Supplemental Information for "Solute Transport through Unsteady Hydrologic Systems Along a Plug Flow-to-Uniform Sampling Continuum"

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November 2021

1 Age-Ranked Storage in Tank 1

In this section we derive the solutions for age-ranked storage under plug-flow sampling that appear as equations (5a) and (5b) in the main text. In Tank 1 only the oldest water in storage is selected for discharge; i.e., a plug flow SAS applies, $\Omega_1(S_{T1}(T,t),t) = H(S_{T1}(T,t) - pS(t))$. The plug flow SAS suffers from the same problem noted in the main text for the shifted uniform SAS; namely, because the dependent variable appears inside the Heaviside function, the corresponding ACE is a non-linear partial differential equation. This complication can be addressed by exploiting the following feature of plug flow sampling: because only the oldest water is sampled for outflow, the age distribution of water in outflow can be stipulated directly (i.e., there is no need for a SAS closure relationship in this particular case). Specifically, at time t, water discharged from Tank 1 must have a single age equal to the maximum age of water in storage at that time, $T_{m1}(t)\,[T]$: $P_{Q1}(T,t) = H(T - T_{m1}(t))$. Thus, under plug flow sampling, the ACE for Tank 1 can be written in the following linear form (compare with equation (1) in the main text):

$$\frac{\partial S_{T1}}{\partial t} = J(t) - H(T - T_{m1}(t))Q_\Delta(t) - \frac{\partial S_{T1}}{\partial T} \tag{1a}$$

$$S_{T1}(T = 0, t) = 0 \tag{1b}$$

$$S_{T1}(T, t = 0) = pS_0 H(T - T_0) \tag{1c}$$

Taking the Laplace Transform of equation (1a) and (1c) with respect to the age variable, T, yields the following rate equation, where $\widetilde{S_{T1}}(r,t) = \int_0^\infty e^{-rT} S_{T1}(T,t)\, dT$ is the Laplace transform of age-ranked storage function, $S_{T1}(T,t)$, r is the Laplace transform variable, and the subscript "1" denotes Tank 1:

$$\frac{d\widetilde{S_{T1}}}{dt} = f_1(r,t) - r\widetilde{S_{T1}}(r,t) \tag{2a}$$

$$f_1(r,t) = \frac{J(t)}{r} - Q_\Delta(t)\frac{e^{-rT_m(t)}}{r} \tag{2b}$$

$$\widetilde{S_{T1}}(r, t = 0) = pS_0 \frac{e^{-rT_0}}{r} \tag{2c}$$

The ACE boundary condition (equation (1b)) has been incorporated into equation (2a). Equation (2a) can be integrated to yield a solution for the Laplace transform of the age-ranked storage function where ν is a dummy integration variable:

$$\widetilde{S_{T1}}(r,t) = pS_0 \frac{e^{-r(t+T_0)}}{r} + e^{-rt} \int_0^t e^{r\nu} f_1(r,\nu)\, d\nu$$

Taking the inverse Laplace transform of both sides we arrive at equation (3) where $\mathcal{L}^{-1}(\cdot)$ denotes an inverse Laplace transform:

$$S_{T1}(T,t) = pS_0 H(T - t - T_0) + \mathcal{L}^{-1}\left(\int_0^t e^{-r(t-\nu)} f_1(r,\nu)\, d\nu\right) \tag{3}$$

Substituting equation (2b), the integral on the right hand side of equation (3) can be expressed as the difference of two integrals:

$$\int_0^t e^{-r(t-\nu)} f_1(r,\nu)\, d\nu \quad = \quad \int_0^t \frac{e^{-r(t-\nu)}}{r} J(\nu)\, d\nu \quad - \quad \int_0^t \frac{e^{-r(t+T_m(\nu)-\nu)}}{r} Q_\Delta(\nu)\, d\nu$$

The inverse Laplace transforms of these two integrals are as follows:

$$\mathcal{L}^{-1}\left(\int_0^t \frac{e^{-r(t-\nu)}}{r} J(\nu)\, d\nu\right) = \int_0^t H\left(T - t + \nu\right) J(\nu)\, d\nu$$
$$\mathcal{L}^{-1}\left(\int_0^t \frac{e^{-r(t+T_m(\nu)-\nu)}}{r} Q_\Delta(\nu)\, d\nu\right) = \int_0^t H\left(T - t - T_m(\nu) + \nu\right) Q_\Delta(\nu)\, d\nu$$

