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Dynamical modelling of concentration–age–discharge in watersheds

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Abstract:

There is now a wide literature on the use of tracer age and transit time distributions to diagnose transport in environmental systems. Theories have been proposed using idealized tracer age modelling for ocean ventilation, atmospheric circulation, soil, stream and groundwater flow. Most approaches assume a steady flow regime and stationarity in the concentration (tracer) distribution function for age, although recent work shows that this is not a necessary assumption. In this paper, dynamic model for flow, concentration, and age in volume-averaged and a spatially distributed watershed system are derived in terms of the moments of the underlying distribution function for tracer age, time, and position. Several theoretical and practical issues are presented: (1) The low-order moments of the age distribution function are sufficient to construct a dynamical system for the mean age and concentration under steady or transient flow conditions. (2) Solutions to the coupled system of equations for flow, concentration and age show that 'age' of solutes stored within the watershed or leaving the watershed is a dynamic process which depends on flow variations as well as the solute or tracer dynamics. (3) Intermittency of wetting and drying cycles leads to an apparent increase in the tracer age in proportional to the duration of the 'dry' phase. (4) The question of how mobile/immobile flow may affect the age of solutes is examined by including a low permeable, passive store that relaxes the well-mixed assumption. (5). A spatially distributed advective and dispersive transport solution for age evolution over a simple 1-D hillslope is developed to demonstrate the age theory for a distributed source of water and tracer, and the solution is shown to have very similar input–output behaviour when compared to the volume-average model for comparable parameters. Copyright © 2010 John Wiley & Sons, Ltd.

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INTRODUCTION

The concept of 'age' in terrestrial watersheds and river basins has long been a useful quantity for the analysis of process timescales (Phillip, 1995) and resource assessment (Allison and Holmes, 1973), and recent reviews of the modelling and experimental strategies have greatly organized our approach to the problem of age of waters (IHP-V, 2001; Kazemi *et al.*, 2006; Brooks *et al.*, 2010). Many authors have noted that the interpretation of 'age' of waters is complicated by the fact that age depends on the fluid path (Botter *et al.*, 2008; Darracq *et al.*, 2010), physical and chemical interactions along the path (Destouni and Graham, 1995; Fiori and Russo, 2008), and the forcing or watershed inputs (Maloszewski and Zuber, 1982).

In this paper equations for the age of solutes in subsurface flow in watersheds governed by transient flow dynamics are investigated. The theory is based on the early work of Nauman (1969), Eriksson (1971), Bolin and Rodhe (1973), Goode (1996) for groundwater, and the recent work for transient systems of Delhez *et al.* (1999) and Gourgue *et al.* (2006). This paper shows that the coupled dynamical system for transient flow, concentration and age can be derived without assuming the particular form of the age distribution function. Several solutions are presented that illustrate the theory and shed some light on the questions of 'old water', such as the role of mobile–immobile tracer flow, the implications of constant, intermittent and random flow and tracer inputs, and the role of advection–dispersion on water 'age' at the hillslope scale.

THE CONCENTRATION–AGE SYSTEM

Solute 'age' is an extensive property which is defined here as the elapsed time since the solute or tracer of interest entered the system, and that the tracer or solute in question has the usual properties of a neutrally buoyant fluid particle (Bolin and Rodhe, 1973). For the watershed, the age might be defined as the time since the tracer entered the soil surface as precipitation. Or in the case of groundwater, the time since the solute entered the aquifer. In general, 'age' is a function of space and time $A(x, t)$ and depends on the particular transport processes, physical and chemical interactions, the boundaries and initial conditions of the watershed. In 1972 Rotenberg proposed a theory for age-dependent biological species that is relevant here. Following Rotenberg's development, we define a joint age–time concentration distribution function $c(\boldsymbol{x}, t, \tau)$, position vector $\boldsymbol{x}$, which describes the

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number of dissolved particles that exist within a specified sub-volume in the time interval $\{t, t + \mathrm{d}t\}$ and the age interval $\{\tau, \tau + \mathrm{d}\tau\}$. In general, the particular form of $c(\boldsymbol{x}, t, \tau)$ would be required to develop information on the joint age–time characteristics of the system. However, as has been shown by Nauman (1969), Rotenberg (1972), and more recently by Delhez *et al.* (1999), it is straightforward to examine moments of $c(\boldsymbol{x}, t, \tau)$ which generally are more accessible for analysis. We assume that the joint age–time distribution is from a population of particles in any sub-volume that is sufficiently large that a continuous distribution exists, and that the time and age correlation of particles in the volume is small relative to other timescales of the system (e.g. statistical independence). From the usual rules of probability, the nth moment of $c(\boldsymbol{x}, t, \tau)$ with respect to τ is written as

$$\mu_n(x, t) = \int_0^\infty \tau^n c(x, \tau, t)\mathrm{d}\tau \tag{1}$$

The tracer concentration $C(x, t)$ for one dimensional flow in x is given by the zeroth moment:

$$C(x, t) = \int_0^\infty c(x, \tau, t)\mathrm{d}\tau \tag{2}$$

Now following Delhez *et al.* (1999) the mean age $A(x, t)$ of our tracer is conveniently defined as the ratio of the first and zeroth moments:

$$A(x, t) = \frac{\int_0^\infty \tau c(x, \tau, t)\mathrm{d}\tau}{\int_0^\infty c(x, \tau, t)\mathrm{d}t} = \frac{\alpha(x, \tau)}{C(x, \tau)} \tag{3}$$

where $\alpha(x, t)$, the first moment of Equation (1), is referred to as the age–concentration function and the denominator is the tracer concentration $C(x, t)$ or zeroth moment. From Equation (3) we see that the mean age $A(x, t)$ is an explicit function of position and time. The purpose of this representation, as we shall see, is to put the mean age in terms of moments of the tracer distribution function $c(x, t, \tau)$ which is developed next for general transport.

