Simulation of groundwater age distributions

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Abstract. The objective of our work is to examine how to simulate the age of groundwater in such a way that it can be compared to actual measurements. We start by showing that the computation of kinematic age, the one obtained by tracking water along streamlines, is ill posed in heterogeneous aquifers. This, together with its inability to account for mixing processes, makes it inadequate for comparison with age measurements, which are the result of some averaging of the age distribution in the water sample (the type of averaging depends on the measurement procedure). Therefore, we go on to write the equations for the cumulative distribution function of residence time under transient flow conditions. This allows us to derive transient equations for the mean age, as well as for the higher-order moments of its distribution, which generalize previous results by others. These moments can be used for approximating age measurements, which need not be equal to the mean age of the water sample. Using both a synthetic and a real example, we show that mean age is an acceptable estimate of radiometric age measurements in many cases, including a second-order correction (variance of residence time distribution) always improves results. On the other hand, higher-order approximations converge slowly for old (compared to half-life) waters, to the point that third-order approximations often worsen the results.

1. Introduction

In a recent article, Goode [1996] presents an equation for the direct simulation of groundwater mean age. The solution of this equation yields the spatial distribution of the mean groundwater age and includes advection, diffusion, and dispersion processes. The objective of groundwater age simulations can be to obtain the spatial distribution of groundwater ages and/or information about flow and transport parameters by comparison between simulation and measurements (model calibration). Our objective is the latter. However, this comparison is not as simple as it might seem because water samples contain a mixture of waters of different ages and the way in which they are averaged in the measurement process needs not be identical to the mean age. This is further complicated by the diversity of measurement methods [Davis and Bentley, 1982] for example, using decays of radioisotopes which have entered the groundwater from contact with the atmosphere [Smith et al., 1976], consideration of certain products of radioactive disintegration to be at an age index [Badi et al., 1979], using stable isotopic relations for relating their spatial distribution to climatic changes [Nearing et al., 1979], and using disequilibrium between origin and product radioisotopes as an age index.

The traditional method for age simulation is based on computing the groundwater travel time from the recharge to the observation point using the effective velocity field [Davis and Bentley, 1982]. Ages thus computed are called kinematic ages in this work. This method allows the simulation of the age distribution, if mean historic Darcy velocities and porosity are known. Kinematic age considers only advection as a transport process, which is a limitation. Nevertheless, it is the approach used most often to validate new dating methods, as the ones described in the above paragraph. This prompted Walter [see Neuman and Nisbetts, 1984; p. 837] to state:

"The problem is that in many systems the geohydraulics of the system are in equilibrium with the geocosmology. And so it's not really right to try and validate the use of an environmental tracer by computing travel times computed from the geotechnical data with those computed from the hydraulic model. There's two different things, and the person using the isotope actually burns his/her case and it were case by case the use of a tracer when actually the tracer represents the reality and the isotope are just a transient artifact of recent history."

It is clear that more sophisticated methods are needed for environmental tracer dating of groundwater. This motivated the development of different models. Those were used often in the interpretation of tracer data [Malyarzinski and Zuber, 1982, 1985; Langan et al., 1982; Campina and Malina, 1985; Zuber, 1986]. However, these models still incorporate significant simplifications. For example, they usually neglect spatial variability of aquifer parameters. Moreover, many of them are solute-specific.

The motivation for this work is similar to that of Goode [1996], to avoid solute-specific modeling in the hope of taking advantage of diverse dating techniques for inverse modeling [Carreras and Neuman, 1986; Harvey and Garrett, 1995a; Medina and Carreras, 1996]. We start by revising the kinematic age concept. This leads us to the need for age distributions, for which we derive the equations under transient flow conditions, thus generalizing previous equations obtained under steady state regime. This generalization is carried out to the temporal
moments equation, derived under steady state by Honey and Glavich [1990b]. Moments of the age distributions can be used for approximating actual age measurements. The validity of such approximations is usually tested by means of numerical examples.

2. Kinematic Age

2.1. Definition and Computation

The oldest and most widely used method for computing water age is based on the advective model. Travel times are derived from Darcy's law combined with an expression of continuity [Davis and Rehfeld, 1982]. This requires establishing the mean isotropic hydraulic gradients, the hydraulic conductivities, and the effective porosities of the aquifer. Then the kinematic age, denoted \( a_k \), is given by

\[
a_k(x) = \frac{1}{n} \int_0^t \frac{ds}{q}
\]

where \( n \) is porosity, \( v \) is seepage and Darcy velocities, \( ds \) is the trajectory element, which is taken parallel to \( q \). Distance along the trajectory is defined by \( s \) with \( s \) representing the point at which water enters the aquifer. Our computation of (1) consists of the following steps [Varni et al., 1994]:

1. First, we solve the flow equation by the finite element method.
2. We then compute the velocity field using Darcy's law. Problems caused by discontinuities at element boundaries were overcome using the method of Cordes and Rehfeld [1982].
3. Finally, we calculate groundwater age at each node by integrating (1) along the stream line that starts at the node. Notice that this prevents us from having internal sinks and sources, which is indeed one of the limitations of the kinematic age concept.