Substituting these results into equation (3) we arrive at the solution for age-ranked storage in Tank 1:

$$S_{T1}(T,t) = pS_0 H(T-t-T_0) + \int_0^t H\left(T - t + \nu\right) J(\nu)\, d\nu - \int_0^t H\left(T - t - T_m(\nu) + \nu\right) Q_\Delta(\nu)\, d\nu$$

Moving the Heaviside function out of the first integral, we obtain the following general solution for age-ranked storage under plug-flow sampling:

$$S_{T1}(T,t) = pS_0 H(T - t - T_0) + \int_0^t J(\nu)\, d\nu - H(t-T)\int_0^{t-T} J(\nu)\, d\nu - \int_0^t H\left(T - t + \nu - T_m(\nu)\right) Q_\Delta(\nu)\, d\nu \quad (4)$$

From the discussion in Sections 2.2 and 2.3.1 of the main text, we can glean the following three results for age-ranked storage under plug flow sampling: (**Result 1**) prior to the critical time, the maximum age of water in Tank 1 is $T_{m1}(t) = T_0 + t$ for $t \leq t_c$; (**Result 2**) after the critical time, the maximum age obeys the inequality $T_{m1}(t) < t$, because only new water remains in the tank for $t > t_c$ and new water, by definition, entered Tank 1 at some time $t > 0$; and (**Result 3**) the critical time, t_c, can be calculated from a simple vadose zone water balance, as the time required to drain all original water from Tank 1 (equation (9a) in the main text)

When Result 1, $T_{m1}(\nu) = T_0 + \nu$, is substituted into the Heaviside function on the right hand side of equation (4), we obtain the following solution for age-ranked storage prior to the critical time:

$$S_{T1}(T, t \leq t_c) = pS_0 H(T - t - T_0) + \int_0^t J(\nu)\, d\nu - H(t-T) \int_0^{t-T} J(\nu)\, d\nu$$
$$- H(T - t - T_0) \int_0^t Q_\Delta(\nu)\, d\nu$$

This last result can be expressed in terms of three sub-equations (depending on the choice of the age variable, T), as summarized in equation (5a) of the main text.

Result 2 ($T_{m1}(t) < t$ when $t > t_c$) has two important implications for age-ranked storage after the critical time: (1) the first term on the right hand side of equation (4) can be dropped, because the Heaviside function appearing in this term is always zero, $H(T{-}t{-}T_0) = 0$; and (2) the last term on the right hand side of equation (4) can also be dropped, because the Heaviside function in the integrand is zero, $H(T{-}t{+}\nu{-}T_{m1}(\nu)) = 0$, over the full range of the dummy integration variable, $\nu \in [0, t]$, as demonstrated next.

Because the maximum age appearing inside the Heaviside function, $T_{m1}(\nu)$, will change abruptly from being equal to $T_{m1}(\nu) = \nu + T_0$ for $0 \leq \nu \leq t_c$ to satisfying the inequality, $T_{m1}(\nu) < \nu$ for $\nu > t_c$ (Results 1 and 2 above), we must evaluate the integral separately for these two ranges of the dummy integration variable:

$$\int_0^t H(T - t + \nu - T_{m1}(\nu))\, Q_\Delta(\nu)\, d\nu = \int_0^{t_c} H(T - t + \nu - T_{m1}(\nu))\, Q_\Delta(\nu)\, d\nu$$
$$+ \int_{t_c}^t H(T - t + \nu - T_{m1}(\nu))\, Q_\Delta(\nu)\, d\nu, \ t > t_c \quad (5)$$

From Result 1, the maximum age $T_{m1}(\nu)$ is equal to the sum of the dummy integration variable and the initial age of original water, T_0, over the range $\nu \in [0, t_c]$. After substituting this result into the Heaviside function appearing in the first integral on the right hand side of equation (5), we find that the Heaviside function is zero over this range of the dummy integration variable: $H(T - t - T_0) = 0$. This last result follows from the fact that, for $t > t_c$, the age of water in Tank 1 will always be less than calendar time, $T < t$. Therefore, the first integral on the right hand side of equation

(5) can be dropped.