Assuming the tracer distribution function is subject to the processes of solute transport and reaction, Rotenberg (1972) and later Delhez *et al.* (1999) show that $c(x, t, \tau)$ satisfies a conservation equation in terms of time, age and position:

$$\frac{\partial c}{\partial t} + \frac{\partial c}{\partial \tau} = \Gamma_c - L(c) \tag{4}$$

where the left-hand represents the total derivative for particles that are allowed to age, $L(c)$ is a general operator for transport (advection, diffusion and dispersion or bulk transport) and the term Γ_c represents sources and sinks. Figure 1 shows the particle control volume within our conceptual watershed. The importance of Equation (4) is that even if the distribution function $c(x, t, \tau)$ is not known explicitly, it provides a means of forming transport equations for the individual moments of the process. The necessary properties of Equation (4) are: $c(x, t, \tau)$ is a continuous density for the time and age distribution of particles in any sub-volume of the system; that the time correlation among the particles in the sub-volume is small relative to other timescales of the system and that $c(x, t, \tau)$ can be approximately described by its first few moments. To calculate the moments for age, we multiply Equation (4) by τ^n and integrate over τ:

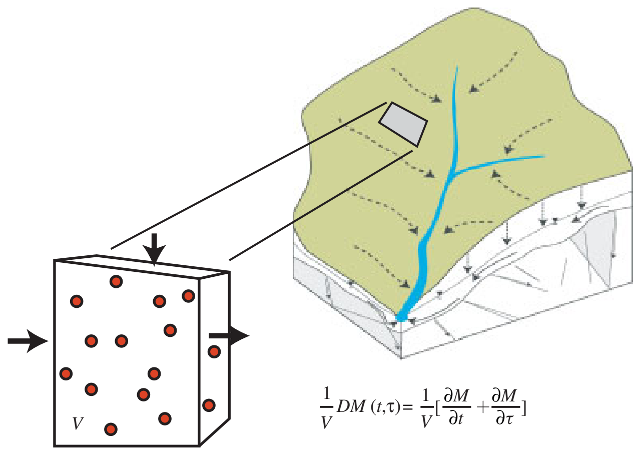

Figure 1. A control volume within the watershed showing the hypothetical distribution of particles of mass M that are allowed to evolve in time and age. $\mathrm{d}M(t,\tau)$ is the total derivative for tracer mass with respect to age and time

$$\int_0^\infty \tau^n \frac{\partial c}{\partial t}\mathrm{d}\tau + \int_0^\infty \tau^n \frac{\partial c}{\partial \tau}\mathrm{d}\tau = \int_0^\infty \tau^n [\Gamma_c - L(c)]\mathrm{d}\tau \tag{5}$$

which yields, after some manipulation, a general equation for the tracer moments:

$$\frac{\partial \mu_n}{\partial t} = n\mu_{n-1} + \Gamma_{\mu_n} - L(\mu_n) \tag{6}$$

The term $n\mu_{n-1}$ is found from integration by parts for the second term on the left-hand side of Equation (6), and making the assumption that the moments of the distribution function for concentration and age have the property (Delhez *et al.*, 1999)

$$\lim_{\tau\to 0}\tau^n c(x, \tau, t) = \lim_{\tau\to\infty}\tau^n c(x, \tau, t) = 0 \tag{7}$$

Evaluating Equation (6) for moments $n = \{0, 1\}$ yields

$$n = 0 \qquad \frac{\partial C}{\partial t} = \Gamma_c - L_C \tag{8}$$

$$n = 1 \qquad \frac{\partial \alpha}{\partial t} = C + \Gamma_{\alpha_1} - L(\alpha) \tag{9}$$

$$A(x, t) = \frac{\int_0^\infty \tau c(x, t, \tau)d\tau}{\int_0^\infty c(x, t, \tau)d\tau} = \frac{\alpha(x, t)}{C(x, t)} \tag{10}$$

Note that Equation (8) is the transport equation for the tracer concentration $C(x, t)$ and Equation (9) represents transport of age concentration $\alpha(x, t)$ which are related by $A(x, t) = \alpha(x, t)/C(x, t)$. Together, Equations (8)–(10) form a coupled system of partial differential equations for concentration and age. Boundary and initial conditions will depend on the particular transport assumed in the model. One implication of the system above is that the mean age can be directly determined using the same transport and reaction operator $L(\alpha)$ as the concentration equation (8). In the following sections, we examine a range of solutions for flow and tracer transport applicable to small watershed settings similar to models developed by Duffy and Cusumano (1998) and Duffy and Lee (1992).

CONCENTRATION–AGE–DISCHARGE FOR A VOLUME-AVERAGED SYSTEM

An elementary model of an upland watershed assumes that the fluid reservoir (e.g. the watershed) has fluid storage volume $V(t)$, input volumetric flow rate $Q_i(t)$ and output flux $Q(t)$. The flow through the reservoir satisfies a balance equation:

$$\frac{dV}{dt} = Q_i - Q \tag{11}$$

where the outflow is some function of the storage $Q = Q(V)$ defined later. The tracer concentration for the input $C_i(t)$ and the output concentration $C(t)$ have the material balance

$$\frac{d(VC)}{dt} = Q_i C_i - QC + V\Gamma_c \tag{12}$$

where Γ_c is an internal source or sink of the tracer including any physical or chemical reactions. Equations (11) and (12) can be simplified by expanding Equation (12) and combining with Equation (11) to yield

$$\begin{aligned} \frac{dV}{dt} &= Q_i - Q \\ \frac{dC}{dt} &= \frac{Q_i}{V}(C_i - C) + \Gamma_c \end{aligned} \tag{13}$$