In homogeneous media the kinematic age concept proved to be well posed [Varni et al., 1994; Glavich, 1996]. However, we are interested in exploring the problems generated when applying it to heterogeneous media.

2.2. Example

Kinematic ages are computed for a synthetic heterogeneous vertical section which consists of a medium with hydraulic conductivity of 1 m d\(^{-1}\) and five embedded layers with conductivities of 25, 46, 74, 134, and 43 m d\(^{-1}\) at zones numbered 2-6, respectively (Figure 1a). Boundary conditions are shown in the Figure 1b, a 10 mm yr\(^{-1}\) recharge was imposed at zone A, and a mixed boundary condition with a leakage coefficient of 10\(^{-4}\) m d\(^{-1}\) and external zero level was imposed at zone B. No flow boundary conditions are specified at the left, right, and bottom boundaries. The effective porosity is 0.1. The flow equation is solved for steady state conditions using the finite element code TRANSFLOW [Muzola et al., 1995].

Figures 1b, 1c, and 1d display the finite element mesh, computed flow net, and age distribution, respectively. Multiple flow paths (zones with water older than the surroundings) can be observed, especially downstream of the high conductivity layers. This problem is caused by interception on a discontinuous field [Varni et al., 1994].

In essence, the basic problem with Figure 1 is that the age field is discontinuous. In fact, it is evident that discrete age differences may appear between two close stream lines, one flowing through a very permeable lens and the other not. Therefore small variations in the measurement point location may cause large variations in age. That is, age computation is unstable with respect to the measurement point location. Moreover, age is undefined at stagnation points, where it tends to infinity (actually, to the age of the rock formation at most).

A problem is said to be well posed in the sense of Hadamard [1902] when a solution exists, and it is unique and stable. The above example shows that in heterogeneous media, kinematic ages may not exist and they may be unstable. Moreover, uniqueness may be questionable when mixing waters of differ-
cent ages, as in the case of recharge. In short, the concept of kinematic age is ill posed.

The need to account for dilution processes, such as dispersion and matrix diffusion, when comparing measured and computed ages, has been pointed out by many authors (e.g., Sturrock and Pratt, 1983; Blumberg and Cook, 1991; Matuszewski and Zuber, 1982, 1991). This, together with the weakness of the kinematic age concept, makes it clear that such a concept should not be used beyond qualitative assessments whenever the system is heterogeneous or dilution processes (e.g., recharge, matrix diffusion, dispersion, and sampling procedure) take place. In such cases it should not be used for direct comparison between age measurements and model outputs aimed at estimating model parameters. Rather, realistic assessments of age, which account for the possible errors in the determination of the age, should be carried out.

3. Age Distribution at a Point

3.1. Transient Flow

If a narrow unit-mass pulse of a conservative tracer is applied uniformly in the aquifer recharge zones and concentration is monitored at a point in the aquifer, the concentration breakthrough curve can be viewed as the travel time probability distribution [Jury and Roth, 1998]. This concept is analogous to that of residence time distribution defined for chemical reactors by Danckwerts [1953] and used in hydrology by a number of authors [see Geuze, 1996]. The travel time probability density function characterizes the distribution of possible travel times that a water molecule might experience in moving from the recharge zones to the measurement points. Usually, the distribution of travel times is computed under steady state flow conditions. In fact, we will do so in section 3.2. However, some insights may be gained by working under transient flow conditions. While the definition is based on a pulse input, it is more convenient to work with cumulative probability functions. Among the particles per unit mass of water located on point $x$ at time $t$, let $F(t, x)$ be the portion of these that have entered the aquifer after time $x$. Note that $t$ and $x$ are here used in a different sense. The physical time convention. They represent time elapsed since the time origin (which is arbitrary), and they grow forward in time. This is contrary to the geological time convention, which grows backward in time and which we will denote age. In fact, they can be related. For example, the age of a water molecule is precisely $t - 	au$. By definition, $P$ behaves as a conservative tracer. In fact, it equals the concentration of a tracer that started entering the aquifer at time $t$ with unit concentration. It can be computed with any conventional solute transport simulator using zero initial concentration and unit boundary concentration for times greater than $t$. Therefore $P$ is governed by