Relative to the second integral on the right hand side of equation (5), Result 2 indicates that, over the integration range $\nu \in (t_c, t]$, the quantity $T - t$ will always be negative while the quantity $\nu - T_{m1}(\nu)$ will always be positive. The question then becomes: is the inequality $\nu - T_{m1}(\nu) \geq T - t$ satisfied over some subset of the integration range $\nu \in (t_c, t]$? If the answer is yes, then the last integral appearing on the right hand side of equation (5) must be retained. If the answer is no, the integral can be dropped.

To answer the above question, we note that the quantity, $\nu - T_{m1}(\nu)$, increases monotonically with ν over the range $\nu \in (t_c, t]$. This conclusion follows from the fact that the maximum age of water in storage, $T_{m1}(\nu)$, periodically declines as old water is selected for discharge, but it can never grow faster than time, ν. Hence, for a fixed choice of the variables t and T, the argument inside the Heaviside function, $H(T - t + \nu - T_{m1}(\nu))$, will be the least negative (or equivalently the most positive) when the dummy integration variable equals its upper integration limit, $\nu = t$. When evaluated at the upper limit, we find that the Heaviside argument is at most zero, $T - T_{m1}(t) \leq 0$, implying that the Heaviside function, $H(T - t + \nu - T_{m1}(\nu))$, is zero over the full range of integration, $\nu \in (t_c, t)$. Thus, for times greater than the critical time, the last integral on the right hand side of equation (5) can be dropped, and the solution for age-ranked storage under plug flow sampling (equation (4)) takes on the following simple form (equation (5b) in the main text):

$$S_{T1}(T, t) = \bar{J}(t) - \bar{J}(t - T), \ 0 \leq T \leq T_{m1}(t), \ t > t_c \tag{6}$$

2 Age-Ranked Storage in Tank 2

Outflow from Tank 2 is randomly selected from storage and therefore the uniform SAS applies in this case (see Figure 1b in the main text): $P_{Q2}(T, t) = \Omega_2(S_{T2}, t) = \frac{S_{T2}(T,t)}{(1-p)S(t)}$. Substituting the uniform SAS and setting the flow and age distribution of water entering Tank 2 equal to the flow and age distribution of water leaving Tank 1, the ACE for Tank 2 can be written in the following linear form:

$$\frac{\partial S_{T2}}{\partial t} = Q_\Delta(t)H(T - T_{m1}(t)) - \frac{S_{T2}(T,t)}{(1-p)S(t)}Q(t) - \frac{\partial S_{T2}}{\partial T} \tag{7a}$$

$$S_{T2}(T = 0, t) = 0 \tag{7b}$$

$$S_{T2}(T, t = 0) = (1-p)S_0 H(T - T_0) \tag{7c}$$

Taking the Laplace Transform of equations (7a) and (7c) with respect to the age variable we arrive at the following rate equation for the Laplace Transformed age-ranked storage function where r is the Laplace transform variable:

$$\frac{d\widetilde{S_{T2}}}{dt} = Q_\Delta(t)\frac{e^{-rT_{m1}(t)}}{r} - \widetilde{S_{T2}}(r,t)\Big(\frac{Q(t)}{(1-p)S(t)} + r\Big) \tag{8a}$$

$$\widetilde{S_{T2}}(r, t = 0) = (1-p)S_0\frac{e^{-rT_0}}{r} \tag{8b}$$

Note that the boundary condition on the ACE for Tank 2 (equation (7b)) has been incorporated into equation (8a). Equations (8a) and (8b) can be integrated to yield the following solution for the Laplace transform of the age-ranked storage function where ν is a dummy integration variable:

$$\widetilde{S_{T2}}(r,t) = (1-p)S_0\frac{e^{-r(t+T_0)}}{r}e^{-\bar{\tau}(t)} + \int_0^t \frac{e^{-r(t+T_{m1}(\nu)-\nu)}}{r}e^{-\bar{\tau}(t,\nu)}Q_\Delta(\nu)\,d\nu \tag{9a}$$

$$\bar{\tau}(t) = \int_0^t \frac{Q(\nu)}{(1-p)S(\nu)}d\,\nu \tag{9b}$$

$$\bar{\tau}(t,\nu) = \int_\nu^t \frac{Q(\nu)}{(1-p)S(\nu)}d\,\nu = \bar{\tau}(t) - \bar{\tau}(\nu) \tag{9c}$$

