = -\rho \phi \mathbf{D} \cdot \nabla \tau, \tag{12}$$

where ∇ is the gradient operator ($\nabla \equiv \partial/\partial x, \partial/\partial y$). Matrix $\mathbf{D}$ is the dispersion tensor

$$\mathbf{D} = \begin{pmatrix} D_{xx} & D_{xy} \\ D_{yx} & D_{yy} \end{pmatrix}, \tag{13}$$

the elements of which (m^2 s^{-1}) are calculated,

$$D_{xx} = D^* + \alpha_L \frac{v_x^2}{|v|} + \alpha_T \frac{v_y^2}{|v|},$$

$$D_{yy} = D^* + \alpha_L \frac{v_y^2}{|v|} + \alpha_T \frac{v_x^2}{|v|}, \tag{14}$$

$$D_{xy} = D_{yx} = (\alpha_L - \alpha_T) \frac{v_x v_y}{|v|}$$

from the self-diffusion coefficient D^* (m^2 s^{-1}) of water within the porous medium and the dispersivities α_L and α_T (m) in the longitudinal and transverse directions. Here, D^* is the product of the diffusion coefficient D in water and the formation factor ω, which accounts for the tortuosity of the porous medium and has typical values in the range 0.01–0.5 (Freeze & Cherry 1979).

Combining the transport laws (Equations 11 and 12) with the conservation principle applied to a control volume, and assuming for the moment that density is constant and porosity uniform, gives the governing equation for age transport,

$$\frac{\partial \tau}{\partial t} = \nabla \cdot \mathbf{D} \cdot \nabla \tau - \nabla \cdot (\mathbf{v}\tau) + 1, \tag{15}$$

where $\nabla \cdot$ is divergence operator ($\nabla \cdot \psi \equiv \partial \psi_x / \partial x + \partial \psi_y / \partial y$). The "+1" term here prescribes that the water ages at unit rate, each molecule getting one year older each year.

Comparing this equation with the equation of solute transport,

$$\frac{\partial C}{\partial t} = \nabla \cdot \mathbf{D} \cdot \nabla C - \nabla \cdot (\mathbf{v}C) + R, \tag{16}$$

where C is volumetric solute concentration (mol m^{-3}) and R is the solute's source rate (mol m^{-3} s^{-1}), we see age transport is analogous to the transport of a reacting solute, with a reaction source rate of one. Just as the time rate of change in solute concentration depends on the accumulation or depletion of solute moles by dispersion and advection, described by the first two terms on the equation's right side, age changes at a rate reflecting the accumulation or depletion of age mass.

Setting the time derivation null in Equation 15 gives the transport equation

$$\nabla \cdot (\mathbf{v}\tau) - \nabla \cdot \mathbf{D} \cdot \nabla \tau = 1 \tag{17}$$

at steady state. If advection alone is to be considered, this equation becomes

$$\nabla \cdot (\mathbf{v}\tau) = 1, \tag{18}$$

which is Equation 1 in multidimensional form.

Age in Aquitards

We can solve Equation 17 for the steady-state profile of groundwater age across an aquitard sandwiched between two aquifers (Bethke & Johnson 2002a; **Figure 4**). We take depth $z = 0$ at the aquitard's centerline and set its half-width to b, so that $-b \le z \le b$. If τ' is excess age, groundwater age in the aquitard in excess of that τ_{aqf} in the aquifers, the steady-state transport equation (Equation 17) written in one dimension becomes

$$v_z \frac{d\tau'}{dz} - D_z \frac{d^2\tau'}{dz^2} = 1, \tag{19}$$
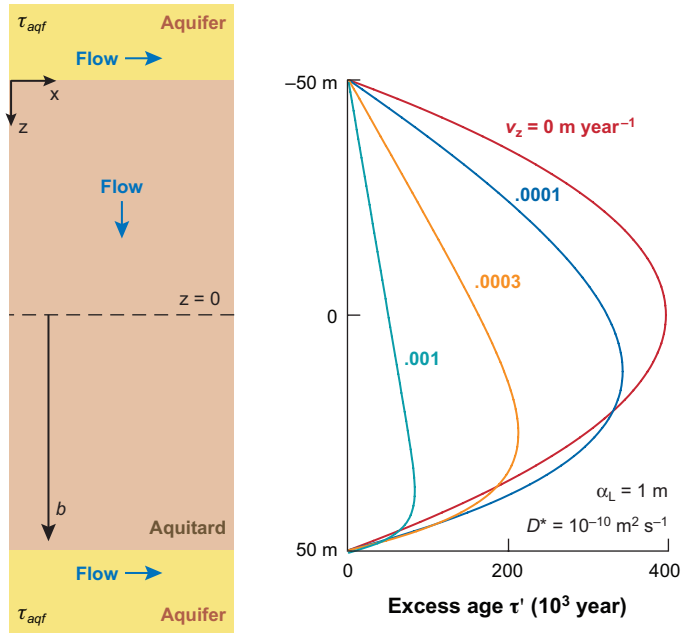
where $\tau' = \tau - \tau_{aqf}$ and D_z is the coefficient of hydrodynamic dispersion along z. In
the absence of cross-formational flow, the equation is

$$\frac{d^2\tau'}{dz^2} + \frac{1}{D^*} = 0 \tag{20}$$

because v_z in this case is zero, and D_z in the absence of flow reduces to the diffusion
coefficient D^* for the porous medium.

Solving the no-flow problem (Equation 20) subject to the boundary conditions
$\tau(z = \pm b) = \tau_{aqf}$, or $\tau'(z = \pm b) = 0$, gives the parabolic result

$$\tau' = \frac{b^2 - z^2}{2D^*}. \tag{21}$$

In the presence of cross-formational flow, the solution is

$$\tau' = \frac{1}{v_z}\left\{ z' - 2b\left[\frac{1 - \exp(v_z z'/D_z)}{1 - \exp(2v_z b/D_z)} \right] \right\}, \tag{22}$$

where $z' = z + b$. The resulting age profiles for the two cases are shown in
Figure 4.

Age Flux into Aquifers

The age profiles across the aquitard (Equations 21 and 22) reflect the generation
of age mass by aging, and its simultaneous dissipation by diffusion, dispersion, and
advection. At the steady state, age mass is generated within the stratum at a rate
balanced by the rate it migrates into the surrounding aquifers.

Substituting Equation 21 into Equation 12 gives the efflux of age mass, in kg m^{-2},

$$J_{z=b} = -J_{z=-b} = \rho\phi b, \tag{23}$$

downward and upward from the aquitard into the aquifers, for the case of no flow. As before, ρ is fluid density, ϕ is porosity of the aquitard, b is its half-thickness. Considering cross-formational flow (Equation 22), the average of these fluxes,

$$\frac{1}{2}(J_{z=b} - J_{z=-b}) = \rho\phi b, \tag{24}$$

takes the same value. The age distribution can also be found assuming a free outlet boundary at the downstream face, and this case gives the same average flux, $\rho\phi b$ (E. LaBolle, written communication).

The Generation and Dissipation of Age

In each case, the age mass efflux from the aquitard can be seen as the mass of water contained in the aquitard, per unit contact area with the aquifers. This result reflects that fact that, at steady state, for each kilogram of water in the aquitard, one kilogram-year of mass must pass each year from the aquitard into the aquifers. As sensible as the result sounds expressed this way, it is nonetheless striking that the efflux depends on no quantity related to transport, such as the diffusion coefficient or the velocity of cross-formational flow.