$$\frac{\partial P}{\partial t} = \nabla \cdot (\Phi \frac{\partial P}{\partial x}) + \frac{\partial F}{\partial x},$$

$$F(t, x) = 0 \quad x = 0, t > 0,$$

$$F(t, x) = H(t - \tau) \quad x \in \Gamma,$$

$$J_d - q \Gamma m = -q \phi m \quad x \in \Gamma,$$

where $\phi$, $m$, and $\tau$ are water density, aquifer porosity, and interflow/strike-slip terms, respectively; $J_d$ is the dispersive flux; $H$ is Heaviside's function; $F(t - \tau) = 1$ if $t > \tau$; otherwise, $H(t - \tau) = 0$; $\Gamma$ is a Dirichlet boundary, and $\Gamma$ is a boundary with prescribed mass fluxes. $\phi$ is the unit vector normal to $\Gamma$ and $F$ and $F$ are the distributions of water particles entering or leaving the aquifer through internal sinks/sources and prescribed mass flux boundaries, respectively. $\Phi$ and $\Phi$ equal $H(t - \tau)$ when water enters the aquifer ($-q \phi m > 0$) and equal 1 when water exits the aquifer ($-q \phi m < 0$).

Several remarks should be made regarding (2). First of all, density, porosity, water flux, sink/source terms, boundary conditions, and dispersion parameters may be time dependent.

This last issue may be important in geologically recent aquifers. One would expect that most shallow aquifers (<1000 m), being many millions of years old, would contain little water from the time the aquifer was formed. In fact, the real difficulties in simulating the age of groundwater in aquifers containing very old waters stem from climatic variations and changes in hydraulic properties and aquifer geometry, rather than from uncertainties about initial water. However, sedimentary aquifers of very recent origin may contain formation water, especially if low $K$ layers are included. In such cases, even if it can be assumed that aquifer sedimentation has taken a very short time, (2) would not be appropriate because it would say nothing about waters with $t < t_0$ ($t_0$ being the "aquifer initial time"). This problem can be approached in two ways. First, if one can assume that all the initial water is of age $t > t_0$ (i.e., depositional age of the aquifer), then

$$F(t, x = t_0, x) = 1$$

(3)

Otherwise, some distribution of ages should be known. Let it be $F(t, x)$. Then, for $t < t_0$, (2) has to be extended to account for the family of equations:

$$\frac{\partial P}{\partial t} = \nabla \cdot (\Phi \frac{\partial P}{\partial x}) + \frac{\partial F}{\partial x},$$

$$F(t, x) = F(t, x),$$

$$F(t, x) = 1 \quad x \in \Gamma,$$

$$J_d - q \phi m = -q \phi m \quad x \in \Gamma,$$

where it should be noticed that now the simulations start at time $t_0$ for all $t < t_0$, while (2) have to be used for $t > t_0$.

A final remark can be made regarding dilution mechanisms in (2) and (3). We have purposely left out matrix diffusion processes for the sake of simplicity. They can be included using any of the standard formulations for conservative solutes [Huggett and Gauthier, 1995; Sánchez-Vila and Camera, 1995]. It does significantly affect the tail of the age distribution and therefore
actual measurements. This issue will be further discussed in section 4.

Probability density functions (pdf) for recharge time (\( r \)) distributions are derived directly from the cumulative distribution functions:

\[
f(r, x, x) = \frac{d}{dr} F(r, x, x)
\]  

(5)

Notice that \( f_i \) is the pdf of the recharge times of the water molecules located in a neighborhood of \( x \) at time \( r \). However, as stated before, it represents a family of functions for varying \( r \). Hence \( f_i \) represents water that entered the aquifer at time \( r_i \), and \( f_r \) represents water that entered the aquifer at time \( r \). Therefore it is not the pdf of travel times \((t - r)\). A simple relationship between the two of them is only possible under steady state flow conditions, as discussed below.

### 3.2. Steady State Flow

The steady state flow case can be derived directly from the transient case (2). It is sufficient to notice that if all hydraulic parameters are time independent, then (2) only depends on \((t - r)\). Thus:

\[
F(t, r, x) = F(t - r, x)
\]  

(6)

Therefore one does not need to solve (2) for each \( r \), but a single solution suffices. Under these conditions it is possible to derive a partial differential equation for the mean age, as the first-order moment of \( f_i \), as shown by Goode [1994, 1996], Varni [1994], and Carrera et al. [1995]. In fact, direct application of the results of Harvey and Goncalves [1995] would allow one to obtain any higher-order moment. Section 3.3 is devoted to showing that this is also possible under transient flow conditions.