If we assume that our tracer has the concentration distribution function $c(t, \tau)$ for time and age, then following the previous development we can immediately write down our dynamical system to include transient flow and tracer age:

$$\begin{aligned} \frac{dV}{dt} &= Q_i - Q \\ \frac{dC}{dt} &= \frac{Q_i}{V}(C_i - C) + \Gamma_c \\ \frac{d\alpha}{dt} &= C - \frac{Q_i}{V}\alpha + \Gamma_\alpha \\ A(t) &= \alpha(t)/C(t) \end{aligned} \tag{14}$$

where it is assumed that $\alpha_i(t) = A_i(t) = 0$, or the tracer input is specified to be of zero age as it enters the system. The zero-age input is of course an arbitrary assumption for the purpose of setting a base condition. The initial conditions for age concentration and age, $\alpha(0) = A(0) = 0$, can also be set to zero but again this is arbitrary. The flow–concentration–age dynamical system (14) is a stable, nonlinear system with the exception of the singularity at $V(t) \to 0$. This nonphysical situation is avoided by adding a small constant to $V(t)$ which assures that $\lim_{V \to 0} \frac{Q(t)}{V(t)} = \text{finite}$. The system (14) represents a fully coupled model of the tracer mixing process with the addition of the equation for the scalar $\alpha(t)$, the age concentration, and the auxiliary equation for age $A(t)$. Solutions to the system (14) follow.

CLOSED-FORM SOLUTION FOR STEADY FLOW

The system (14) admits a closed-form solution for steady flow conditions ($Q_i = Q$), constant input (C_o) and initial conditions (C_i):

$$\begin{aligned} C(t) &= C_i e^{-kt} + C_o(1 - e^{-kt}) \\ \alpha(t) &= k^{-1}C_o(1 - e^{-kt}) + tC_i e^{-kt} - tC_o e^{-kt} \\ A(t) &= \frac{\alpha(t)}{C(t)} = \frac{k^{-1}C_o(1 - e^{-kt}) + t(C_i - C_o)e^{-kt}}{C_i e^{-kt} + C_o(1 - e^{-kt})} \end{aligned} \tag{15}$$

The steady-state solution $A(t \to \infty) = A^*$ shows that the age depends on C_o:

$$\begin{aligned} C_o &\neq 0, \qquad A^*(\infty) = k^{-1} = V/Q \\ C_o &= 0, \qquad A(\infty) = t \end{aligned} \tag{16}$$

As expected, for large time, the age of the solute tends to a constant value defined by the steady-state age or steady-state residence time (V/Q) of the system. While for $C_o = 0$, the age of the solute grows in proportional to time, a simple clock. The implications of these two solutions will be discussed further in the next section. A^* will also serve as a comparison for other solutions developed in the paper.

NUMERICAL SOLUTIONS FOR TRANSIENT FLOW AND TRACER INPUTS

Next, we examine numerical solutions for the system (14) for unsteady flow with step, pulse and random inputs for the tracer and flow with particular attention paid to the tracer mean age $A(t)$. In Figure 2, the solution is given for a unit step input $Q_i = C_i = 1$ (t > 0), with $\Gamma_{c,\alpha} = 0$ and initial conditions $Q(0) = C(0) = A(0) = 0$. The figure shows that age $A(t)$ for constant inputs evolves to the expected result, the mean residence time or the steady-state age. As the age of the tracer tends to a constant value, the 'ageing process' stops as the flow and the tracer approach steady state. For this case and subsequent cases, the volume–discharge relation is assumed to have the form:

$$Q = a(V - V_0)^b \tag{17}$$

with the parameters arbitrarily assigned to be $V_0 = 3$, $a = 5$ and $b = 1$, which were found to be convenient

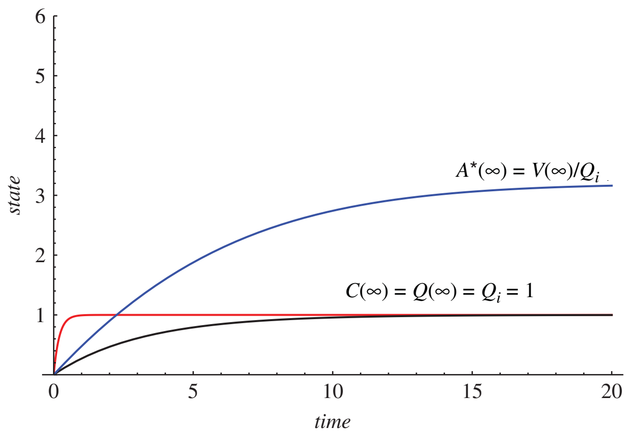

Figure 2. Numerical solution to the system (14) for unit step inputs Q_i and C_i and zero-state initial conditions. Note that $A^*(\infty) = V(\infty)/Q_i$ is the steady-state age or residence time. $A^*(\infty)$ with constant input is used as a reference for later results

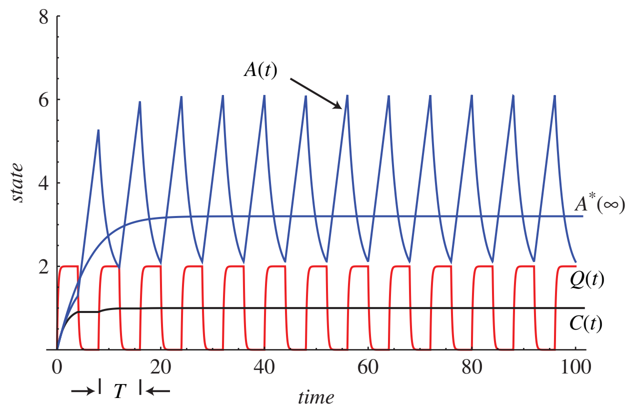

Figure 4. The evolution of solute age $A(t)$ for an intermittent pulse input of Q_i and C_i. Note that the intermittency increases the age of the tracer over the steady state for constant inputs $A^*(\infty)$ (Figure 2). Also note that the concentration $C(t)$ is almost unaffected by the intermittent inputs as compared to the age in this example, suggesting the importance of transient flow on tracer ages