Aquitards, then, affect the age of groundwater in aquifers simply by existing. This conclusion belies the underlying assumption of basing age dating on the piston flow model, that too few old water molecules migrate from aquitards to affect age in aquifers. In fact, the transfer of water molecules not only increases age in the aquifer, but decreases it in the aquitard. Where exchange is slow, a few very old molecules move into the aquifer; where it is rapid, more molecules enter the aquifer, but they are not as old.

Accounting for the transfer of age mass between formations, the age gradient along an aquifer is

$$\frac{d\tau}{dx} = \frac{1}{v_x}\left(1 + \frac{\phi_{aqt}b}{\phi_{aqf}B}\right), \tag{25}$$

where x is the direction along the aquifer, v_x is flow velocity in that direction, B is the aquifer's half-thickness, and ϕ_{aqt} and ϕ_{aqf} are porosity of aquitard and aquifer. The flow velocity implied by the ages τ_1 and τ_2 of samples taken from wells separated by a distance Δx is

$$v_x = \left(1 + \frac{\phi_{aqt}b}{\phi_{aqf}B}\right)\Bigg/\left(\frac{\tau_2 - \tau_1}{\Delta x}\right). \tag{26}$$

We see that these relations reduce to the piston flow model only in the case for which $b = 0$, which is in the absence of aquitards.

Considering these concepts on a larger scale, we see groundwater flow regimes in a new light: as engines within which age, or more specifically age mass, is generated

and dissipated continuously. Generation is distributed across the flow regime, in aquitards as well as aquifers. For each kilogram of groundwater anywhere in the flow regime, each year one kilogram-year of age mass is created. At the steady state, those kilogram-years must dissipate, either by being carried to a discharge point, or by diffusing or dispersing to the surface.

REACTIVE TRANSPORT MODELING

Reactive transport modeling provides a generalized alternative to the piston flow model for evaluating groundwater age that avoids many of the limitations and biases of the age-dating techniques in common use (e.g., Goode 1996, Zhao et al. 1998, Bethke et al. 1999, Bethke & Johnson 2002b, Park et al. 2002, Castro & Goblet 2005, Kazemi et al. 2006, Zinn & Konikow 2007). Instead of using the standard methods, such as evaluating Equations 4, 5, 7, or 9, to figure the age of each sample individually, the hydrologist assumes a distribution of permeability in his field area and uses it to construct a two- or three-dimensional model of groundwater flow there. He then uses the resulting velocity field $\mathbf{v}$, assumed values for the transport parameters (the diffusion coefficient D^* and dispersivities α_L and α_T), and any data needed to calculate the source or decay rate R to evaluate the distribution in the flow regime of the marker solute, by solving Equation 16. In practice, the two steps are generally accomplished in a single run because most software for modeling reactive transport in the subsurface includes provision for calculating the groundwater flow field.

Adjusting the input data, the modeler strives to reproduce the measured concentrations of a marker isotope or molecule, or several markers, across the flow regime, and perhaps variables such as hydraulic head, while honoring various constraints to within their associated uncertainties. The constraints might include the reasonable range of measured or inferred permeabilities, diffusion coefficients, or dispersivities; the likely distribution in rocks or sediments of U and Th; or an isotope's flux into the base of the flow regime.

A successful model gives a groundwater flow field consistent with the observed marker concentrations. The marker distribution has been inverted to give rates of groundwater flow along and across stratigraphy, or vertically and horizontally in crystalline rock, as well as diffusive and dispersive fluxes. With these results, transit times, recharge rates, and so on can be calculated directly.

Evaluating Equation 15 using these rates gives the distribution of groundwater age across the flow regime, according to the new definition of age. Perhaps ironically, this final step is not strictly necessary: The resulting flow velocities and transport rates can be reported directly, without specifying the age distribution they imply.

[36]Cl Distribution in Hypothetical Flow Regime

As an example of the application of reactive transport modeling, we consider the distribution of [36]Cl across a hypothetical flow regime, following Park et al. (2002). In the model (**Figure 5**), groundwater flows left to right through a 100-m-thick aquifer, in response to 300 m of topographic relief across the 240-km-long section. The
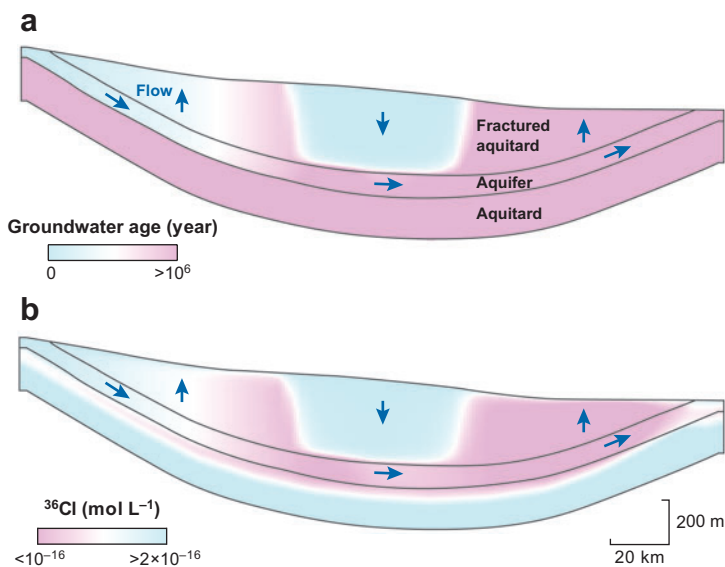
a

Flow

Fractured aquitard

Aquifer

Aquitard

Groundwater age (year)

0   >10^6

b

^{36}Cl (mol L^{-1})

<10^{-16} >2×10^{-16}

200 m

20 km

Figure 5

Numerical simulation of groundwater flow and reactive transport at steady state along a cross
section through a hypothetical flow regime. An aquifer is confined above and below by
aquitards, and the overlying aquitard is fractured. Groundwater flows left to right along the
aquifer, and recharges and discharges across the fractured confining layer. (*a*) The distribution
of groundwater age, accounting for the generation of age mass within the three stratigraphic
units. (*b*) The predicted distribution of ^{36}Cl, calculated accounting for radioactive decay and,
secondarily, subsurface production.

aquifer is confined above by a fractured aquitard, and underlain by another aquitard.
Variation in the slope on the water table creates a secondary recharge area near the
center of the cross section, driving cross-formational flow downward into the aquifer.
The model was calculated using the Basin2 software package (Bethke 1985; Bethke
et al. 2002)[2]; Park et al. (2002) give details of the hydrologic properties assumed.

Groundwater flows along the aquifer at a velocity ranging from approximately
0.5 m year^{-1} upgradient to 0.2 m year^{-1} in deeper strata. The ^{36}Cl concentration
is 2 × 10^{-16} mol L^{-1} in the meteoric recharge, and decreases from this value in
water flowing away from the upper boundary, as the isotope decays. To the left of
the regime, ^{36}Cl is gradually lost in water passing along the aquifer. Near the center,
relatively young water from the surface recharges the aquifer, replenishing some of
its ^{36}Cl content (**Figure 6**).