Taking the inverse Laplace transform of this last result, we obtain the following solution for age-ranked storage in Tank 2:

$$S_{T2}(T,t) = (1-p)S_0H(T - t - T_0)e^{-\bar{\tau}(t)} + \int_0^t H(T - t + \nu - T_{m1}(\nu))e^{-\bar{\tau}(t,\nu)}Q_\Delta(\nu)\,d\nu \tag{10}$$

The functional form this solution takes (equations (9a) and (9b) in the main text) depends on whether elapsed time is before or after the critical time (at which all original water has been removed from Tank 1), and the choice of age variable T. These different functional forms are derived next.

2.1 Age-Ranked Storage in Tank 2 *before* the Critical Time

2.1.1 Solution for $t \leq t_c$ and $T = T_0 + t$

Before the critical time, all water in Tank 2 is of age $T = T_0 + t$, where T_0 is the initial age of water in the vadose zone (see equation (1c) and discussion thereof in the main text). Furthermore, before the critical time the oldest water in Tank 1 is original water, and therefore the maximum age of water in Tank 1 is: $T_{m1}(t) = T_0 + t$. Substituting these results into equation (10) we obtain the following:

$$S_{T2}(T,t) = (1-p)S_0 H(0) e^{-\bar{\tau}(t)} + \int_0^t H(0) e^{-\bar{\tau}(t,\nu)} Q_\Delta(\nu)\, d\nu,\ T = T_0 + t,\ 0 \leq t \leq t_c \quad (11)$$

Setting $H(0) = 1$, we arrive at the upper solution in equation (9a) of the main text:

$$S_{T2}(T,t) = (1-p)S_0 e^{-\bar{\tau}(t)} + \int_0^t e^{-\bar{\tau}(t,\nu)} Q_\Delta(\nu)\, d\nu,\ T = T_0 + t,\ 0 \leq t \leq t_c \quad (12)$$

2.1.2 Solution for $t \leq t_c$ and $T < T_0 + t$

For times before the critical time, $t \leq t_c$, and water age less than the age of original water, $T < T_0 + t$, the arguments of both Heaviside functions in equation (10) are negative and therefore the lower solution in equation (9a) of the main text applies:

$$S_{T2}(T,t) = 0,\ T < T_0 + t,\ 0 \leq t \leq t_c \quad (13)$$

2.2 Age-Ranked Storage in Tank 2 *after* the Critical Time

Here there are four functional forms of the age-ranked storage function for Tank 2 depending on the choice of the age variable, T.

2.2.1 Solution for $t > t_c$ and $T = T_0 + t$

When the age variable is set equal to the age of original water, $T = T_0 + t$, the two Heaviside functions appearing in equation (10) reduce to unity and the upper solution in equation (9a) of the main text applies:

$$S_{T2}(T,t) = (1-p)S_0 e^{-\bar{\tau}(t)} + \int_0^t e^{-\bar{\tau}(t,\nu)} Q_\Delta(\nu)\, d\nu,\ T = T_0 + t,\ t > t_c \tag{14}$$

This last result follows from the fact that the maximum age of water in Tank 1 is always less than or equal to the elapsed time: $\nu - T_{m1}(\nu) \geq 0$. Thus, after substituting $T = T_0 + t$, the following inequality applies, $T_0 + \nu - T_{m1}(\nu) > 0$, which implies that the Heaviside function appearing inside the integral is always unity.

2.2.2 Solution for $t > t_c$ and $t \leq T < T_0 + t$

When the age variable is less than the age of original water, $T < T_0 + t$, and calendar time is greater than zero, $t \geq 0$, the first term on the right hand side of equation (10) drops out:

$$S_{T2}(T,t) = \int_0^t H(T - t + \nu - T_{m1}(\nu)) e^{-\bar{\tau}(t,\nu)} Q_\Delta(\nu)\, d\nu,\ 0 \leq T < T_0 + t,\ t \geq 0$$