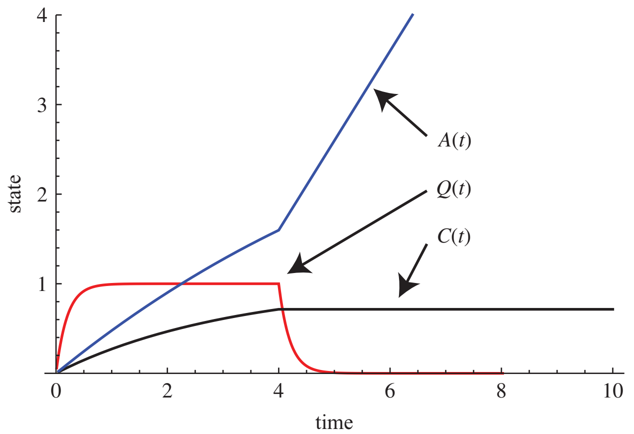

Figure 3. The evolution of solute age $A(t)$ for a finite duration pulse input for Q_i and C_i. Note that during the drying phase $A(t) \sim t$

for illustrating the results. V_0 can be thought of as the residual storage volume in the system under static or no-flow conditions.

Figure 3 shows a solution to Equation (14) for discrete pulse inputs of flow and solute, and represents the case when the ageing process of the tracer is intermittent due to an abrupt change in the hydrological forcing. The inputs are defined as

$$\begin{aligned} C_i = Q_i &= 1, \ \ (0 < t \leq 4) \\ &= 0, \ \ \text{otherwise} \end{aligned} \tag{18}$$

The initial conditions are the same as for the continuous unit step input. During the transient period, the flow, tracer and age all tend to an equilibrium value governed by the forcing as before. As the flow relaxes to no flow, the concentration remains constant, and the age increases as linear function of time.

The important point here is that, as the flow stops the tracer age evolves in time, a simple clock, or $A(t) \sim t$. The implications for watershed systems that have extended periods without hydrological inputs (e.g. arid regions or extended drought conditions) is that no-flow conditions will increase the tracer age in proportion to the duration of the dry period, until wetter conditions return and the 'clock' slows as shown in Figure 1.

Figure 4 shows the 'clock' effect for periodic pulse inputs of wet–dry or on–off cycles for the flow and the tracer. The first observation is that even though the tracer is subject to intermittent pulses just like the flow, the longer time constant for the solute produces very little fluctuation in $C(t)$. So, age fluctuations are almost entirely due to the intermittency in the flow. The second point is the age of the system $A(t)$ is on-average greater than the steady-state age $A^*(t)$. This simulation suggests that the age of tracers in upland ephemeral channels or arid zone ephemeral streams will increase in proportion to the duration of the seasonal drought or the length of the dry period.

Next, we examine the role of stationary random inputs $Q_i(t)$ and $C_i(t)$ to illustrate the effect of continuous variation in forcing conditions on flow, concentration and age dynamics (Figure 5). In this case $A(t)$ is sensitive to variability in both the flow and the tracer concentration. $A(t)$ tends to increase during dry periods and to slow down during wet cycles but with a phase lag that depends on both the flow and the tracer. It was found that even when the input concentration was constant, the output age can have fairly large variations due to the flow dynamics alone. Once the initial conditions wear off, fluctuations in tracer and flow vary about a constant value as does the age. In general, the amplitudes of $A(t)$ are large in comparison to the concentration. Although the results discussed above will depend on the timescale for mixing in the system, they suggest the importance of transient flow conditions in estimating the age of waters in the field. Note that all simulations use the same mean parameters to allow the above comparisons.

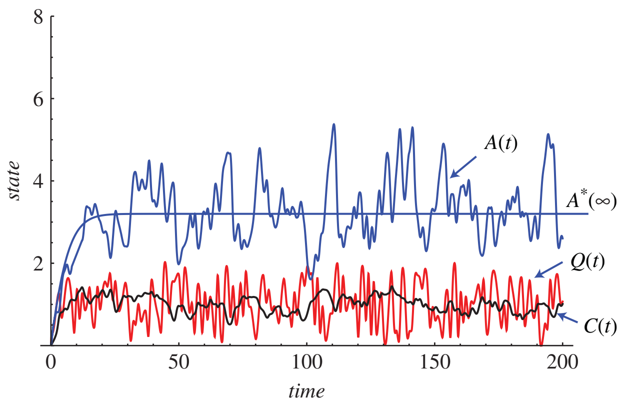

Figure 5. Age evolution of $C(t)$ and $Q(t)$ due to stationary random inputs $Q_i(t)$ and $C_i(t)$ and initial condition Q(0)=C(0)=0. The inputs are generated from a uniform distribution with range {0, 2}. It was found that even when the input concentration is relatively constant, the age can exhibit significant time fluctuations due to the flow dynamics