### 3.3. Mean Age and Higher-Order Moments

#### Under Transient Flow Conditions

The mean age is defined as the mean of the residence times \((t - r)\) of all water particles in the neighborhood of any point:

\[
a_i(t, x) = \int_0^\infty (t - r) f_i(t, r, x) dr
\]  

(7)

Higher-order moments of the residence time distributions are given by

\[
a_n(t, x) = \int_0^\infty (t - r)^n f_i(t, r, x) dr
\]  

(8)

In order to derive the equations for the moments of the age distributions it is sufficient to apply the \( n \)-th moment operator \( \int (t - r)^n d\tau \) to (2). The application is straightforward except for the time-derivative term, where one has to recall that

\[
\frac{d}{dr} \int_a b (t - r)^n \phi(t, r) dr = \int_a b (t - r)^n \frac{\partial \phi(t, r)}{\partial r} dr + \int_a \frac{\partial}{\partial r} \left( (t - r)^n \phi(t, r) \right) dr
\]  

(9)

Applying the first moment operator to (2) while using (9) for the time derivative term and recalling that \( a_n = 1 \) leads to the mean age equations:

\[
\frac{\partial a_i}{\partial t} = \nabla \cdot \left( \left[ a_i \phi_i \right] - \rho q_i \right) + \rho_i \rho - \rho \phi
\]  

(10a)

\[
a_i(0, x) = a_i
\]  

(10b)

\[
a_i(t, x) = 0 \quad x \in \Omega_i,
\]  

(10c)

\[
[a_i(t, x)] - \rho q_i \n = - q_i \rho, \quad x \in \Gamma_T
\]  

(10d)

where \( \rho_i \) is the age of water sinks and sources, which is equal to zero when water enters the aquifer \((r = 0)\) and is equal to \( a_i \) otherwise; \( a_i \) is the mean age at the initial time. This equation is comparable to those derived by Goode [1994, 1996], Varni [1994], and Carrera et al. [1995], all of them using mass balance considerations. It should also be noticed that it represents the transport of a conservative species in which all external inputs are zero. The only difference stems from the "aging" term, the last one in (10a), which expresses nothing but the fact that water ages one unit time per unit time. Hence modifying any transport code to accommodate age simulation simply needs to include this additional term.

Derivation of higher-order moments is analogous. Basicly, it consists of applying the \( n \)-th moment operator to (2). Using, again, equation (5) to solve for the time-derivative term leads to the equations for the \( n \)-th order moments of the age distribution:

\[
\frac{\partial a_n}{\partial t} = \nabla \cdot \left( \left[ a_i \phi_i \right] - \rho q_i a_n \right) + \rho_i \rho_n + n \rho \frac{\partial a_n}{\partial t}
\]  

(11a)

\[
a_n(0, x) = a_n
\]  

(11b)

\[
a_n(t, x) = 0 \quad x \in \Omega_i
\]  

(11c)

\[
[a_n(t, x)] - \rho q_i a_n = - q_i \rho_n, \quad x \in \Gamma_T
\]  

(11d)

where \( a_n \) is the \( n \)-th order moment of the age of water sinks and sources (normally zero for sources and \( a_i \) for sinks); \( a_n \) is the \( n \)-th order moments of the age distribution at the initial time.

The only difference between (10) and (11) is the aging term, which is equal to \( \rho \phi \) for the mean age equation and equal to \( \rho \phi a_n \) for the \( n \)-th moment equation (as the former is the particular case of the latter for \( n = 1 \)). Therefore modifying any transport code to simulate \( a_n \) simply requires adding this term. It should be noted that this is the modification derived by Harvey and Goncalves [1995] for steady state flow and concentration distributions. Therefore (11) can be viewed as a generalization of the work by these authors for the case of transient flow and residence time distributions.

In practice, it is more useful to compute moments with respect to the mean time with respect to the origin \( \omega_n \) in (11). Deriving the equations of the former is not conceptually difficult but is complex. We have derived those equations and show them in the appendix. However, because of their complexity, we prefer to work with (11) and derive the moments with respect to the mean from those with respect to the origin, which is trivial.
3.4. Radiometric Age

We denote as radiometric the age calculated according to the radioactive decay equation

$$a_r = \frac{1}{\lambda} \ln \left( \frac{c_r}{c} \right)$$  \hspace{1cm} (12)

where $\lambda$ is the radioactive decay constant and $c$ and $c_r$ are the measured and initial isotope concentrations, respectively. Actually, if we view each sample as containing a distribution of residence times, the real concentration would be

$$c(t) = \int c(x) f(x) dx$$  \hspace{1cm} (13)

in the case of steady state flow and constant input concentration it would be

$$a_r(x) = \frac{1}{\lambda} \ln \left( \int_{x_0}^{x} e^{-\lambda t} f(x) dx \right)$$  \hspace{1cm} (14)

where $t = r - t_r$ is the residence time and $f(x)$ is computed by means of (2) and (3).

