WHY DO WE NEED TO DATE GROUNDWATER?

Groundwater is an important resource with concerns in regard to both its quality and quantity. In all climate regimes, but particularly in arid regions, groundwater represents a viable source of water and it is important to determine if specific sites represent a renewable or a minable resource. “Groundwater age” at a specific site would be useful in defining the rate of groundwater renewal or an acceptable rate of water mining. In many urban, industrial, and agricultural sites, groundwater may be contaminated and it is necessary to quantify the timescale of processes that transport (mix and advect) this contaminant. Groundwater may also need to be a key barrier at nuclear waste disposal or carbon dioxide sequestration sites. Knowing the velocity and mixing of the groundwater can be used to evaluate the effectiveness of this barrier. Furthermore, groundwater is an integral component of Earth/environmental systems that facilitates mass transport of dissolved substances and couples surface hydrology, landforms, crustal weathering and soil formation to the deep metamorphism and the mechanical properties of the crust. It enables the existence of life forms, sometimes under extreme climate, geochemical or physical conditions. Thus, the understanding of processes and timescales by which groundwater is mixed and transported remain of paramount importance to understanding the controls on its quantity and quality. In this context, temporal information about the groundwater system in question is needed and hence the subject of “groundwater dating” remains a viable area of research and application.

WHAT DOES “GROUNDWATER AGE” MEAN?

The idea of “dating” groundwater was originally proposed as an extension of traditional radiocarbon dating as applied to solid materials that contain carbon (e.g., wood, shells, charcoal, travertine) (Münnich, 1957). However, early practitioners of isotopic dating of groundwater approached the problem in a rather naïve fashion and did not fully appreciate the differences between traditional radiocarbon dating and groundwater “dating”. The materials used for traditional radiocarbon dating are solids with a (presumably) well-defined initiation time (e.g., the year a tree ring was laid down or a band of travertine precipitated). The difference between this initiation time and the current time is the actual age of the sample. The atoms of carbon within the object are presumed to have remained fixed in place, with no new carbon added, until the sample is analyzed for its radiocarbon content. The object is then “dated” by applying the radioactive decay equation using the current measured radiocarbon content and an assumed initial radiocarbon content. We can call the interval of time calculated in this fashion the “model age”. Provided that the basic assumptions (the initial radiocarbon content and that atoms of carbon have been neither gained nor lost) are correct, the “model age” should equal the actual age.
In reality, in many cases, the basic assumptions are not valid and the model age may significantly differ from the actual age.

Early practitioners of groundwater dating failed to fully appreciate the fundamental differences caused by the fungible nature of water. The “age” of a single molecule of water can readily be defined as the length of time since the molecule crossed the water table and became part of the saturated zone. However, we can actually sample and date only finite volumes of groundwater that contain very large numbers of molecules. Groundwater moves in a bulk fashion in response to spatial gradients in fluid potential. In addition to this, inasmuch as water is a fluid and the relative positions of the molecules are not fixed, those molecules move in such a way as to increase the entropy of the system. These potential-driven and entropy-driven transport processes interact in a complex fashion to produce transport processes variously described as “advection”, “diffusion”, “hydrodynamic dispersion”, “turbulent dispersion” and so on (see (Phillips and Castro, 2003) for a discussion of the influence of the various transport processes on groundwater age tracers). One implication of this type of transport is that the transport path of any individual molecule of water may (and almost certainly does) differ from the mean path obtained by averaging many molecules (see Figure 1). The result is that any finite-sized sample of groundwater contains water molecules that have resided in the system for differing periods of time. This being the case, groundwater cannot be characterized by any single-valued “age”, rather, it is characterized by an age distribution.

What might this age distribution look like? At one extreme, one can imagine groundwater systems that are very well mixed. One example might be an aquifer that has a large volume but very small recharge and discharge rates. In this case diffusion will tend to effectively mix the water molecules within the reservoir. An alternative example might be a very actively recharged karstic aquifer in which a complex, anastamosing conduit network produces efficient turbulent mixing. In both cases the average residence time is simply equal to the pore volume of the aquifer ($L^3$) divided by the recharge rate ($L^3 T^{-1}$), but the distribution of ages around that mean would be both broad and flat (i.e., no prominent mode).

An alternative extreme example would be an extensive, very uniform aquifer with a high recharge rate that is spatially localized (e.g., at a small area of outcrop of the formation). This system will be advection-dominated because the spatially uniform aquifer minimizes dispersive mixing and the high recharge rate produces small gradients of residence time with flow distance. In this case the age distribution of a small sample of the aquifer water will have a prominent mode with relatively little spreading around it.

It is tempting to try to characterize the “age” of a water sample by calculating some central tendency, but unless the system is strongly advection-dominated, this can yield quite misleading results. For example, imagine a small, rapidly recharged aquifer that is bounded by thick shale of extremely low permeability. The shale is still diffusing out connate water that was present when the shale was deposited in the Cretaceous. If 99.9% of the water discharged
from the aquifer was recharged 5 years ago and 0.1% is water from the shale, the average age of the discharge is 65,000 years. This number conveys no useful information about the system and is in fact quite misleading if taken at face value. However, in the case that the system is strongly advection-dominated an estimate of the mode of the groundwater age distribution can provide useful information. In this case we refer to that estimate of the mode as the “estimated groundwater age” (single valued).