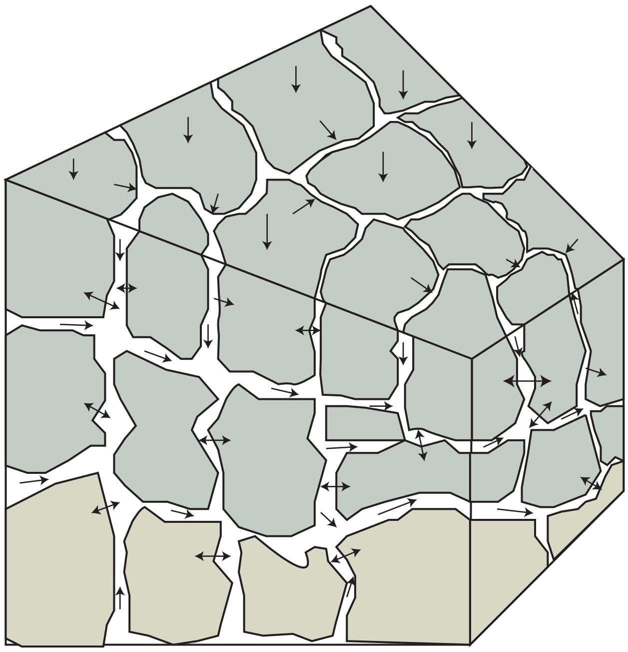

Figure 6. Conceptual model for mobile–immobile flow and tracer transport

CONCENTRATION–DISCHARGE–AGE DYNAMICS FOR MOBILE–IMMOBILE FLOW SYSTEMS

In a recent paper by Brooks *et al*. (2010) the authors present experimental stable isotope data that bring into question the assumption of complete mixing (or volume averaging) as developed in the previous section. The authors show that a significant fraction of tightly bound water stored in the soil does not participate in the advective component of stormflow during precipitation–runoff events. The conceptual model applied here (Figure 6) allows for a linear exchange between the immobile and mobile solute states. The goal of this section is to examine the age dynamics when the solute is partitioned into mobile and immobile components. The formulation follows the development of Gerke and van Genuchten (1993); however, we apply their approach to a volume-average system. The resulting dynamical system, derived in the same way as Equation (14), is given by:

$$\begin{aligned}
\frac{dV_m}{dt} &= Q_i - Q \\
\frac{dC_m}{dt} &= \frac{Q_i}{V_m}(C_i - C_{im}) - k_1\frac{V_{im}}{V_m}(C_m - C_{im}) \\
\frac{dC_{im}}{dt} &= k_1(C_m - C_{im}) \\
\frac{d\alpha_m}{dt} &= C_m - \frac{Q_i}{V_m}\alpha_m - k_1\frac{V_{im}}{V_m}(\alpha_m - \alpha_{im}) \\
\frac{d\alpha_{im}}{dt} &= C_{im} + k_1(\alpha_m - \alpha_{im}) \\
A_m(t) &= \alpha_m(t)/C_m(t) \\
A_{im}(t) &= \alpha_{im}(t)/C_{im}(t)
\end{aligned} \tag{19}$$

where $C_m, C_{im}, \alpha_m, \alpha_{im}$ are the mobile and immobile tracers and age concentration respectively, and A_m and A_{im} are the mobile and immobile water ages. k_1 in this case is the rate constant for exchange between the mobile and immobile solute states. Note that the system of equations (19) has seven state variables, five dynamic and two algebraic states. The assumption of an immobile fluid volume implies $\dot{V}_{im} = 0$, and the volume ratio is defined as

$$\frac{V_{im}}{V_m} = \frac{(1-\beta)nV_0}{\beta n V(t)} \tag{20}$$

where β is the fraction of the porosity n that is occupied by the mobile storage volume, and V_0 is the mean residual saturated volume of the system. Figure 7 shows the unit step input case for the age of mobile and immobile flows. The asymptotic value for mobile and immobile ages is given by:

$$\begin{aligned}
A_m(\infty) &= \frac{V_m(\infty) + V_{im}}{Q_i} \\
A_{im}(\infty) &= \frac{V_m(\infty) + V_{im}}{Q_i} + \frac{1}{k}
\end{aligned} \tag{21}$$

It is interesting to note that the age of the mobile fraction is increased by the magnitude of the immobile volume (21) as compared to the well-mixed case, and that the age of the immobile fraction is further increased by k^{-1}. The implications for watershed systems may be significant where immobile storage volume represents an adequate model and k^{-1} is large enough. In this case $k = 0{\cdot}1$ (time units^{-1}) and the mobile volume fraction is $\beta = 0{\cdot}8$. Clearly, the simple model proposed here for immobile/mobile tracer storage cannot entirely explain the apparent 'old water' often observed in upland watersheds. However, combined with the transient hydrology effects described earlier, it does provide useful insight into the path to a more complete understanding of the contributing processes.

The solution for age was extended to cyclic wet–dry input sequences. In Figure 8 we see that the on–off flow

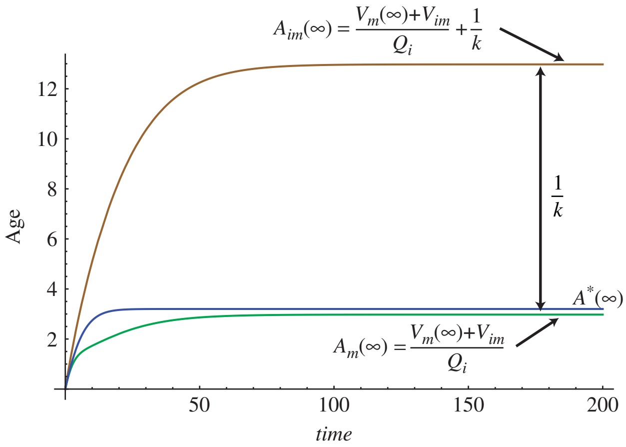

Figure 7. Numerical solution for the mobile–immobile flow and tracer transport system (Equation 19) for unit step inputs Q_i and C_i and the corresponding steady-state age for mobile and immobile storage (shown). Note that both $A_m(\infty)$ and $A_{im}(\infty)$ are larger than the steady-state age for constant inputs $A^*(\infty)$ by constant factors given in Equation (21)