Isotopic data can be interpreted using (12), which assumes that groundwater obeys the piston flow model or that dispersion is very small. The age distribution at a point, assumed unimodal, can vary between the delta distribution, corresponding to piston flow, and the exponential distribution (Eriksson, 1950), that assumes perfect mixing in the aquifer. The only case in which the radiometric age equals the mean age is when the piston flow model can be applied, that is, when the sample is not the consequence of a waters mixture (Taylor, 1960). In general, the actual age distribution is affected by many factors (heterogeneity and dilution mechanisms), so that it does not equal the piston flow distribution. Hence the mean age is different from the radiometric age. However, if the age distribution is known, the mean and radiometric ages can be related.

Starting from the radiometric age equation (14) and expanding $e^{-\lambda t}$ in Taylor series around $a_r$ (mean age) leads to

$$a_r = \frac{1}{\lambda} \ln \left( \sum_{n=0}^{\infty} \frac{(-\lambda a_r)^n}{n!} \right)$$  \hspace{1cm} (15)

$$a_r = a_r = \frac{1}{\lambda} \ln \left( 1 + \frac{a_r}{\lambda} \right)$$  \hspace{1cm} (16)

where $a_r$ are the nth order moments with respect to the mean ($m_0 = 1, m_1 = 0$, and $m_n = a_r^n$). This series is alternating and converges, provided that $a_r$ does not grow faster than $n!$. In fact, this type of series tends to converge very fast. Moreover, the error caused by truncating the summation is smaller than the first neglected summation. This prompts us to neglect terms of order higher than 2, which leads to

$$a_r = a_m = \frac{1}{\lambda} \ln \left( 1 + \frac{a_r}{\lambda} \right)$$  \hspace{1cm} (17)

where $a_1$ can be computed from (16) and $a_r = a_1 - a_0$, where $a_0$ is obtained from (11) with $n = 2$. This expression establishes the approximate relationship between radiometric and mean groundwater ages, for both resident- or flux-averaged ages. Since dispersion of the residence time distribution grows more or less proportionally to the mean residence time, one should anticipate problems whenever $a_1$ is large compared to $a_0$. This is examined in section 4.

4. Application Example

The example of section 2.2 is now used to compare radiometric (assuming they are measured with $^{14}C$) and mean ages. First, mean ages are computed using TRANSN-11 (Meadow et al., 1995) with longitudinal and transversal dispersivities of 25 and 10 m, respectively. They are shown in Figure 2. Kinematic age problems have been overcome. The effect of mixing due to dispersion causes a gentle age skew distribution, which nonetheless reproduces the global trends of Figure 1d.

Radiometric age will now be compared with the approximations obtained from (16) up to the second- and third-order moments, respectively. We start by showing the age pdf at three points (Figure 3a). These distributions show that a good deal of mixing is taking place between adjacent flow paths. Yet one can still observe several modes, which suggests that information about each path is not totally lost by dilution. Also shown in Figure 3a are the kinematic ages. It is worth noting that they can fall anywhere within the age pdf, which makes them somewhat erratic.

Knowing the pdf, we can easily compute not only the moments of the age distribution but also any type of weighted average. We have done so, first, for verification purposes, and found that the moments computed using up to fourth-order moments (10) and (11) are indeed equal to those derived from the pdf. Second, we have computed radiometric ages using the integral expression (equation 13) and truncating the series in (16) both at the second- and third-order moments, the former leading to (17). Results are summarized in Figure 4 not only for the points of Figure 3b but for all points identified in Figure 1a.

The analysis of Figure 4 allows us to summarize some of the discussions of sections 2 and 3. First, mean age is consistently
larger than the radiometric age, a consequence of the skewness of the age pdf coupled with the fact that the radiometric age (equation (14)) gives more weight to small ages. Second, the second-order approximation (equation (17)) leads to some improvement, and in most cases the true radiometric ages falls between the mean and this approximation. Third, the third-order approximation only leads to improvements for very young waters. In fact, this approximation cannot be used for old waters because the truncated series (in parentheses in (16)) becomes negative. Finally, the kinematic ages display a some-
what erratic behavior. They can take up any value within the age pdf. In fact, in the absence of matrix diffusion this pdf can be viewed as the distribution of kinematic ages and the measurement location. This interpretation helps in explaining why kinematic age is comparable to either the mean or the radiometric age in many points (those in which the kinematic age falls within the bulk of the pdf, such as 1.5 in Figure 3a). This interpretation also helps in explaining why kinematic age is similar to the mean age in all but three points (the pdf are so skewed that the probability of falling above the mean is small). However, kinematic age falls far from either the mean or the radiometric ages in 7 out of 17 points of Figure 3 (4-12 in Figure 3a is one of them).