The base of the lower aquitard serves as a source of salinity, which is allowed to
diffuse upward into the flow regime. Groundwater in the underlying aquitard is saltier
than in the aquifer, varying in salinity up to about 30 mmol L^{-1} at its base, compared
with less than 4 mmol L^{-1} along most of the aquifer. ^{36}Cl forms within the aquitard,

---

[2]The Basin2 software may be downloaded from **http://www.geology.uiuc.edu/Hydrogeology.**

and to a lesser extent in the aquifer, from the chloride in the dissolved salt, by neutron capture. As a result of the subsurface production, ^{36}Cl concentrations at the base of the lower aquitard are the highest of any point in the simulation, up to approximately 3.5×10^{-16} mol L^{-1}. The ^{36}Cl, however, diffuses upward into the aquifer too slowly to have more than a secondary effect on concentration in the aquifer, relative to the meteoric source. If the groundwater had been taken to be more saline, in contrast, or the sediments richer in uranium and thorium, the subsurface production could have overwhelmed the meteoric signature.

The predicted pattern of ^{36}Cl concentration across the aquifer and overlying aquitard in **Figure 5** mirrors, in an antithetic sense, the distribution of ground-water age there. High ^{36}Cl concentrations occur where groundwater is young, and low concentrations where water is old. This result indicates that ^{36}Cl decay can serve as an effective proxy for aging in a regime of this configuration. A reactive transport model reproducing the ^{36}Cl distribution observed in such a basin would give a valid estimate of the flow velocity along the aquifer, as well as the rate of recharge across the overlying aquitard.

Along the left-most 100 km of the aquifer, the ^{36}Cl concentration predicted by the reactive transport model closely tracks that expected from the piston flow model (**Figure 6**). Flow across the upper aquitard is upward, so no ^{36}Cl is carried into the aquifer, and the isotope mass lost by diffusion into the upper aquitard is balanced approximately by the gain from below. Age dates made here in our hypothetical basin on the basis of the piston flow model, using Equation 4, would accurately depict groundwater flow along the aquifer.

At the center of the flow regime, in contrast, the piston flow model gives misleading results. Where ^{36}Cl concentration increases from left to right, Equation 4 would predict a trend of decreasing age, incorrectly suggesting the flow had locally reversed. The high ^{36}Cl concentrations in the deep aquifer, furthermore, lead to erroneously young sample ages, and overly short transit times from the aquifer's primary recharge point. A reactive transport model accounting for flow and transport across, as well as along, stratigraphy would be required to quantitatively interpret the ^{36}Cl distribution in these sediments.

^{4}He and ^{36}Cl in Great Artesian Basin

The distribution of ^{4}He observed in the Jurassic or "J" aquifer of the Great Arte-
sian Basin of Australia (Torgersen et al. 1992) has been difficult to reconcile with
the pattern of groundwater flow mapped out there, and this disagreement has led to
considerable controversy (Bethke et al. 1999). By the piston flow model (Equation 8),
^{4}He concentration would be expected to increase along the aquifer linearly, but in
fact, the trends are more nearly linear in semilog coordinates (**Figure 7**), and hence
the increase is roughly exponential. Concentration in the discharge area, further-
more, is considerably greater than expected from the piston flow model. Sample ages
determined by the ^{4}He method (Equation 9), then, conflict with ages figured from
groundwater velocity in the aquifer.

To investigate this discrepancy, Bethke et al. (1999) constructed a simple re-
active transport model (**Figure 8**) accounting for ^{4}He passing into basal strata
from the underlying crystalline crust, as well as a somewhat smaller amount of the
isotope generated by uranium and thorium decay in the basin sediments themselves.
The simulation carries two stratigraphic units, the J aquifer and its confining layer,
and two types of sedimentary rocks, coarse-grained and fine-grained. The J aquifer
in the model is an interlayering of 60% coarse-grained and 40% fine-grained rocks,
and the confining layer contains only fine-grained rocks.

Groundwater migrates from the northeast end of the cross section to the south-
west end. Flow conditions are artesian, as the basin's name suggests, so groundwa-
ter discharges upward across the confining layer. The primary hydraulic parameters
controlling the distribution of ^{4}He in the model are the hydraulic conductivities of
the two rock types. Conductivity of the coarse-grained rocks controls how rapidly
groundwater flows along the aquifer, and that of the fine-grained rocks controls the
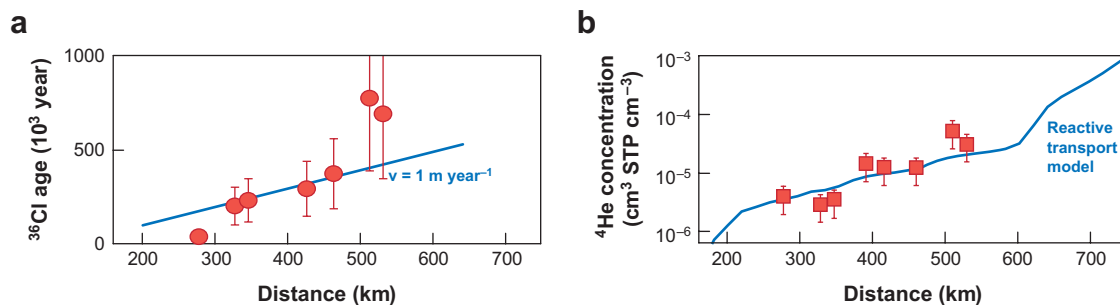rate of cross-formational flow.

Figure 7

Linear plot of ^{36}Cl sample ages (Bentley et al. 1986, Torgersen et al. 1991) and plot in semilog
coordinates of ^{4}He concentration (Torgersen et al. 1992) in groundwater from the J aquifer,
along a northeast-southwest transect through the Great Artesian Basin. Line in (*a*) is the trend
in sample age over a portion of the aquifer; the reciprocal slope of the line is groundwater
velocity there. Line in (*b*) is the result of the reactive transport model for the flow regime,
shown in **Figure 8**, along the top of the aquifer.

Figure 8

Results of a steady-state
reactive transport model
along a northeast-
southwest cross section
through the Great
Artesian Basin of
Australia, showing
groundwater age (*a*) and
the distribution of ^{4}He
(*b*). Groundwater age is
calculated accounting for
the generation of age mass
in basin sediments as well
as in the top 5 km of the
crystalline crust, in
fractures comprising 1%
of the rock volume there.
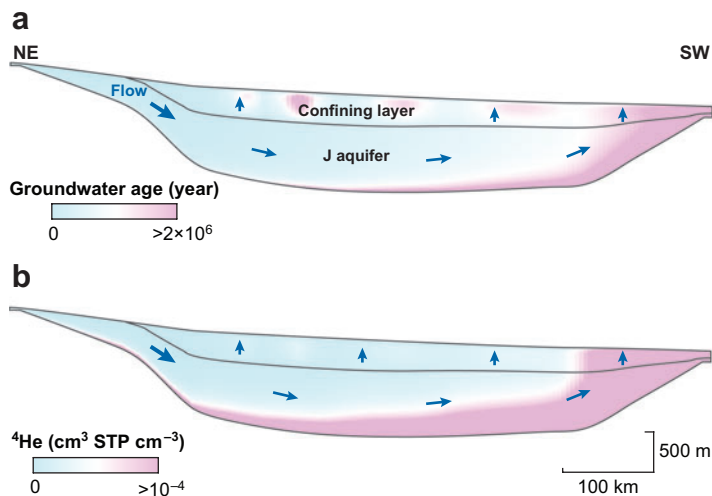
Velocity along an upgradient section of the aquifer can be inferred from the distribution of ^{36}Cl ages, which are considered reliable because the aquifer is thick and not subject to recharge from the surface, to be about 1 m year^{-1}, as shown in **Figure 7**. Given the head gradient and porosity there, this result suggests a conductivity for the coarse-grained rocks of 1–2 m day^{-1}, within the range 0.1–10 m day^{-1} observed in well tests. In a more complicated scenario, of course, the ^{36}Cl distribution could be included directly in the reactive transport model, rather than used as an external constraint. A conductivity for the fine-grained sediments of 10^{-3} m day^{-1}, within the range of 10^{-4}–10^{-2} m day^{-1} reported by previous studies, reproduces well the ^{4}He distribution.