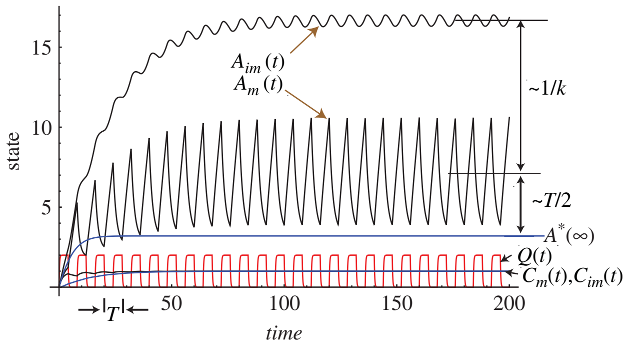

Figure 8. Numerical solution for the mobile–immobile flow, tracer and age for the system (19) for an intermittent sequence (wet–dry) of unit step inputs Q_i and C_i. The corresponding age for mobile and immobile storage fractions are very sensitive to the input fluctuations, while the mobile and immobile concentrations are not. It was estimated that the time-averaged age of mobile and immobile tracers were larger than $A^*(\infty)$ by the factors $\sim T/2$ and k^{-1} respectively

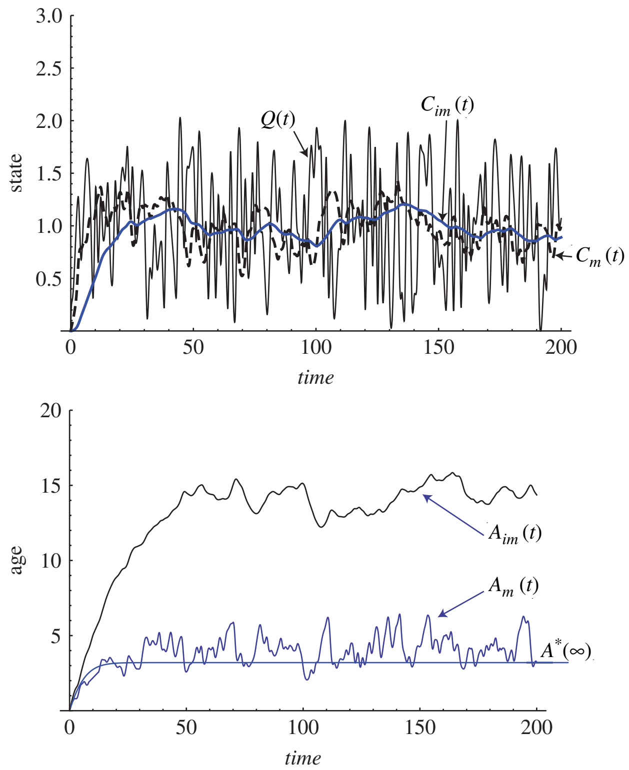

Figure 9. Solution to the mobile–immobile flow system (19) for uniform random inputs for Q_i and C_i showing the evolution of age for the mobile and immobile storage volume (lower graph) under fluctuating input conditions. The inputs were generated from a uniform distribution in the range {0, 2}. The initial conditions are zero-state as in the previous cases. The steady-state age for constant inputs (Figure 2) is also shown for reference

cycle has only a small effect on the concentration but a very large effect on the age of mobile and immobile solutes. The solution shows that although a dynamic steady state is reached, during the drying cycle, the age of the mobile state increases in proportion to clock time, and both mobile and immobile states are significantly older than the steady-state age $A^*(\infty)$.

The case of random inputs with mobile–immobile solute storage was simulated and the results are shown in Figure 9. The inputs were chosen to fluctuate about unit values with the same assumptions and parameters as for the earlier case (Figure 5). The results are consistent with the previous interpretations; however, we note that the immobile solute concentration has filtered the high-frequency solute fluctuations observed in the mobile volume.

The commentary by Kirchner (2003) is relevant here in that, this simple model provides one explanation for the 'rapid mobilization of old water', where the immobile storage of solute increases the age of the mobile state in proportion to k^{-1}. We also notice that the age of solutes in runoff will depend on the fluctuations in $Q(t)$. Overall, the simple model provides useful insight into the behaviour for field settings where immobile storage is suspected, and the approach could provide a tool for estimating the immobile volume and the rate constant k^{-1}.

CONCENTRATION–AGE FOR A DISTRIBUTED SOURCE WITH ADVECTION AND DISPERSION

The final example is motivated by an attempt to extend the age solution to spatially distributed inputs over a hillslope, and the setting is shown in Figure 10. Following the same strategy outlined earlier, the transport operator $L(C)$ in Equation (8) is now defined in terms of the advective and dispersive flux. The limited goal of this section is to demonstrate that the age-simulation strategy also applies to advective–dispersive systems, and to compare these solutions to the volume-average system (14) results given earlier. Assuming a steady flow, the 1-D hillslope system is given by (Bear, 1972; Duffy and Cusumano, 1998):

$$
\begin{aligned}
&\nabla \cdot (Kh\nabla h) + \varepsilon = 0 \\
&\theta_s \frac{\partial (Ch)}{\partial t} + \nabla \cdot F = \varepsilon C_i \\
&F = QC - hJ \\
&J = -\theta_s D \nabla C
\end{aligned}
\tag{22}
$$