This example can also be used to study the effect of matrix diffusion. For this purpose we simulated the same example with diffusivity of $10^{-12}$ m$^2$ s$^{-1}$ and planar matrix (thickness 1 m and porosity 0.04). The porosity of the mobile zone was 0.8, so that total porosity was kept equal to that of the above example. The resulting pdf are shown in Figure 3b. By comparing them with those of the mobile zones (Figure 3a) it is clear that reduction of the mobile porosity causes an earlier breakthrough, while diffusion in the matrix leads to a longer tail (in Figure 3b this latter effect can only be seen for point 1.5). The net effect is that the mean age remains unaltered, as predicted by Harvey and Gocens (1995b), an observation which we have verified both from the pdf and by solving the mean age equations (10), both with and without matrix diffusion. Since matrix diffusion causes an increase in the variance and skewness of the residence time distribution, radiometric ages (which give large weight to small ages), will be smaller with than without matrix diffusion. In our case the difference is small (Figure 5) because matrix porosity was small compared to mobile porosity. In general, matrix porosity is much bigger than mobile porosity, so that the effect of matrix diffusion on radiometric ages will be much more marked than is implied in Figure 5. This issue is discussed in detail by Maleczewski and Zuber (1993) and Zuber and Metzka (1994).

5. Field Example
This example is aimed at analyzing the applicability of the equations derived in section 5 under realistic conditions. Data come from a low-permeability mountainide located at El Cabrito in southern Spain (Figure 6). The site consists of quartaries (to the west) and gneisses (to the east). The gneisses are cut by two thin subvertical metazoic layers (Figure 7). These layers are subparallel to the equipotential lines. Despite this, they drain a large portion of the recharge to the north because they contain highly transmissive fractures (Departamento de Ingeniería de Terreno-Departamento de Matemática Aplicada y Matemáticas Informáticas, Universidad Politécnica de Madrid (DT-DMAT), 1990). Figure 7).

Issues requiring clariﬁcation include whether the metamotorses indeed act as drains, what their active depth is, and what total depth should be adopted for the model. A vertical cross section has been built perpendicular to the equipotential lines (that is why it is curved and why it displays an angular point at Los Morales bridge, which is efﬁcient). Fracture density is quite high, and a porous medium approach was adopted.

5.1. Flow Models
Six models have been considered. They result from combining two possibilities for aquifer thickness (thin and thick) and three for representing the role of metazoic layers (fully penetrating, draining only through half of the thickness, and no draining), as shown in Figure 7. All models consist of three forma-
ovals (1, Albarrana quartzite; 2, El Cabril gneisses; and 3, Albarrica gneisses) that are treated as homogeneous and isotropic. Recharge rates have also been taken as homogeneous for each formation and equal to 34.5, 33.5, and 11.2 m yr⁻¹, respectively. Heads are prescribed at the intersections between the brooks and cross sections (heads of 530, 390, and 247 m at the three intersections shown in Figure 7).

The six models were calibrated against five head measurements taken close to the sections and averaged over time to represent steady state heads. Results of the calibration are shown in Table 1, which shows that only the models with metamorphoses lead to good agreement between measured and computed heads. While each result is consistent with the conceptual model of DFT-DNAM [1998], they do not allow us to discriminate among the remaining four models (those including metamorphoses).

5.2. Age Simulations

The task of discriminating among these four models was left to isotopic data, which are available at three piezometers, one of them at two depths (Table 2). Tritium data were interpreted using rainfall tritium data from Barcelona, available since 1945, and two extreme models: piston flow model, which assumes no mixing, and exponential model, which assumes total mixing. Resulting ages are shown in Table 2. It should be noticed here that because of bomb effect, neither estimate is comparable to radiometric ages but both radiometric and mean ages should belong to the interval spanned by the two estimates. On the other hand, ¹⁴C data were interpreted using the conventional radioactive decay equations, both with and without a ¹⁴C correction for isotopic dilution.