In the calculation results (**Figure 8**), as ^{4}He passes upward from the crystalline crust into the J aquifer, it is entrained by the flowing groundwater, forming a concentrated layer along the base of the flow regime. Where there is no upward flow, the isotope can reach the top of the aquifer, where water wells are completed and hence the groundwater sampled, only by diffusing across the fine-grained interbeds. This process is rather slow, so most of the ^{4}He remains sequestered at depth, where the modeled ^{4}He concentration along much of the cross section is more the two orders of magnitude higher than along the top of the aquifer. Downgradient, where the groundwater upwells toward the surface, however, the upwelling carries the deep, ^{4}He-rich water into shallow strata.

This pattern of deep sequestration followed by upwelling explains the nonlinear trend in concentration observed along the top of the aquifer, as well as the high ^{4}He levels found downgradient in the flow regime. ^{4}He transport is seen to be an inherently two-dimensional problem, so it is not surprising that the isotope's distribution is not described by the piston flow model, and that age calculated using Equation 9 poorly reflects groundwater flow in the aquifer.

The results show how ^{36}Cl and ^{4}He can be used together to define the flow pattern and age distribution in the basin. Each isotope serves a unique purpose. Whereas

the ^{36}Cl delimits the flow rate along the aquifer and hence hydraulic conductivity there, the ^{4}He distribution is sensitive to cross-formational flow and constrains the conductivity of the confining layer. Interestingly, if we calculate age accounting for the generation of age mass not only in the sedimentary section, but within fractures in the top 5 km of the crystalline crust (using Equation 23, with $\phi = 1\%$), the distribution of ^{4}He in the flow regime serves as a quite direct proxy for groundwater age (**Figure 8**).

Optimized Model of the Paris Basin

The process of matching a reactive transport model to observed marker concentrations is, in the simplest cases, straightforward. For a scenario like that shown in **Figure 5**, for example, two variables affect the ^{36}Cl distribution most directly: the horizontal permeability of the aquifer and the vertical permeability of the confining aquitard; variables such as dispersivity and the diffusion coefficient are of secondary importance. The aquifer permeability controls how rapidly the ^{36}Cl concentration decreases along the direction of flow owing to radioactive decay, and the aquitard permeability determines how much of the isotope is replenished by recharge from the surface. The modeler adjusts the two values until the model results reflect as closely as possible the observed ^{36}Cl distribution.

As more data points are collected, more types of markers and other data are to be matched, and more adjustable parameters are included in a model, however, calibrating the model to observations quickly becomes a difficult task. Optimization methods provide an alternative to fitting a model by hand (e.g., Hill & Tiedeman 2007), and software packages such as PEST (Doherty 2004) and UCODE (Poeter et al. 2005) are suitable for this purpose. The codes work by iteration, improving an initial guess to the values of the adjustable parameters, such as the permeabilities of the hydrologic units.

Iteration continues until the value of an objective function, a statistical measure of how much the model results deviate from the observations, stops decreasing. At this point, the function is assumed to be minimized, at least locally, and the model is taken as a candidate best-fit solution. The optimizing software can typically report the sensitivities of the solution to each of the adjustable parameters, and the correlation between each pairing of parameters. The value of a highly sensitive parameter not well correlated to another can be taken with confidence, at least in a mathematical sense. There is, however, little special meaning to the value reported for an insensitive or highly correlated parameter; such cases occur in models in which the adjustable variables have been chosen poorly.

Berger (2008) used optimization methods to construct a groundwater age model along an east-west cross section through the Paris Basin (**Figure 9**). Deep groundwater there flows through the Trias and Dogger aquifers, which are confined by the Lias and Malm aquitards. These units are overlain by Cretaceous and Tertiary strata. The Bray and Sennelay fault zones cut across the deep aquitards in the model and are taken to be hydraulically conductive.

The model accounts for the generation and transport of ^{4}He, the transport of dissolved salt, and heat transfer by conduction and advection. ^{4}He is generated within basin sediments by uranium and thorium decay, and a flux of the magnitude of the
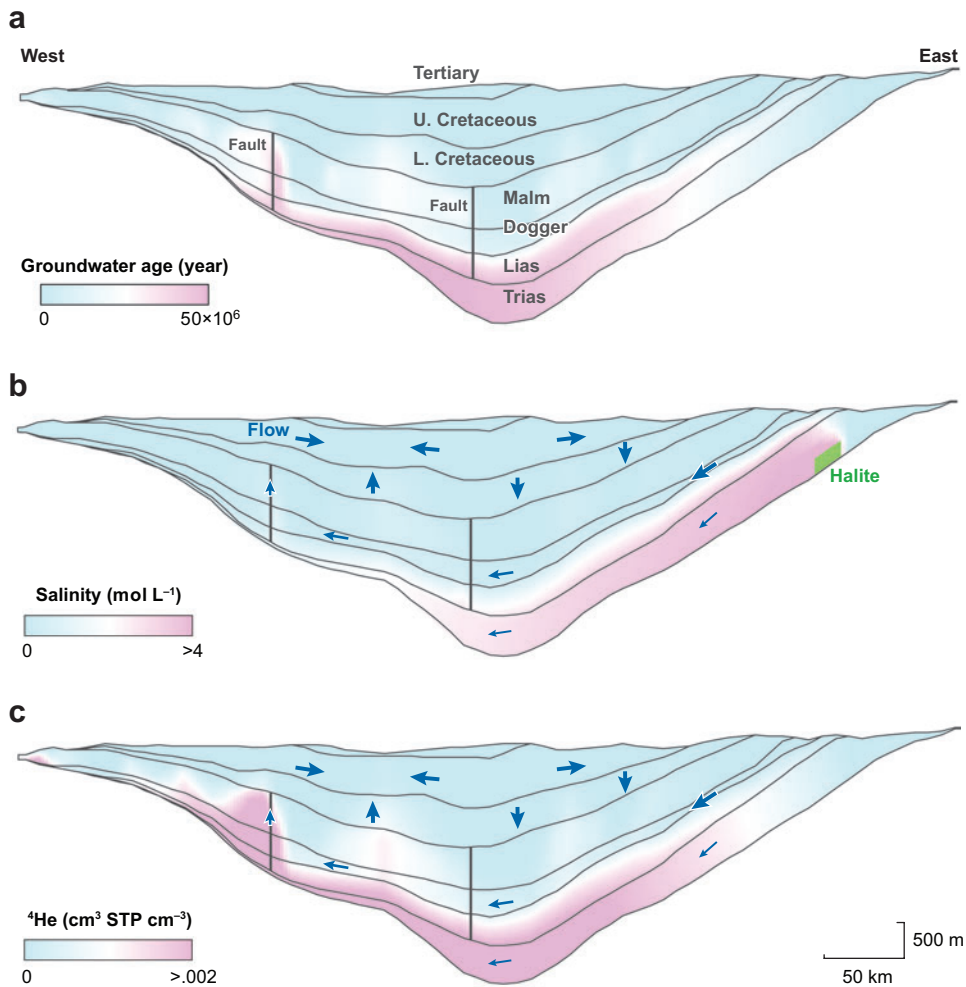
Figure 9

Distribution of (*a*) groundwater age, (*b*) salinity, and (*c*) ^{4}He in a steady-state model of groundwater flow and reactive transport along an east-west cross section through the Paris Basin (Berger 2008). Groundwater age reflects effects of the generation of age mass within the stratigraphic units shown. Salinity is derived by dissolution of halite beds, shown in (*b*). ^{4}He is produced by radioactive decay within the sedimentary section, and supplied across the lower boundary as a basal flux.

isotope's crustal production passes into basin strata from below. Groundwater salinity is derived from dissolution of halite beds in the lower Trias, to the east of the cross section. A heat flux was supplied across the basal boundary, and the top boundary was held at constant temperature.