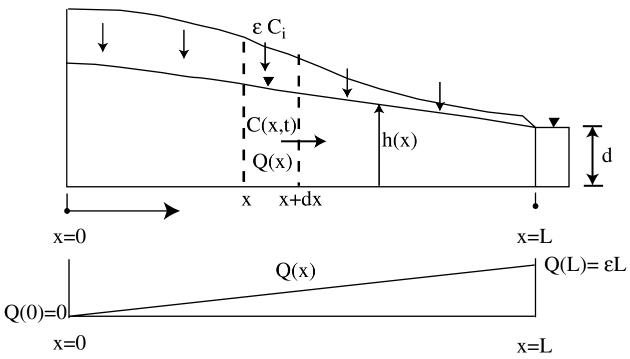

Figure 10. A distributed tracer and recharge in a steady, 1-D non-uniform flow. The constant recharge rate produces the advective flux $Q(x) = \varepsilon x$ which varies linearly along the flow path. The parameters were assigned such that the spatially distributed solution could be compared to the volume-average solutions developed earlier

where $C(x,t)$ is the solute concentration, $h(x)$ is the saturated thickness, K is the hydraulic conductivity and ε is the recharge rate to the aquifer. In Equation (8) $L[C] = \nabla \cdot F$ is the advective–dispersive flux term and D is the dispersion coefficient. Expanding the transport equation in (22) and including the age concentration equation (9) lead to the following system for concentration and age in a steady 1-D flow with recharge:

$$\begin{aligned} \frac{\partial C}{\partial t} + u(x)\frac{\partial C}{\partial x} - D(x)\frac{\partial^2 C}{\partial x^2} &= K(C_i - C) \\ \frac{\partial \alpha}{\partial t} + u(x)\frac{\partial \alpha}{\partial x} - D(x)\frac{\partial^2 \alpha}{\partial x^2} &= C - k\alpha \end{aligned} \tag{23}$$

where for steady flow the lateral flux of groundwater and the parameters are given by:

$$\begin{aligned} Q(x) &= -Kh\frac{\partial h}{\partial x} = qh = \varepsilon x \\ k &= \frac{\varepsilon}{\theta_s d}; \quad u(x) = k(x - a_L) \\ D(x) &= kxa_L \end{aligned} \tag{24}$$

As before, the age concentration is assumed to have the initial condition $\alpha(0) = 0$, and the external source or the recharge age concentration is taken to be $\alpha_i = 0$, which states that the input of solute is zero age as it enters the system as before. Figure 11 shows the space–time solution for constant inputs. It is clear that the depth-averaged model (23) has a nearly constant solution in space. In fact, we get essentially the same solution at any location along the flow as we do for the volume-averaged case. To demonstrate this point, the unit step solution for volume-averaged age and concentration are superimposed in Figure 11 with almost no difference between 1-D advective–dispersive transport with unit inputs. Duffy and Lee (1992) found a similar result for a more general 2-D flow system with stationary spatial variability in $K(x,z)$, $\varepsilon(x)$ and $C_i(x,z)$. We see in this comparison that the age and concentration for well-mixed and spatial inputs are essentially the same for comparable conditions. One practical implication is that the simple

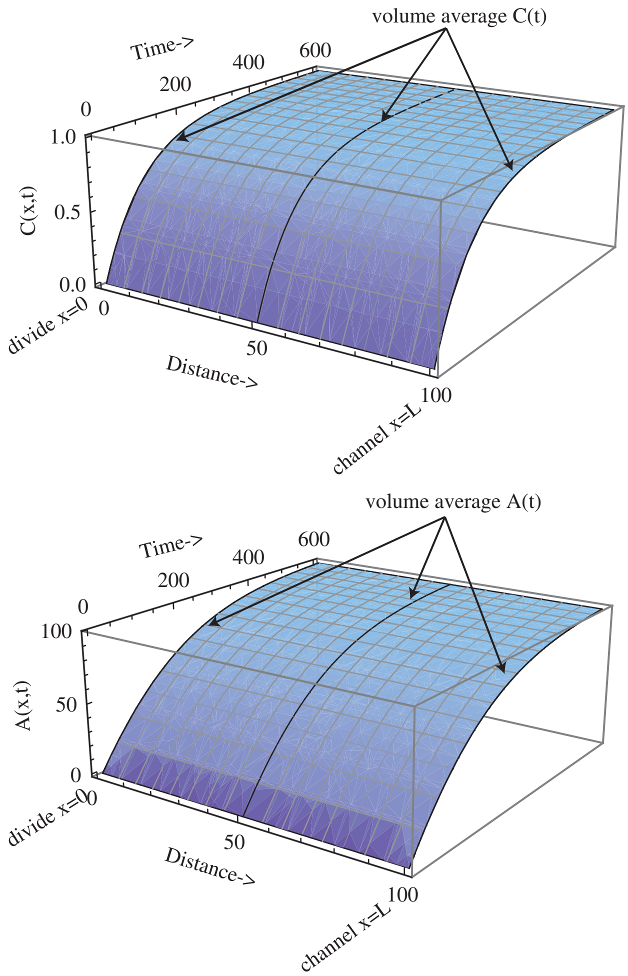

Figure 11. The space and time distribution of tracer concentration (upper) and age (lower) for the system (23) including the effects of non-uniform flow and advective–dispersive transport, with uniform constant ε_i and C_i. The solutions for $C(x,t)$ and $A(x,t)$ are nearly constant in space as shown by Duffy and Lee (1992). The solid lines are superimposed from the volume-average solution from Equation (14) shown in Figure 2

volume-average model has very similar dynamics and input–output behaviour to the spatially distributed flow along a hillslope, and that simple models continue to have an important role to play in watershed studies. It must be noted that in real field settings, the processes encountered will be more complex including the role of bedrock slope, displacement dynamics, transient contributing area, etc. The comparisons made here can only serve as a step towards a more comprehensive theory that includes these processes.