To summarize, a sample of groundwater does have a well-defined “age”. It is defined as the frequency distribution of the times since each of the individual water molecules crossed the water table. We term this the “actual groundwater age distribution” or “actual age distribution”. Unfortunately, this actual age distribution is very difficult to obtain, except in numerical experiments. For estimating groundwater age in real systems we must rely on either inferences from the concentration of tracers in a water sample or on calculations based on the physics of fluid mass transport. If the age estimate is obtained from tracer data, then a conceptual/mathematical model must be employed to convert tracer concentrations into an age; we therefore term the age value that results a “model tracer age”. For example, a groundwater age obtained using $^{14}$C data and the radioactive decay equation would be called the “model $^{14}$C age”. This terminology reinforces the principle that the calculated age is inseparable from the conceptual/mathematical model employed, and is therefore a useful measure of the actual age distribution only to the extent that the model corresponds to the actual system.

In the majority of cases the mathematical models employed to interpret tracer data do not include mixing processes. These then yield single-valued model tracer ages. The single-valued model tracer ages may correspond to a mean age obtained from the actual age distribution, but in most cases probably do not. Multiple tracers, combined with a good grasp of the hydrogeology, can often help to understand in at least a qualitative fashion the relation between the single-valued model tracer ages and the actual age distribution.

If the age estimate is obtained from application of the physics of fluid mass transport, we term it the “hydraulic age”. In many cases such calculations include only advective transport, in which case a single value for the hydraulic age is obtained. In more complete models additional processes may be included and in this case a “hydraulic age distribution” may be calculated. Figure 2 illustrates conceptually the effects on the hydraulic age distribution of including successively more realistic combinations of transport processes in a numerical model. Figure 3, from Goode (1996), provides a quantitative example illustrating how changes in the dispersion parameter affect the mean hydraulic age in a simple groundwater system.

Real groundwater flow systems are typically very complex. Hydraulic conductivity can vary over something like 14 orders of magnitude (Freeze and Cherry, 1979) and large variations in hydraulic conductivity can cause different transport processes to predominate in different parts of the system. For example, advection may dominate in a highly permeable aquifer whereas diffusion dominates in a low-permeability shale that bounds the aquifer. Further
complexity is introduced by spatial heterogeneities in recharge and discharge, particularly mixing promoted by convergent flow lines at focused discharge points. The marked differences in residence time effected by the different transport processes and spatial heterogeneity can produce highly skewed or multimodal actual age distributions. Any practical value obtained from model tracer ages or hydraulic ages depends on having a good understanding of the hydrogeology and aquifer dynamics and applying that understanding to interpreting the model or hydraulic age results. In general, the chances of usefully interpreting the tracer data or hydraulic modeling increase as the number of methods applied increases.

TRACERS IN THIS BOOK

For times scales of greater than 1000 years, the tracers available for application and interpretation in terms of model tracer ages are limited. $^4$He, $^{14}$C, $^{36}$Cl, $^{81}$Kr and U-Th-series analyses provide valuable information and are discussed in the chapters that follow. However, the value of model tracer ages is of greater value when two or more methodologies can be compared and contrasted in order to understand the relation between the generally simplified assumptions inherent in the tracer models and the more complex real system.

The geochemical groundwater tracers discussed in this book ($^4$He, $^{36}$Cl, $^{14}$C, $^{81}$Kr, U-Th-series ratios) have been used to calculate model tracer ages in multiple, groundwater basins with sufficient cross checks to ensure at least a minimal level of confidence in the results. In the following chapters, tracer-specific processes will be defined and discussed that contribute to the calculation of model tracer ages as well as how various processes affect the interpretation of the model tracer ages. We will refer to the "model tracer age" as a generality and in specific cases refer to, for example, the "model $^{14}$C age" or the "model $^4$He age" to differentiate which specific tracer has been used.

The case studies that we cover reinforce the principle that multiple sampling points with multiple tracers including temperature, water chemistry, hydraulic head, stable isotopes and well-bore tests will provide information that is generally necessary for adequately characterizing groundwater basins. These can then be interpreted with the aid of detailed reaction and transport models. Additional constraints can often be imposed on the interpretation by optimizing hydraulic models to best simulate the tracer transport data (Berger, 2008). Yet even for the best tracers and the simplest groundwater basins, the system of equations describing reaction and transport in the groundwater basin will be under-constrained. In order to solve the equations that describe flow in a groundwater basin, assumptions and simplifications must be made with regard to the structure of the basin, the heterogeneity of the basin properties and the evolution of the basin as a steady-state or unsteady-state flow system subject to temporally controlled uplift and erosion. Given this complexity, physics-based models (e.g., Torgersen and Ivey, 1985; Castro, et al, 2000) that include transport and mixing of groundwater as well as the source and sink functions that control the tracer distribution (Zhao et al, 1998; Bethke et al. 1999, 2000; Castro
et al. 1998ab; Castro and Goblet, 2003; Bethke and Johnson, 2008) are a great help in evaluating the actual controls on groundwater movement.

Flow in real groundwater systems is dependent on a typically complex spatial distribution of hydraulic properties. Actual data to constrain this distribution are generally sparse. The spatial distribution of hydraulic head is relatively insensitive to the distribution of hydraulic properties unless the materials of differing properties are arrayed in continuous layers of strongly contrasting values (Gomez-Hernandez and Gorelick, 1989). It is within this context that estimates of the groundwater age can provide significant constraints on the structure of the system. However, even given this additional information, real groundwater systems are always underconstrained with regard to the data requirements and the resulting models are always non-unique. To some extent this limitation can be overcome by employing geostatistically based multiple conditional simulations, but even this computationally intensive approach provides only an indication of the possible range of behavior of the system. It behooves groundwater scientists to maintain an appropriate degree of humility in the face of the complex natural systems they study.

REFERENCES

Berger, 2008?