The model includes 11 adjustable parameters: the permeabilities of each of seven stratigraphic units, the fault permeability, thermal conductivities for deep and shallow
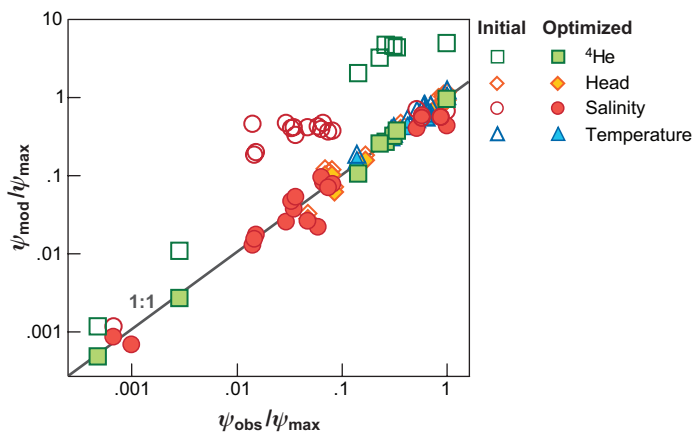
Figure 10

Modeled (ψ_{mod}) versus observed (ψ_{obs}) values of [4]He concentration, hydraulic head, salinity, and temperature in the Paris basin, for the simulation shown in **Figure 9**, plotted as a ratio to the maximum value (ψ_{max}) observed for each variable. Open symbols show results for the initial simulation, before optimization, and solid symbols are results after the simulation was optimized. The simulation matches observed conditions closely when points fall along the diagonal line.

strata, and the formation factor $\omega = D^*/D$ for diffusion within aquitards. It is constrained by a total of 50 observations of [4]He concentration, hydraulic head, salinity, and temperature of groundwater across the basin, as reported by Pinti & Marty (1995), Castro et al. (1998b), and references therein; Castro et al. (1998a) have previously attempted a hand calibration to the [4]He data.

A rough initial model was constructed using Basin2 and then refined with the UCODE software to find optimum values for the adjustable parameters. As shown in **Figure 10**, the optimized model reproduces the observations considerably better than the rough model, especially with respect to the distribution in the flow regime of [4]He and salinity.

Optimizing a model in this way is of obvious value, but, far from being an automatic process, requires of the modeler a considerable level of expertise. The set of adjustable parameters needs to be chosen with care, making sure the variables are not too numerous, have independent effects on the model results, and that each is fully constrained by the observations. The modeler must be alert for roots that are valid statistically, but unlikely physically. And local minima in the objective function need to be identified so the global best-fit solution can be sought. Hill & Tiedeman (2007) give concrete advice on parameterizing groundwater models and calibrating them to observations.

ERROR ANALYSIS

There have been a number of attempts to analyze and correct for the conceptual errors that stem from applying the piston flow model to describe groundwater age. By conceptual error, we mean the error that arises in formulating the problem, as

opposed to uncertainty owing to practical factors such as analytical accuracy, sampling bias, and the distribution and completeness of data. Sudicky & Frind (1981), Sanford (1997), and LaBolle et al. (2006), for example, considered how to correct for loss of the marker from water flowing along aquifers, as the marker diffuses into aquitards, and Maloszewski & Zuber (1991) and Shapiro (2001) looked at marker diffusion from fractures into the rock matrix.

A global analysis of the sources of conceptual error in age dating groundwater, however, has proved elusive. The difficulty in constructing such an analysis arises in large part because the three-dimensional migration of water through the subsurface differs so radically from the piston flow model. In using reactive transport modeling to analyze the distribution of groundwater age in a flow regime, in contrast, the sources of conceptual error can be identified directly (Bethke & Johnson 2002b). To do so, we need only compare the origin and transport of age mass, described by Equation 15, with that of the marker solute, by Equation 16.

Age mass and the marker solute are both transported by advection, dispersion, and diffusion. The flow velocity $\mathbf{v}$ controls advective transport, and dispersion (Equation 14) is described by $\mathbf{v}$ and the dispersivities α_L and α_T. Neither velocity nor dispersivity depends on the quantity being transported, so no conceptual mismatch arises from using the advective and dispersive transport of the marker as a proxy for the transport of age mass.

The diffusion coefficient D^* for age mass, which is the value for water molecules, however, can differ from that of a marker solute (**Figure 11**), so differential diffusion can represent a source of conceptual error (e.g., LaBolle et al. 2006). As well, the unit source rate for age mass (the "+1" term in Equation 15) may differ in form from R in Equation 16 because it is not common for the source rate of a marker solute to be both invariant in time and uniformly distributed over the domain. **Table 1** compares the origin and transport of age mass with that of two markers, ^{36}Cl and ^{4}He.
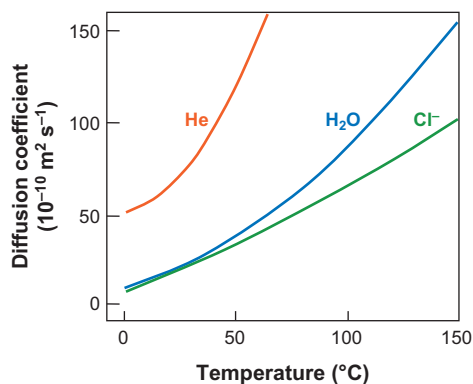

Figure 11

Diffusion coefficient in water of He atoms, water molecules, and Cl ions, as a function of temperature. From Wise & Houghton (1966), Krynicki et al. (1978), and Oelkers & Helgeson (1988).

Table 1 Origin and transport of age mass, ^{36}Cl, and ^{4}He

	Age mass	^{36}Cl	^{4}He
Diffusion coefficient D (in water at 20°C)	20×10^{-10} m^2 s^{-1}	20×10^{-10} m^2 s^{-1}	70×10^{-10} m^2 s^{-1}
Source (or sink)	Zero-order production	First-order decay; zero-order secondary source	Zero-order source
Diffusion length	Over distance, as allowed by D^*	Limited to approximately 30 m per half life ($t_{1/2} \simeq 300,000$ years)	Over distance, as allowed by D^*
Source distribution	Uniform per unit fluid mass	Secondary source varies with U, Th mass in sediments, ^{35}Cl concentration	Varies with U, Th mass in sediments, per unit fluid mass
Reaction	Nonreactive	^{36}Cl/^{35}Cl may be affected by dissolution of halide minerals, otherwise nonreactive	May partition into gas phase, otherwise nonreactive

^{36}Cl Method

The diffusion coefficient for chloride is almost the same as for water, especially at low temperature (**Figure 11**), so conceptual error for the ^{36}Cl method arises largely from differences in source rate (**Table 1**). Whereas age mass is produced at a constant, or zero-order rate per kilogram of groundwater, ^{36}Cl decays with time at a first-order rate. For this reason, as is broadly appreciated, the isotope's decay cannot be observed within the method's precision until a significant fraction of its half-life ($t_{1/2} \simeq 300,000$ years) has elapsed, nor after passage of more than several half-lives.