Furthermore, if calendar time is greater than the critical time, $t > t_c$ then the right hand side of this last equation can be written as the sum of two integrals:

$$\begin{aligned} S_{T2}(T,t) = & \int_0^{t_c} H(T - t + \nu - T_{m1}(\nu)) e^{-\bar{\tau}(t,\nu)} Q_\Delta(\nu)\, d\nu \\ & + \int_{t_c}^t H(T - t + \nu - T_{m1}(\nu)) e^{-\bar{\tau}(t,\nu)} Q_\Delta(\nu)\, d\nu,\ 0 \leq T < T_0 + t,\ t > t_c \end{aligned}$$

Because the upper limit of the first integral is the critical time, t_c the dummy integration variable appearing in this integral conforms to the inequality, $\nu \leq t_c$, and therefore the maximum age of water in Tank 1 over this integration range is $T_{m1}(\nu) = T_0 + \nu$. Given this result, the Heaviside function appearing in the first integral can be written as follows: $H(T - t + \nu - T_{m1}(\nu)) = H(T - t - T_0) = 0$ for $T < T_0 + t$. Thus, the first integral on the right hand side of this last equation is exactly zero:

$$S_{T2}(T,t) = \int_{t_c}^{t} H(T - t + \nu - T_{m1}(\nu))e^{-\bar{\tau}(t,\nu)}Q_{\Delta}(\nu)\,d\nu,\ T < T_0 + t,\ t > t_c \qquad (15)$$

Finally, for the age range stipulated, $t \leq T < T_0 + t$, the Heaviside function appearing on the right hand side of equation (15) is unity based on the following argument. For the integration range, $\nu \in [t_c, t]$, the dummy integration variable is always greater than the critical time, $\nu \geq t_c$ and therefore the following inequality applies to the maximum age of water in Tank 1: $T_{m1}(\nu) \leq \nu$. This last inequality together with the stipulation that, $T \geq t$, implies that the argument of the Heaviside function will always be equal to or greater than zero: $T - t + \nu - T_{m1}(\nu) \geq 0$. Hence, the Heaviside function appearing in equation (15) is unity over the full integration range and the second solution in equation (9b) of the main text applies:

$$S_{T2}(T,t) = \int_{t_c}^{t} e^{-\bar{\tau}(t,\nu)}Q_{\Delta}(\nu)\,d\nu,\ t \leq T < T_0 + t,\ t > t_c$$

2.2.3 Solution for $t > t_c$ and $T_{m1}(t) \leq T < t$

For the same reasons articulated in the last section, the stipulation that $t > t_c$ and $T < t < T_0 + t$ implies that the age-ranked storage function for this range of the age variable can be simplified to equation (15). To make further progress we must consider the argument inside the Heaviside function, $H(T - t + \nu - T_{m1}(\nu))$. The stipulation that $T < t$ implies that the first two terms in the argument are negative, $T - t < 0$. On the other hand, the difference $\nu - T_{m1}(\nu)$ will be positive and increases monotonically with increasing ν. This last conclusion follows from the fact that $T_{m1}(\nu)$ will periodically decrease as older water is flushed out of Tank 1, but it can never grow faster than ν. Thus, the Heaviside function appearing in the integrand, $H(T - t + \nu - T_{m1}(\nu))$, will be zero up until the dummy integration variable equals the single root, $\nu = t_{i,2}$, of the equation, $t_{i,2} - T_{m1}(t_{i,2}) = t - T$, where $t_{i,2} > t_c$. For values of the dummy integration variable greater than or equal to this root, $\nu \geq t_{i2}$, the Heaviside function will be unity because, as noted above, the difference $\nu - T_{m1}(\nu)$ grows monotonically with ν. Therefore, age ranked storage in this limit is equal to the third solution in equation (9b) of the main text, where the root t_{i2} is a function solely of $t - T$:

$$S_{T2}(T,t) = \int_{t_{i,2}(t-T)}^{t} e^{-\bar{\tau}(t,\nu)} Q_{\Delta}(\nu)\, d\nu,\ T_{m1}(t) \leq T < t,\ t > t_c$$