Groundwater ages were first simulated following the same

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<th>Observed Heads</th>
<th>Computed Heads</th>
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<td></td>
<td>a°</td>
<td>b°</td>
</tr>
<tr>
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<tr>
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<tr>
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</tr>
<tr>
<td>S-235</td>
<td>288.6</td>
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</table>

Footnotes:
1. The a and d models do not include metamorphoses, the b and e models include only the upper half of metamorphoses, and the c and f models include fully penetrating metamorphoses. The a, b, and c models assume a thin system, and the d, e, and f models assume a deep system.
2. Models a, b, and c represent the thin domain (see Figure 7a) with no, partial, and full metamorphoses penetration, respectively.
3. Models d, e, and f represent the thick domain (see Figure 7b) with no, partial, and full metamorphoses penetration, respectively.
methodology as in section 4 and using the four flow models with longitudinal and transversal dispersivities of 10 and 5 m, respectively, and a 0.05 porosity, which had been derived from two field rectangular flow tracer tests. The computed ages are much smaller than those of Table 2. We attributed such differences to the retardation effect of matrix diffusion, which would affect age computations but would have a negligible effect on short-term tracer tests. Hence we repeated the simulations but assumed matrix diffusion to occur throughout the domain. The matrix was treated as 2 m thick slabs of 0.05 porosity and a diffusion coefficient of \( 5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \) (Carneiro et al. [1999] show that the solution should not be overly sensitive to matrix shape and that it depends on \( D_m \)).

Sensitivity to this parameter will be analyzed later. Results are summarized in Table 3 which contains the mean age (\( \langle \alpha \rangle \)) obtained by solving (16), the exact radiometric age computed from the residence times pdf (\( \langle \alpha_r \rangle \)), and the second-order approximation (\( \langle \alpha_{approx} \rangle \)). Figure 8 displays the ages compared with varying diffusion coefficients. Reducing matrix diffusion brings computed radionic age closer to the one obtained with only mobile water.

None of the models reproduces well the measured head data. Yet, model f performs better (for less poorly) than the others. SH-5 data are reproduced by all models, although the tritium data probably favor models d and f, which lead to the youngest waters. No model produces ages within the \( 1^\sigma \) interval, but model f is quite close. Data from upper interval (b) of S-223 are not reproduced by any model, but model e is the closest, followed by model f. On the other hand, model f is the only one which clearly misses the \( 1^\sigma \) age interval for S-223 b.

In summary, model f is the only one with fair results. These could probably be improved by modifying some of the assumptions. For example, computed ages correspond to the midpoint of the sampling interval, and it is likely that most water in S-223 b is formed from near the surface, which was not reproduced by our models. We could have introduced other modifications to improve the fit between measured and computed data. However, that would not have modified the general conclusions from this example. That is, isotopic data have been used for model discrimination without the need for solution-specific simulations.

### Summary and Conclusions

We have shown that kinematic age computations in heterogeneous media can be unstable (small perturbations in the point coordinates can lead to very large changes in computed age). This, together with the need to account for diffusion processes, restricts its use to qualitative assessments on homogeneous media. This motivates the derivation of age equations. We have obtained equations for mean age and for the moments of the groundwater age distribution at a point. Our equations are valid under steady state and transient flow conditions, which is a generalization of previous results.

The distribution of groundwater residence times is quite independent and can be used for reproducing any groundwater dating procedure on the basis of conservative solutes. In general, under transient flow conditions it is very tedious to compute this distribution. However, groundwater age measurements can also be reproduced using its moments. We have derived the equations for the moments of the age distribution. These can be easily computed from minor modifications on any standard advection transport simulator. We have used these models to compute radiometric ages (those obtained from radioactive decays). It would seem then that the road is paved for using ages as quantitative data for model calibration, in the same fashion as heads. Yet the issue is not as clear cut. In fact, aside from the usual conceptual difficulties that affect any

### Table 3. Measured Interval (from Table 2), Radiometric (1^\sigma), and Approximate Radiometric Ages for the Models

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Measured Interval</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>SH-5</td>
<td>0-1200</td>
<td>0.67</td>
<td>0.42</td>
<td>0.45</td>
<td>0.44</td>
</tr>
<tr>
<td>S-200</td>
<td>200-2400</td>
<td>0.51</td>
<td>0.29</td>
<td>0.34</td>
<td>0.32</td>
</tr>
<tr>
<td>S-223b</td>
<td>200-5800</td>
<td>0.80</td>
<td>0.51</td>
<td>0.56</td>
<td>0.54</td>
</tr>
<tr>
<td>S-223 ti</td>
<td>2100-5800</td>
<td>0.66</td>
<td>0.40</td>
<td>0.45</td>
<td>0.44</td>
</tr>
</tbody>
</table>

The abbreviations are as follows: b, thin, meteoric on upper half; c, thin, with fully penetrating meteoric; d, deep, with fully penetrating meteoric; f, the computed mean age; \( \alpha_{approx} \), the computed radiometric age and \( \alpha_{approx} \), the second order approximation to radiometric age.
model construction process, age computations are very sensitive to matrix diffusion, and measurements may be open to several interpretations. In our real example these two effects are so marked that we have given up a formal (even automatic) quantitative calibration and have instead settled with using age data for qualitative model discriminations (by means a negligible one).