This fact poses immediate limitations on the accuracy of using reactive transport modeling to invert for groundwater age. A model might be successfully inverted, for example, to give the flux into an aquifer of ancient, isotopically dead (i.e., ^{36}Cl depleted) groundwater from below. Lacking constraining data beyond the ^{36}Cl distribution, however, the model cannot reliably predict flow conditions in underlying, ^{36}Cl-dead aquifers.

The isotope's half-life also limits the distance over which it can trace transport by diffusion. Taking D^* as 10^{-10} m^2 s^{-1}, the isotope diffuses only 30 m, calculated as $2\sqrt{D^*t_{1/2}}$, over its half-life, a distance considerably less than the thicknesses of many aquitards. There is, in contrast, no inherent limitation on the diffusion length for age mass, beyond the time available.

Secondarily, as already mentioned, the isotope can be produced in the subsurface from ^{35}Cl by neutron capture. Error in a model involving saline groundwater, then, may depend on how well the distribution of chlorinity in the flow regime, as well as the uranium and thorium content of sediments, is known. Finally, ^{36}Cl in groundwater can be diluted by the addition of dead chloride where evaporite minerals dissolve. When the ^{36}Cl distribution is represented in a model by the ^{36}Cl/^{35}Cl ratio, a lack of knowledge of the dissolution rate of chloride minerals, or amount of chloride migrating from depth, can contribute significant error.

[4]He Method

Of the dating methods in common use, the source and transport of [4]He meshes most closely with that of age mass. As an uncharged atom, [4]He moves through water more easily than a water molecule, which is hydrogen bonded to the other molecules of the solvent. The isotope, then, has a higher diffusion coefficient than water (**Figure 11**, **Table 1**), and this mismatch can lead to error. [4]He might escape from an aquifer by diffusing across an aquitard to the surface, for example, or diffuse upward across fine-grained interbeds rapidly enough to make the isotope's distribution insensitive to flow along the aquifer.

Assuming [4]He is released from sediments as quickly as it is produced, the isotope's source rate R is constant when the uranium and thorium concentrations, expressed as mass U and Th in the sediments per unit mass of groundwater, are uniformly distributed across the flow regime. Differential diffusion, in this case, represents the sole source of error in using [4]He concentration as a proxy for age mass. Where aquitards are richer in U and Th than aquifers, however, the contrast needs to be recognized in the reactive transport model, to avoid miscalculating age and flow rates. In an aquifer containing unrecognized roll-front uranium deposits, as a second example, the unexpected accumulation of [4]He could lead to the erroneous conclusion that flow is nearly stagnant.

SIGNIFICANCE FOR AGE DATING

Perhaps the most striking facet of the new thinking about groundwater age is that it transcends the apparent inconsistencies that have plagued the field of age dating. Groundwater age dates, as already mentioned, commonly fail to agree with ages inferred from flow rates given by Darcy's law, and age dates obtained by various methods tend to conflict with each other. The disagreement cannot be resolved within the framework of the piston flow model, but is a natural outcome of the new thinking, in which a groundwater sample is taken as a mixture of water from various origins.

Consider as an example water flowing along a shallow confined aquifer. From the flow velocity given by Darcy's law and the distance to the recharge point, we believe the water to be hundreds of thousands of years old. The ^{14}C activity, however, is about a tenth the (prebomb) recharge value, suggesting only several half-lives, or less than 20,000 years, have elapsed since recharge. The water's [4]He content, in turn, is high enough to give an age of millions of years, according to Equation 9.

With the new thinking, the sample can be viewed as water that has flowed from the aquifer's recharge point and mixed with modern water recharged from the surface, and ancient water discharging into the aquifer from below. Given data along the aquifer, reactive transport modeling can give estimates of the relative importance of water from the three sources, and the rates of cross-formational flow from above and below. Seemingly contradictory observations can be seen not only to mesh but also to give important information about the flow regime.

Recognizing groundwater samples as mixtures of waters of differing origin, age dating studies in the future will likely sample for sets of markers that, ensemble,

reflect a broad spectrum of sample age, rather than considering a single marker, or a set of markers applicable to a specific range of ages. In studying shallow groundwater, for example, samples may be analyzed for markers commonly applied to date deep, old groundwater. In this way, it might be possible to map discharge areas from deep flow cells, or characterize discharge along faults. A study of deep groundwater might include markers used to date young waters, to check for direct recharge from the surface, or down-flow along fractures and faults. With the reactive transport modeling approach, the markers would be inverted together in a single step.

At the same time, age daters will likely work to sample groundwater from differing strata, shallow and deep, over the entire flow regime, instead of concentrating on a single aquifer or aquifer system, or a portion thereof, as is common practice today. They might, in a single study, sample groundwater from shallow household wells, deeper municipal wells, and still deeper petroleum reservoirs. In this way, they will be able invert for flow along and across stratigraphy, in shallow and deep layers, rather than characterizing flow velocity in one direction, along a single aquifer. And it may be possible to better characterize flow in fractured crystalline rocks, inherently a multidimensional problem, in a way not possible with the current one-dimensional concepts of age dating.

Age daters will probably find themselves collecting a broader range of data, including not only marker concentrations but also groundwater salinity and temperature, hydraulic head, the permeabilities of various units, and so on. Salinity, as in the Paris Basin example, can serve as a tracer for deep groundwater flow, and temperature can help delimit rates of cross-formational flow, especially along fault zones. Observed permeabilities can be compared with those found by inverting marker concentrations. Perhaps more significantly, permeability measurements can constrain reactive transport models in areas of the flow regime where marker concentrations have not been observed. In this way, the distinction between using physical hydrologic methods and age dating techniques to characterize groundwater flow may fade, and physical and chemical hydrologists may with time find they have much in common.

There are, unfortunately, practical limitations to such broad-based strategies. The age dating techniques available today do not cover a continuous spectrum; in fact, there are broad ranges in sample age for which no technique may be available. As is frequently noted, age dating techniques that could bridge these gaps, if such methods can be developed, would be especially useful. As well, absent funds to pay for scientific drilling, groundwater samples can be collected only from wells drilled for other purposes. Water wells are generally screened in the shallowest interval encountered that can supply sufficient water. For this reason, all the water wells in an area may tap the top of a single aquifer. Oil wells, of course, are completed only in petroleum reservoirs, which may be absent from an area, or found in a single formation.

The piston flow model, despite being deprecated in the new thinking, has undeniable practical advantages over a reactive transport approach to age dating. The model is unambiguously defined and fully parameterized. An age date can be calculated for a single sample, using a simple equation. A reactive transport model, in contrast, can be parameterized in various ways. The stratigraphic section, for example, can be divided into many layers, or a few, and each hydrologic unit can be taken to be

homogeneous or heterogeneous in its permeability. There are guidelines for parameterizing a model effectively (e.g., Hill & Tiedeman 2007), but no rules. Groundwater age is calculated for a set of observations, following an involved modeling procedure, rather than individually, for each observation. And the ages are not necessarily unique because parameterizing the model differently may give a different result, and they may change as new data are collected.