2.2.4 Solution for $t > t_c$ and $0 \leq T < T_{m1}(t)$

For the same reasons outlined above, the stipulation that $t > t_c$ and $T < T_{m1}(t) < T_0 + t$ implies that the age-ranked storage function for this range of the age variable can be simplified to equation (15). From the stipulation that $T < T_{m1}(t)$ and the fact, over the integration range, $\nu \in [t_c, t]$, the dummy integration variable is always less than or equal to time, $\nu \leq t$, we can infer that the the argument of the Heaviside function appearing in equation (15) is always negative: $T - t + \nu - T_{m1}(\nu) < 0$. Therefore the Heaviside function is zero over the full range of integration, and we arrive at the last solution in equation (9b) of the main text:

$$S_{T2}(T,t) = 0,\ 0 \leq T < T_{m1}(t),\ t > t_c$$

3 PDF form of the Age Distribution in Outflow

In this section we derive the PDF form of the age distribution of water leaving the vadose zone under shifted uniform selection. Water discharged from Tank 2 is selected randomly from storage (i.e., a uniform SAS was adopted for Tank 2). Under uniform sampling, the age distribution of water in outflow is the same as the age distribution of water in storage and therefore the PDF form of the age distribution of water leaving Tank 2 can be represented as follows:

$$p_{Q2}(T,t) = \frac{1}{(1-p)S(t)} \frac{\partial S_{T2}}{\partial T} \tag{16}$$

The goal in this section is to derive an expression for the derivative of age-ranked storage in Tank 2 with respect to the age variable, $\frac{\partial S_{T2}}{\partial T}$. From the solution derived in the last section for age-ranked storage in Tank 2 (equation (10)), its derivative with respect to age can be written as follows where $\delta(\cdot)$ is the Dirac Delta function:

$$\frac{\partial S_{T2}}{\partial T} = (1-p)S_0\delta(T-t-T_0)e^{-\bar{\tau}(t)} + \int_0^t \delta(T-t+\nu-T_{m1}(\nu))e^{-\bar{\tau}(t,\nu)}Q_\Delta(\nu)\,d\nu \quad (17)$$

To simplify the integral term on the right hand side, we apply the following identity for Dirac Delta functions: $\delta(f(\nu)) = \sum_{f(\nu_j)=0} \frac{\delta(\nu-\nu_j)}{f'(\nu_j)}$, where $f'(\nu_j)$ is the derivative of f with respect to ν evaluated at $\nu = \nu_j$, and ν_j is the jth root of the equation, $f(\nu_j) = 0$. In our case, the function f is defined as follows, $f(\nu) = T - t + \nu - T_{m1}(\nu)$, and its derivative with respect to the dummy integration variable ν is: $f'(\nu) = 1 - T'_{m1}(\nu)$, where $T'_{m1}(\nu)$ is the time derivative of the maximum age of water in Tank 1 (see equation (7) in the main text and discussion thereof). Thus, the Dirac Delta function appearing inside the integral in the equation above can be expressed as follows where the function $t_{i,2}(t-T)$ is the single root of the equation, $t_{i,2} - T_{m1}(t_{i,2}) = t - T$ for times greater than the critical time, $t > t_c$, and the maximum age is bounded as follows, $0 \leq T_{m1}(\nu) \leq \nu$ (these last two inequalities apply because we are interested in characterizing the breakthrough of solute, which can occur only after the critical time, when new water is entering Tank 2):

$$\delta(T-t+\nu-T_{m1}(\nu)) = \frac{\delta(\nu - t_{i,2}(t-T)}{1 - T'_{m1}(t_{i,2}(t-T))} \quad (18)$$

As noted in the main text, the function $t_{i,2}(t-T)$ can be interpreted as the time a water parcel enters Tank 2, conditioned on the same water parcel entering Tank 1 at time $t_i = t - T$ (or, equivalently, conditioned on the same water parcel having age T at time t). The quantity $1 - T'_{m1}(t_{i,2})$ that appears in the denominator on the right hand side can be simplified by manipulating the implicit equation for the maximum age in Tank 1, $T_{m1}(t)$ (see equation (7) in the main text): $pS(t) = \bar{J}(t) - \bar{J}(t - T_{m1}(t))$. Here, the function $\bar{J}(t)$ represents the cumulative volume flowing into Tank 1 (across the top boundary of the vadose zone) over time, t: $\bar{J}(t) = \int_0^t J(\nu)\,d\nu$. Taking the time derivative of this implicit equation for $T_{m1}(t)$, we arrive at the following result: $pS'(t) = J(t) - J(t - T_{m1}(t))(1 - T'_{m1}(t))$. Furthermore, the change in storage with respect to time can be written as the difference between inflows and outflows across the vadose zone control volume: $S'(t) = J(t) - Q(t)$. Combining these last two results and solving for the quantity $(1 - T'_{m1}(t))$, we obtain equation (19), where the variable $Q_\Delta(t) = (1 - p)J(t) - pQ(t)$ represents the rate at which water is transferred from Tank 1 to 2 (see equation (3) in the main text).