Our emphasis on solute independent simulations of groundwater age was partly motivated by the objective of using age measurements, possibly obtained with a large number of techniques, for hard calibration (actually for automatic calibration). Our findings suggest that such an approach may be quite difficult. Second, one needs at least two solute transport simulations (mean and variance of the age distribution) and even so, the result is just an approximation (see the discussion by Harvey and Gorkoff [1990] on the derivation of the whole pdf from its moments). Finally, tritium and \(^{14}C\) are the only dating techniques usually available; in which case, two solute-specific runs would suffice to obtain exact values by comparison with measurements. This, together with the fact that solute-specific simulations allow for incorporating solute-specific processes, suggests that calibration may be best performed by explicit treatment of every solute contributing dating information. Direct simulation of groundwater ages would then be useful for preliminary calibrations.

Appendix: Moments With Respect to the Mean

Derivation of the equations governing the moments with respect to the mean (\(\mu_s\)) is analogous to that of the moments with respect to the origin (\(\mu_o\)). In essence, one has to apply the following operator,

\[
M_t = \int_0^t (t - \tau - \beta \tau^2) \hat{D}^* d\tau
\]

\[\hat{D}^* = \int \left( \frac{\partial}{\partial t} \right) d\tau \]

(2)

The fact that \(\alpha_s\) is a function of space complicates the derivation a little bit, but it suffices to use relationships analogous to (9). The time derivative term requires

\[
\int_0^t \left[ \int (t - \tau - \beta \tau^2) \frac{\partial}{\partial \tau} \hat{D}^* d\tau \right] d\tau
\]

where the last term is what results from applying operator (A1) to the time derivative term in (2a). Analogously, the term arising from applying (A1) to the advection term in (2a) can be obtained from

\[
\int_0^t \left[ \int (t - \tau - \beta \tau^2) \frac{\partial}{\partial \tau} \hat{D}^* d\tau \right] d\tau = 0
\]

(3)

The first application of the "df" operator to \(\mu_s\) leads to

\[
\int_0^t \left[ \int (t - \tau - \beta \tau^2) \frac{\partial}{\partial \tau} \hat{D}^* d\tau \right] d\tau = \mu_s + \int \int \left[ \int (t - \tau - \beta \tau^2) \frac{\partial}{\partial \tau} \hat{D}^* d\tau \right] d\tau
\]

(4)

After some algebraic manipulations the second application of \(\hat{D}^*\) leads to

\[
\int_0^t \left[ \int (t - \tau - \beta \tau^2) \frac{\partial}{\partial \tau} \hat{D}^* d\tau \right] d\tau = \mu_s + \frac{\int \int \left[ \int (t - \tau - \beta \tau^2) \frac{\partial}{\partial \tau} \hat{D}^* d\tau \right] d\tau}{\int \int \left[ \int (t - \tau - \beta \tau^2) \frac{\partial}{\partial \tau} \hat{D}^* d\tau \right] d\tau}
\]

(5)

The equation we are seeking is obtained by applying (A1) to (2), using the last term of (A2) for substituting the storage term, that of (A3) for the advective term, and that of (A5) for the dispersive term. Using the mean age equation (equation (10)) and the flow equation to eliminate some of the resulting terms leads to the partial differential equation (PDE) of the \(n\)th moment with respect to the mean:

\[
\frac{\partial}{\partial \tau} \left( \rho \mu_s \hat{D}^* \right) + \frac{\partial}{\partial \tau} \left( \rho \mu_s \hat{D}^* \right) - \mu_s \frac{\partial}{\partial \tau} \hat{D}^* = -\int \int \left[ \int (t - \tau - \beta \tau^2) \frac{\partial}{\partial \tau} \hat{D}^* d\tau \right] d\tau
\]

\[\int \int \left[ \int (t - \tau - \beta \tau^2) \frac{\partial}{\partial \tau} \hat{D}^* d\tau \right] d\tau
\]

(6)

where \(\sigma_s\) equals \(\mu_s\) for discharge zones (\(r < 0\)) and equals \(\sigma_s\) \((\sigma_s + r) \sigma_s - (r + 1) \sigma_s - (r - 1) \sigma_s)\) for recharge zones. The same procedure, only simpler, is followed for boundary and initial conditions, which are derived by applying operator (A1) to (2b) - (2d).

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