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

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Introduction This supporting information contains details on the derivation of age-ranked storage in Tank 1 (**Text S1**), a graphical interpretation of the age-ranked storage solution for Tank 1 (**Text S2**), derivation of age-ranked storage in Tank 2 (**Text S3**), a graphical interpretation of the age-ranked storage solution for Tank 2 (**Text S4**), derivation of the probability density function (PDF) form of the age distribution of water in outflow under shifted-uniform selection (**Text S5**), and derivation of age-ranked storage and solute breakthrough solutions under pure plug flow sampling (**Text S6**) and uniform sampling (**Text S7**).

Text S1. 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 (9a) and (9b) in the main text. In Tank 1 only the oldest water in storage is selected for discharge; i.e., a plug flow SAS applies, $\Omega_1(S_{T1}(T,t),t) = H(S_{T1}(T,t) - pS(t))$. Because the dependent variable appears inside the Heaviside function, the corresponding ACE is a non-linear partial differential equation. This non-linearity 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 equations (3a)-(3c) 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:

$$S_{T1}(T,t) = pS_0H(T-t-T_0) + \int_0^t H\left(T-t+\nu\right)J(\nu)\,d\nu - \int_0^t H\left(T-t-T_m(\nu)+\nu\right)Q_\Delta(\nu)\,d\nu$$

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

$$\begin{aligned} S_{T1}(T,t) = pS_0H(T-t-T_0) + \int_0^t J(\nu)\,d\nu - H(t-T)\int_0^{t-T} J(\nu)\,d\nu \\ - \int_0^t H\left(T-t+\nu-T_m(\nu)\right)Q_\Delta(\nu)\,d\nu \end{aligned} \quad (4)$$

From the discussion in Section 3.2 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 (12) 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:

$$\begin{aligned} S_{T1}(T,t\leq t_c) = pS_0H(T-t-T_0) + \int_0^t J(\nu)\,d\nu - H(t-T)\int_0^{t-T} J(\nu)\,d\nu \\ - H\left(T-t-T_0\right)\int_0^t Q_\Delta(\nu)\,d\nu \end{aligned}$$

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 (9a) 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 $0 \le \nu \le t_c$ 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:

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

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: $H\left(T - t - T_0\right) = 0$. 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, $H\left(T - t + \nu - T_{m1}(\nu)\right)$, 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 (9b) in the main text):

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

Thus, age-ranked storage in Tank 1 can be written as follows (equations (9a) and (9b) in the main text):

$$S_{T1}(T,t) = \begin{cases} pS_0 - \bar{Q}_\Delta(t) + \bar{J}(t), \ T = T_0 + t \\ \bar{J}(t), \ t \le T < T_0 + t \\ \bar{J}(t) - \bar{J}(t-T), \ 0 \le T < t \end{cases} \qquad 0 \le t \le t_c \tag{7a}$$

$$S_{T1}(T,t) = \bar{J}(t) - \bar{J}(t-T), \quad 0 \le T \le T_{m1}(t), \quad t > t_c \tag{7b}$$

The cumulative volume functions $\bar{J}(t)$, $\bar{Q}(t)$, and $\bar{Q}_\Delta(t)$ are defined as follows (equations (10a)-(10c) in the main text):

$$\bar{J}(t) = \int_0^t J(\nu)\, d\nu \tag{8a}$$

$$\bar{Q}(t) = \int_0^t Q(\nu)\, d\nu \tag{8b}$$

$$\bar{Q}_\Delta(t) = (1-p)\bar{J}(t) + p\bar{Q}(t) \tag{8c}$$

The critical time, t_c, at which all old water has drained from Tank 1 can be written as the time required to discharge all original water in Tank 1, pS_0 where S_0 is the volume of original water in the control volume (equation (12) in the main text):