$$1 - T'_{m1}(t_{i,2}(t - T)) = \frac{Q_\Delta(t_{i,2}(t - T))}{J(t_{i,2}(t - T) - T_{m1}(t_{i,2}(t - T))} \tag{19}$$

Combining equations (18) and (19) we arrive at the following result for the Dirac Delta function, where the functional dependence of the variable $t_{i,2}$ on $t-T$ has been dropped for clarity:

$$\delta(T - t + \nu - T_{m1}(\nu)) = \frac{\delta(\nu - t_{i,2})J(t_{i,2} - T_{m1}(t_{i,2}))}{Q_\Delta(t_{i,2})} \tag{20}$$

Substituting this last result into the integral appearing on the right hand side of equation (17) we obtain the following:

$$\int_0^t \delta(T - t + \nu - T_{m1}(\nu))e^{-\bar{\tau}(t,\nu)}Q_\Delta(\nu)\, d\nu$$
$$= \int_0^t \frac{\delta(\nu - t_{i,2})J(t_{i,2} - T_{m1}(t_{i,2}))}{Q_\Delta(t_{i,2})}e^{-\bar{\tau}(t,\nu)}Q_\Delta(\nu)\, d\nu = J(t - T)e^{-\bar{\tau}(t,t_{i,2})}$$

The last equal sign on the right hand side follows by invoking the combing property of the Dirac Delta function and applying the implicit equation, $t_{i,2} - T_{m1}(t_{i,2}) = t - T$, for the function $t_{i,2}(t - T)$. Substituting this last result into equation (17) we can write the derivative of the age-ranked storage for Tank 2 in the following compact form:

$$\frac{\partial S_{T2}}{\partial T} = (1 - p)S_0\delta(T - t - T_0)e^{-\bar{\tau}(t)} + J(t - T)e^{-\bar{\tau}(t,t_{i,2}(t-T))} \tag{21}$$

The first and second terms on the right hand side of this last result represent the contributions of old and new water, respectively, to the age structure of water leaving the vadose zone. Dropping the first term (for old water) and substituting the result into equation (16) we obtain the PDF form of the transit time distribution of new water exiting the vadose zone (equation (14) in the main text).

4 Plug Flow Sampling Limit

In this section we derive an expression for solute breakthrough under pure plug flow sampling. In this case, the age-ranked storage function can be easily derived by making the following replacements in equation (5) of the main text: $p \to 1$, $Q_\Delta(t) \to Q(t)$, $T_{m1}(t) \to T_m^{\mathrm{PF}}(t)$ and $t \to t_c^{\mathrm{PF}}$:

$$S_T^{\mathrm{PF}}(T,t) = \begin{cases} S_0 - \bar{Q}(t) + \bar{J}(t),\ T = T_0 + t \\ \bar{J}(t),\ t \leq T < T_0 + t \\ \bar{J}(t) - \bar{J}(t-T),\ 0 \leq T < t \end{cases} \qquad 0 \leq t \leq t_c^{\mathrm{PF}} \tag{22a}$$

$$S_T^{\mathrm{PF}}(T,t) = \bar{J}(t) - \bar{J}(t-T), \quad t > t_c^{\mathrm{PF}}, \quad 0 \leq T \leq T_m^{\mathrm{PF}}(t) \tag{22b}$$