There are also obstacles of scientific culture and training. Few groundwater age daters are experienced in reactive transport modeling, much less in handling issues such as the parameterization and optimization of numerical models. A reactive transport modeler, in turn, may know little about groundwater age dating, including issues of sampling and analysis. Modeling expertise is needed not only in interpreting data collected by age daters but also in designing sampling strategies, before data collection begins.

Age daters and modelers will need to learn much about each other's specialties, form effective partnerships, or—most likely—both. In any event, in light of the compelling logic of the new thinking, and the insights and information that follow from it, we believe the practical issues will inevitably be overcome. If we are correct, today's practitioners may hardly recognize tomorrow's age-dating studies.

SUMMARY POINTS

1. A groundwater sample is composed not of water that recharged at a point in the past, but of a mixture of waters that have resided in the subsurface for varying lengths of time.

2. Conventional age-dating techniques applied to mixed waters predict sample ages that in most cases are strongly biased toward youth; the bias can be extreme.

3. The distribution of groundwater age across a flow regime can be calculated in a rigorous way by tracking the generation and transport of "age mass," the product of groundwater age and mass.

4. Reactive transport modeling can be used to invert the distribution of a marker isotope or molecule, or a set of markers, for flow rates and the distribution of age in a flow regime.

5. Inversion for age in this manner allows for a global analysis of the sources of conceptual error in the dating study.

6. The reactive transport modeling can incorporate to advantage not only marker concentrations but also chemical and physical observations such as salinity and permeability.

7. The models can be constrained using data collected from various stratigraphic units, not just a single aquifer or aquifer system, to characterize flow and transport in two or three dimensions over an entire flow regime.

DISCLOSURE STATEMENT

ACKNOWLEDGMENTS

LITERATURE CITED

Bentley HW, Phillips FM, Davis SN, Gifford S, Elmore D, et al. 1982. Thermonuclear Cl-36 pulse in natural water. *Nature* 300:737–40

Bentley HW, Phillips FM, Davis SN, Habermehl MA, Airey PL, et al. 1986. Chlorine 36 dating of very old groundwater 1. The Great Artesian Basin, Australia. *Water Resour. Res.* 22:1991–2001

Berger PM. 2008. *An optimization approach to groundwater age dating: How old is water in the Paris basin*? PhD thesis. Univ. Illinois, Urbana. In review

Bethke CM. 1985. A numerical model of compaction-driven groundwater flow and heat transfer and its application to the paleohydrology of intracratonic sedimentary basins. *J. Geophys. Res.* 90:6817–28

Bethke CM, Johnson TM. 2002a. Paradox of groundwater age. *Geology* 30:385–88

Bethke CM, Johnson TM. 2002b. Ground water age. *Ground Water* 40:337–39

Bethke CM, Lee M-K, Park J. 2002. *Basin Modeling with Basin2, Release 5*. Urbana: Hydrogeol. Prog., Univ. Illinois. 205 pp. **http://www.geology.uiuc.edu/Hydrogeology**

Bethke CM, Zhao X, Torgersen T. 1999. Groundwater flow and the ^{4}He distribution in the Great Artesian Basin of Australia. *J. Geophys. Res.* 104:12999–13011

Busenberg E, Plummer LN. 2000. Dating young groundwater with sulfur hexafluoride: natural and anthropogenic sources of sulfur hexafluoride. *Water Resour. Res.* 36:3011–30

Castro MC, Goblet P. 2005. Calculation of ground water ages—a comparative analysis. *Ground Water* 43:368–80

Castro MC, Goblet P, Ledoux E, Violette S, de Marsily G. 1998a. Noble gases as natural tracers of water circulation in the Paris Basin. 2. Calibration of a groundwater flow model using noble gas isotope data. *Water Resour. Res.* 34:2467–83

Castro MC, Jambon A, de Marsily G, Schlosser P. 1998b. Noble gases as natural tracers of water circulation in the Paris Basin 1. Measurements and discussion of their origin and mechanisms of vertical transport in the basin. *Water Resour. Res.* 34:2443–66

Clark ID, Fritz P. 1997. *Environmental Isotopes in Hydrology*. Boca Raton, FL: Lewis. 328 pp.

Cook PG, Solomon DK, Plummer LN, Busenberg E, Schiff SL. 1995. Chlorofluo-rocarbons as tracers of groundwater transport processes in a shallow, silty sand aquifer. *Water Resour. Res.* 31:425–34

Doherty J. 2004. *PEST: Model-Independent Parameter Estimation, User Manual.* Brisbane, Aust.: Watermark Numer. Comput. 5th ed.

Drimmie RJ, Aravena R, Wassenaar LI, Fritz P, Hendry MJ, Hut G. 1991. Radiocarbon and stable isotopes in water and dissolved constituents, Milk River aquifer, Alberta, Canada. *Appl. Geochem.* 6:381–92

Etcheverry D, Perrochet P. 2000. Direct simulation of groundwater transit-time distributions using the reservoir theory. *Hydrogeol. J.* 8:200–8

Ekwurzel B, Schlosser P, Smethie WM Jr, Plummer LN, Busenberg E, et al. 1994. Dating of shallow groundwater: comparison of the transient tracers ^{3}H/^{3}He, chlorofluorocarbons and ^{85}Kr. *Water Resour. Res.* 30:1693–708

Fontes JC. 1983. Dating of groundwater. In *Guidebook on Nuclear Techniques in Hydrology.* IAEA Tech. Rep. Ser., 91:285–317. Vienna: Int. At. Energy Agency

Fontes JC, Garnier JM. 1979. Determination of initial ^{14}C activity of total dissolved carbon: a review of existing models and a new approach. *Water Resour. Res.* 15:399–413

Freeze RA, Cherry JA. 1979. *Groundwater.* Engelwood Cliffs, NJ: Prentice Hall. 604 pp.

Gat JR. 1980. The isotopes of hydrogen and oxygen in precipitation. In *Handbook of Environmental Isotope Geochemistry*, ed. P Fritz, JC Fontes, pp. 21–48. Amsterdam: Elsevier

Glynn PD, Plummer LN. 2005. Geochemistry and the understanding of groundwater systems. *Hydrogeol. J.* 13:263–87

Goode DJ. 1996. Direct simulation of groundwater age. *Water Resour. Res.* 32:289–96

Goode DJ. 1998. *Ground-water age and atmospheric tracers: simulation studies and analysis of field data from the Mirror Lake site, New Hampshire.* PhD thesis. Princeton Univ. 194 pp. **http://pa.water.usgs.gov/projects/frhr/thesis.html**

Hill CH, Tiedeman CR. 2007. *Effective Groundwater Model Calibration.* Hoboken, NJ: Wiley-Intersci. 455 pp.

Johnson TM, DePaolo DJ. 1996. Reaction-transport models for radiocarbon in groundwater: the effects of longitudinal dispersion and the use of Sr isotope ratios to correct for water-rock interaction. *Water Resour. Res.* 32:2203–12

Kazemi GA, Lehr JH, Perrochet P. 2006. *Groundwater Age.* Hoboken, NJ: John Wiley and Sons. 325 pp.