CONCLUSIONS

A theoretical interpretation of tracer and solute ages for a transient hydrological systems is developed based on constructing the moments of the underlying concentration age distribution function $c(x, t, \tau)$. The results are applicable to spatially distributed and volume-averaged systems and the method requires limited assumptions on the particular form of the distribution function. Particular examples or numerical experiments are conducted using *Mathematica* simulation software (Wolfram, 2010) which demonstrate a number of points: (1) The first two moments of the age distribution function are sufficient to construct a dynamical system for the mean age and concentration under steady or transient flow conditions. (2) Solutions to the coupled system of equations for flow, concentration and age show that 'age' of solutes stored within the watershed or leaving the watershed is a dynamic process which depends on flow variations as well as the solute or tracer dynamics. (3) Intermittency of wetting and drying cycles leads to an apparent increase in the tracer age in proportional to the duration of the 'dry' phase. It is noted that transient effects may be a particular problem for regions where intermittent rainfall–runoff has long periods of no flow. This would be the case in arid regions or for small upland humid watersheds where vegetation tends to consume all the summer precipitation. (4) The question of how mobile/immobile flow may affect the age of solutes is examined by including a low permeable, passive store that drops the well-mixed assumption in the first model. In this case, we see explicitly how an immobile storage of tracer will increase the age of the stored or exiting waters as compared to the steady-state age often used. The presence of immobile storage in the watershed serves to increase these time constants in a predictable way based on the magnitude of the rate constant k. (5) Comparison of the volume-averaged model with spatially distributed advective–dispersive transport along a 1-D hillslope trajectory is shown to compare well with the volume-average results for similar hydraulic parameters. The comparisons extend earlier work (Duffy and Lee, 1992; Duffy and Cusumano, 1998) by including age in the comparison. Finally, the paper shows that relatively few additional parameters are necessary to include dynamic hydrology in age modelling. In general, including transient flow added additional information that complements steady-state age results widely used in the literature.

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REFERENCES

Allison G, Holmes J. 1973. The environmental tritium concentration of under ground water and its hydrological interpretation. *Journal of Hydrology* **19**(2): 131–143.

Bear J. 1972. *Dynamics of fluids in porous media*, Elsevier pub.; 764 p.

Bolin B, Rodhe H. 1973. A note on the concepts of age distribution and transit time in natural reservoirs. *Tellus* **25**(1): 58–62.

Botter G, Peratoner F, Putti M, Zuliani A, Zonta R, Rinaldo A, Marani M. 2008. Observation and modeling of catchment-scale solute transport in the hydrologic response: a tracer study. *Water Resources Research* **44**(5): W05409. DOI: 10.1029/2007WR006611.

Brooks J, Barnard H, Coulombe R, McDonnell J. 2010. Ecohydrologic separation of water between trees and streams in a Mediterranean climate, *Nature Geoscience* **3**: 100–104.

Darracq A, Destouni G, Persson K, Prieto C, Jarsjö J. 2010. Quantification of advective solute travel times and mass transport through hydrological catchments. *Environmental Fluid Mechanics* **10**(1–2): 103–120.

Delhez EJM, Campin J-M, Hirst AC, Deleersnijder E. 1999. Toward a general theory of the age in ocean modeling. *Ocean Modelling* **1**(1): 17–27.

Destouni G, Graham W. 1995. Solute transport through an integrated heterogeneous soil groundwater system. *Water Resources Research* **31**(8): 1935–1944.

Duffy CJ, Cusumano J. 1998. A low-dimensional model for concentration-discharge dynamics in groundwater stream systems. *Water Resources Research* **9**(34): 2235–2247.

Duffy CJ, Lee DH. 1992. Baseflow response from nonpoint source contamination: simulated spatial uncertainty in source, structure and initial condition. *Water Resources Research* **28**(3): 905–914.

Eriksson E. 1971. Compartment models and reservoir theory. *Annual Reviews Ecological Systems* **2**: 67–84.

Fiori A, Russo D. 2008. Travel time distribution in a hillslope: insight from numerical simulations. *Water Resources Research* **44**(12): W12426. DOI: 10.1029/2008WR007135.

Gerke HH, van Genuchten MTh. 1993. Evaluation of a first order water transfer term for variably saturated dual-porosity models. *Water Resources Research* **29**(4): 1225–1238.

Goode D. 1996. Direct simulation of groundwater age. *Water Resources Research* **32**(2): 289–296.

Gourgue O, Deleersnijder E, White L. 2006. Toward a generic method for studying water renewal, with application to the epilimnion of Lake Tanganyika, Estuarine. *Coastal and Shelf Science* **74**(4): 628–640.

IHP-V. 2001. *Environmental Isotopes in the Hydrological Cycle*, Mook W (ed). *IHP Technical Documents in Hydrology*, No. 39 Unesco: Paris, Vol. VI, 117 p.

Kazemi A, Lehr J, Perrochet P. 2006. *Groundwater Age*. Wiley: New Jersey USA; 325 p.

Kirchner JW. 2003. A double paradox in catchment hydrology and geochemistry, *Hydrologic Processes* **17**: 871–874.

Maloszewski P, Zuber A. 1982. Determining the turnover time of groundwater systems with the aid of environmental tracers. 1. Models and their applicability. *Journal of Hydrology* **57**(3–4): 207–231.

Nauman E. 1969. Residence time distribution theory for unsteady stirred tank reactors. *Chemical Engineering Science* **24**(9): 1461–1470.

Phillip F. 1995. The use of isotopes and environmental tracers in subsurface hydrology. *Reviews in Geophysics* **33**: 1029–1033 (Supplement, July 1995, U.S. Nat. Rept. To Int. Union Geod. Geophys. 1991–1994).

Rotenberg M. 1972. Theory of population transport. *Journal of Theoretical Biology* **37**(2): 291–305.

Wolfram Research, 2010. Mathematica 7.0, (software) www.wolfram.com.