Implicit solutions for the critical time at which all original water has drained from the vadose zone and the maximum age of water in the vadose zone under plug flow sampling are as follows:

$$S_0 = \bar{Q}(t_c^{\mathrm{PF}}) \tag{23a}$$

$$S(t) = \bar{J}(t) - \bar{J}(t - T_m^{\mathrm{PF}}(t)) \tag{23b}$$

The CDF and PDF forms of the age distribution in outflow are $P_Q^{\mathrm{PF}}(T,t) = H(T - T_m^{\mathrm{PF}}(t))$ and $p_Q^{\mathrm{PF}}(T,t) = \delta(T - T_m^{\mathrm{PF}}(t))$, respectively. Convolving the PDF form of the outflow age distribution with the inflow solute concentration and assuming that there is no solute in the original water, we arrive at the breakthrough concentration solution (equation (19a) in the main text):

$$C_Q^{\mathrm{PF}}(t) = \begin{cases} 0,\ 0 \leq t \leq t_c^{\mathrm{PF}} \\ C_J(t - T_m^{\mathrm{PF}}(t)),\ 0 \leq T_m^{\mathrm{PF}} < t,\ t > t_c^{\mathrm{PF}} \end{cases} \tag{24}$$

5 Uniform Sampling Limit

In this section we derive the expression for solute breakthrough under uniform sampling in the main text (equation (20a)). In this case, the ACE and associated initial and boundary conditions takes the form:

$$\frac{\partial S_T^{\mathrm{U}}}{\partial t} = J(t) - \frac{S_T^{\mathrm{U}}(T,t)}{S(t)}Q(t) - \frac{\partial S_T^{\mathrm{U}}}{\partial T} \tag{25a}$$

$$S_T^{\mathrm{U}}(T=0,t) = 0 \tag{25b}$$

$$S_T^{\mathrm{U}}(T,t=0) = S_0 H(T-T_0) \tag{25c}$$

Taking the Laplace Transform of these equations with respect to the age variable yields the following ordinary differential equation where r is the Laplace transform variable:

$$\frac{d\widetilde{S_T^{\mathrm{U}}}}{dt} = \frac{J(t)}{r} - \widetilde{S_T^{\mathrm{U}}}(r,t)\Big(\frac{Q(t)}{S(t)} + r\Big) \tag{26a}$$

$$\widetilde{S_T^{\mathrm{U}}}(r,t=0) = S_0\frac{e^{-rT_0}}{r} \tag{26b}$$

Equations (26a) and (26b) can be integrated to yield the following solution for the Laplace transform of the age-ranked storage function where t_i is a dummy integration variable:

$$\widetilde{S_T^{\mathrm{U}}}(r,t) = S_0\frac{e^{-r(t+T_0)}}{r}e^{-\bar{\tau}^{\mathrm{U}}(t)} + \int_0^t \frac{e^{-r(t-t_i)}}{r}e^{-(\bar{\tau}^{\mathrm{U}}(t)-\bar{\tau}^{\mathrm{U}}(t_i))}J(t_i)\,dt_i \tag{27a}$$

$$\bar{\tau}^{\mathrm{U}}(t) = \int_0^t \frac{Q(\nu)}{S(\nu)}d\,\nu \tag{27b}$$

Taking the inverse Laplace transform of this last result, we obtain the following solution for age-ranked storage in the vadose zone under uniform sampling for outflow:

$$S_T^{\mathrm{U}}(T,t) = S_0H(T-t-T_0)e^{-\bar{\tau}^{\mathrm{U}}(t)} + \int_0^t H(T-t+t_i)e^{-(\bar{\tau}^{\mathrm{U}}(t)-\bar{\tau}^{\mathrm{U}}(t_i))}J(t_i)\,dt_i \tag{28}$$

Under uniform sampling the age distribution of water in outflow is identical to the age distribution in storage. Therefore, the PDF form of the age distribution of water in outflow can be written as follows:

$$p_Q^{\mathrm{U}}(T,t) = \frac{1}{S(t)}\frac{\partial S_T^{\mathrm{U}}}{\partial T} \tag{29}$$

Taking the derivative of equation (28) and substituting it into equation (29) we arrive at the following expression for the PDF form of the age distribution of water in outflow:

$$p_Q^{\mathrm{U}}(T,t) = \frac{S_0\delta(T-t-T_0)}{S(t)}e^{-\bar{\tau}^{\mathrm{U}}(t)} + \frac{J(t-T)}{S(t)}e^{-(\bar{\tau}^{\mathrm{U}}(t)-\bar{\tau}^{\mathrm{U}}(t-T))} \tag{30}$$

Provided that the original water is solute free, the last result can be convolved with the inflow concentration to yield the expression in the main text (equation (20a)) for solute breakthrough concentration in outflow from the vadose zone under uniform sampling.