Kipfer R, Aeschbach-Hertig W, Peeters F, Stute M. 2002. Noble gases in lakes and ground waters. In *Noble Gases in Geochemistry and Cosmochemistry*, ed. D Porcelli, C Ballentine, R Wieler, pp. 615–700. Chantilly, VA: Mineral. Soc. Am.

Krynicki K, Green CD, Sawyer DW. 1978. Pressure and temperature dependence of self-diffusion in water. *Faraday Discuss. Chem. Soc.* 66:199–208

LaBolle EM, Fogg GE, Eweiss JB. 2006. Diffusive fractionation of ^{3}H and ^{3}He in groundwater and its impact on groundwater age estimates. *Water Resour. Res.* 42:W07202, doi:10.1029/2005WR004756

Lehmann BE, Davis SN, Fabryka-Martin JT. 1993. Atmospheric and subsurface sources of stable and radioactive nuclides used for groundwater dating. *Water Resour. Res.* 29:2027–40

Loosli HH, Lehmann BE, Smethie WM Jr. 2000. Noble gas radioisotopes: ^{37}Ar, ^{85}Kr, ^{39}Ar, ^{81}Kr. In *Environmental Tracers in Subsurface Hydrology*, ed. P Cook, AL Herczeg, pp. 379–96. Dordrecht: Kluwer

Maloszewski P, Zuber A. 1991. Influence of matrix diffusion and exchange reactions on radiocarbon ages in fissured carbonate aquifers. *Water Resour. Res.* 27:1937–45

Mazor E, Nativ R. 1992. Hydraulic calculation of groundwater flow velocity and age: examination of the basic premises. *J. Hydrol.* 138:211–22

Morgenstern U. 2000. Silicon-32. In *Environmental Tracers in Subsurface Hydrology*, ed. P Cook, AL Herczeg, pp. 498–502. Dordrecht: Kluwer

Oelkers EH, Helgeson HC. 1988. Calculation of thermodynamic and transport properties of aqueous species at high pressures and temperatures: dissociation constants for supercritical alkali metal halides at temperatures from 400 to 800°C and pressures from 500 to 4000 bars. *J. Phys. Chem.* 92:1631–39

Park J, Bethke CM, Torgersen T, Johnson TM. 2002. Transport modeling applied to the interpretation of groundwater ^{36}Cl age. *Water Resour. Res.* 38:1043, doi:10.1029/2001WR000399

Pearson FJ, White DE. 1967. Carbon-14 ages and flow rates of water in Carrizo sand, Atascosa County, Texas. *Water Resour. Res.* 3:251–61

Phillips FM, Bentley HW, Davis SN, Elmore D, Swanick GB. 1986. Cl-36 dating of very old groundwater. 2. Milk River aquifer, Alberta, Canada. *Water Resour. Res.* 22:2003–16

Phillips FM, Castro MC. 2003. Groundwater dating and residence-time measurements. In *Treatise on Geochemistry*, ed. HD Holland, KK Turekian, Vol. 5: *Surface and Ground Water, Weathering, and Soils*, ed. JI Drever, pp. 451–97. Oxford: Elsevier. 626 pp.

Pinti DL, Marty B. 1995. Noble gases in crude oils from the Paris Basin, France: implications for the origin of the fluids and constraints on the oil-water-gas interactions. *Geochim. Cosmochim. Acta* 59:3389–404

Pinti DL, Marty B. 1998. The origin of helium in deep sedimentary aquifers and the problem of dating very old groundwaters. In *Dating and Duration of Fluid Flow and Fluid-Rock Interaction*, ed. J Parnell, Spec. Publ., 144:53–68. London: Geol. Soc. London. 300 pp.

Plummer LN, Friedman LC. 1999. Tracing and dating young ground water. *U.S. Geol. Surv. Fact Sheet-134-99*, U.S. Geol. Surv., Reston, Virginia **http://water.usgs.gov/pubs/FS/FS-134-99/pdf/fs-134-99.pdf**

Poeter EP, Hill MC, Banta ER, Mehl S, Christensen S. 2005. UCODE_2005 and six other computer codes for universal sensitivity analysis, calibration, and uncertainty evaluation. *U.S. Geol. Surv. Tech. Methods 6-A11*. Virginia: Reston

Sanford WE. 1997. Correcting for diffusion in carbon-14 dating of ground water. *Ground Water* 35:357–61

Shapiro AM. 2001. Effective matrix diffusion in kilometer-scale transport in fractured crystalline rock. *Water Resour. Res.* 37:507–22

Schlosser P, Stute M, Dorr H, Sonntag C, Munnich KO. 1988. Tritium He-3 dating of shallow groundwater. *Earth Planet. Sci. Lett.* 89:353–62

Smethie WM, Solomon DK, Schiff SL, Mathieu GG. 1992. Tracing groundwater-flow in the Borden aquifer using Kr-85. *J. Hydrol.* 130:279–97

Sudicky EA, Frind EO. 1981. Carbon 14 dating of groundwater in confined aquifers: implications of aquitard diffusion. *Water Resour. Res.* 17:1060–64

Torgersen T. 1980. Controls on pore-fluid concentration of He-4 and Rn-222 and the calculation of He-4-Rn-222 ages. *J. Geochem. Explor.* 13:57–75

Torgersen T, Clarke WB. 1985. Helium accumulation in groundwater. 1. An evaluation of sources and the continental flux of crustal He-4 in the Great Artesian Basin, Australia. *Geochim. Cosmochim. Acta* 49:1211–18

Torgersen T, Habermehl MA, Clarke WB. 1992. Crustal helium fluxes and heat flow in the Great Artesian Basin, Australia. *Chem. Geol.* 102:139–52

Torgersen T, Habermehl MA, Phillips FM, Elmore D, Kubik P, et al. 1991. Chlorine 36 dating of very old groundwater. 3. Further studies in the Great Artesian Basin, Australia. *Water Resour. Res.* 27:3201–13

Torgersen T, Kennedy BM, Hiyagon H, Chiou KY, Reynolds JH, Clarke WB. 1989. Argon accumulation and the crustal degassing flux of Ar-40 in the Great Artesian Basin, Australia. *Earth Planet. Sci. Lett.* 92:43–56

Varni M, Carrera J. 1998. Simulation of groundwater age distributions. *Water Resour. Res.* 34:3271–81

Weissmann GS, Zhang Y, LaBolle EM, Fogg GE. 2002. Dispersion of groundwater age in an alluvial aquifer system. *Water Resour. Res.* 38:1198, doi:10.1029/2001WR000907

Wigley TML, Plummer LN, Pearson FJ. 1978. Mass transfer and carbon isotope evolution in natural water systems. *Geochim. Cosmochim. Acta* 42:1117–39

Wise DL, Houghton G. 1966. The diffusion coefficients of ten slightly soluble gases in water at 10–60°C. *Chem. Eng. Sci.* 21:999–1010

Zhao X, Fritzel TLB, Quinodoz HAM, Bethke CM, Torgersen T. 1998. Controls on the distribution and isotopic composition of Helium in deep ground-water flows. *Geology* 26:291–94

Zinn BA, Konikow LF. 2007. Potential effects of regional pumpage on groundwater age distribution. *Water Resour. Res.* 43:W06418, doi:10.1029/2006WR004865

Contents

Indexes

Errata

An online log of corrections to *Annual Review of Earth and Planetary Sciences* articles
may be found at http://earth.annualreviews.org