$$pS_0 = \bar{Q}_\Delta(t_c) \tag{9}$$

Text S2. Graphical Interpretation of Solution for Tank 1 Age-ranked storage can be represented graphically as a vertical water column with height equal to the area-normalized volume of water in storage, ordered by age from youngest at the top to oldest at the bottom (Figure 1). The age-ranked storage function for Tank 1, $S_{T1}(T,t)$, then represents the portion of storage in Tank 1 at time t with ages T or younger (gray vertical arrow in Figures (S1a) and (S1b)). Different functional forms for the Tank 1 age-ranked storage function apply before and after the critical time (equation (7a) and (7b), respectively) and depending on the choice of the age variable, T. Prior to the critical time t_c, the age-ranked storage function consists of three separate solutions that apply over different ranges of T (Figure 1a). When the age variable is set equal to the maximum age of water in storage, $T = T_0 + t$ (top solution in equation (7a)), age-ranked storage includes all water in Tank 1 storage, including all new water that flowed into the vadose zone up to time t (volume (i), Figure (S1a)) plus the volume of original water that is still in Tank 1 (volume (iii) minus volume (iv), Figure (S1a)). When the age variable falls in the range, $t \leq T < T_0 + t$ (middle solution in equation (7a)), the age-ranked storage function includes all new water that flowed into the vadose zone up to time t (volume (i), Figure (S1a)). When the age variable falls in the range, $0 \leq T < t$ (bottom solution in equation (7a)), the age-ranked storage function includes only the portion of new water in storage with ages T or younger (volume (i) minus volume (ii), Figure (S1a)).

Past the critical time, $t > t_c$, all original water has been discharged to Tank 2, and therefore Tank 1 storage consists only of new water (Figure (S1b)). The corresponding solution for the Tank 1 age ranked storage function (equation (7b)) equals the total volume of new water that flowed into the vadose zone up to time t (volume (v), Figure (S1b)), minus the portion of that new water that flowed into the vadose zone up to time $t - T$ (volume (vi), Figure (S1b)).

A graphical interpretation can also be ascribed to the implicit solution for the maximum age of water in Tank 1 after the critical time (see equation (11) in the main text):

$$pS(t) = \bar{J}(t) - \bar{J}(t - T_{m1}(t)), \;\; t > t_c \tag{10}$$

The total storage present in Tank 1 at time t (left hand side of equation (10) and solid bordered box in Figure (S1b)) equals the cumulative volume of new water added up to time t (first term on the right hand side of equation (10) and volume (v) in Figure (S1b)) minus the cumulative volume of new water added up to time $t - T_{m1}(t)$ (second term on right hand side of equation (10) and volume (vii) in Figure (S1b)).

In summary, while the mathematics required to solve the ACE for Tank 1 are somewhat involved (Text 1 above), the final result (equations (7a) and (7b)) can be easily understood graphically as a kinematic problem involving the inflow and discharge of age-ranked water. Provided that the water balance over the vadose zone is known (i.e., time series for inflow $J(t)$, discharge $Q(t)$ and storage $S(t)$ are given), numerical implementation of the age-ranked storage function for Tank 1 involves three steps: (1) the critical time, t_c, is determined by solving for the root of equation (9); (2) for elapsed times less than the critical time, the maximum age of water in Tank 1 storage, $T_{m1}(t)$, is set equal to the sum of the initial age of original water plus elapsed time ($T_{m1}(t) = T_0 + t$), while past the critical time the maximum age of water in Tank 1 storage is obtained for any elapsed time of interest by solving for the root of equation (10); and (3) with these results, the age-ranked storage function can be calculated from the algebraic expressions listed in equations (7a) or (7b).

Text S3. 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:

$$\frac{\partial S_{T2}}{\partial t} = Q_\Delta(t)H(T - T_{m1}(t)) - \frac{S_{T2}(T,t)}{(1-p)S(t)}Q(t) - \frac{\partial S_{T2}}{\partial T} \tag{11a}$$

$$S_{T2}(T = 0, t) = 0 \tag{11b}$$

$$S_{T2}(T, t = 0) = (1-p)S_0 H(T - T_0) \tag{11c}$$

Taking the Laplace Transform of equations (11a) and (11c) 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:

$$\frac{d\widetilde{S_{T2}}}{dt} = Q_\Delta(t)\frac{e^{-rT_{m1}(t)}}{r} - \widetilde{S_{T2}}(r,t)\Big(\frac{Q(t)}{(1-p)S(t)} + r\Big) \tag{12a}$$

$$\widetilde{S_{T2}}(r, t = 0) = (1-p)S_0\frac{e^{-rT_0}}{r} \tag{12b}$$

Note that the boundary condition on the ACE for Tank 2 (equation (11b)) has been incorporated into equation (12a). Equations (12a) and (12b) 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:

$$\widetilde{S_{T2}}(r,t) = (1-p)S_0\frac{e^{-r(t+T_0)}}{r}e^{-\bar{\tau}(t)} + \int_0^t \frac{e^{-r(t+T_{m1}(\nu)-\nu)}}{r}e^{-\bar{\tau}(t,\nu)}Q_\Delta(\nu)\,d\nu \tag{13a}$$

$$\bar{\tau}(t) = \int_0^t \frac{Q(\nu)}{(1-p)S(\nu)}d\,\nu \tag{13b}$$

$$\bar{\tau}(t,\nu) = \int_\nu^t \frac{Q(\nu)}{(1-p)S(\nu)}d\,\nu = \bar{\tau}(t) - \bar{\tau}(\nu) \tag{13c}$$

Here, discharge weighted time functions, $\bar{\tau}(t)$ and $\bar{\tau}(t,\nu)$ are defined as follows:

$$\bar{\tau}(t) = \int_0^t \frac{Q(r)}{(1-p)S(r)}\,dr \tag{14a}$$

$$\bar{\tau}(t,\nu) = \bar{\tau}(t) - \bar{\tau}(\nu) \tag{14b}$$

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

$$
\begin{aligned}
S_{T2}(T,t) = (1-p)S_0 H(T-t-T_0)e^{-\bar{\tau}(t)} \\
+ \int_0^t H(T-t+\nu-T_{m1}(\nu))e^{-\bar{\tau}(t,\nu)}Q_\Delta(\nu)\,d\nu
\end{aligned}
\quad (15)
$$

The functional form this solution takes (equations (13a) and (13b) 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.

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

0.1.1. Solution for $t \le t_c$ 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 (3c) 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 (15) we obtain the following:

$$
S_{T2}(T,t) = (1-p)S_0 H(0)e^{-\bar{\tau}(t)} + \int_0^t H(0)e^{-\bar{\tau}(t,\nu)}Q_\Delta(\nu)\,d\nu,\ T = T_0 + t,\ 0 \le t \le t_c \quad (16)
$$

Setting $H(0) = 1$, we arrive at the upper solution in equation (13a) of the main text:

$$
S_{T2}(T,t) = (1-p)S_0 e^{-\bar{\tau}(t)} + \int_0^t e^{-\bar{\tau}(t,\nu)}Q_\Delta(\nu)\,d\nu,\ T = T_0 + t,\ 0 \le t \le t_c \quad (17)
$$

0.1.2. Solution for $t \le t_c$ 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 (15) are negative and therefore the lower solution in equation (13a) of the main text applies:

$$S_{T2}(T,t) = 0,\ T < T_0 + t,\ 0 \leq t \leq t_c \tag{18}$$

0.2. 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.

0.2.1. 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 (15) reduce to unity and the upper solution in equation (13a) of the main text applies:

$$S_{T2}(T,t) = (1-p)S_0 e^{-\bar{\tau}(t)} + \int_0^t e^{-\bar{\tau}(t,\nu)} Q_\Delta(\nu)\, d\nu,\ T = T_0 + t,\ t > t_c \tag{19}$$

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.

0.2.2. 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 (15) 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:

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

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, $\nu \le t_c$, 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:

$$S_{T2}(T,t) = \int_{t_c}^{t} H(T - t + \nu - T_{m1}(\nu))e^{-\bar{\tau}(t,\nu)}Q_\Delta(\nu)\,d\nu,\ T < T_0 + t,\ t > t_c \qquad (20)$$

Finally, for the age range stipulated, $t \le T < T_0 + t$, the Heaviside function appearing on the right hand side of equation (20) 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, $\nu \ge t_c$ and therefore the following inequality applies to the maximum age of water in Tank 1: $T_{m1}(\nu) \le \nu$. This last inequality together with the stipulation that, $T \ge t$, implies that the argument of the Heaviside function will always be equal to or greater than zero: $T - t + \nu - T_{m1}(\nu) \ge 0$. Hence, the Heaviside function appearing in equation (20) is unity over the full integration range and the second solution in equation (13b) of the main text applies:

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

0.2.3. Solution for $t > t_c$ and $T_{m1}(t) \le T < t$

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 (20). 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, $\nu = t_{\mathrm{BT}}$, of the equation, $t_{\mathrm{BT}} - T_{m1}(t_{\mathrm{BT}}) = t - T$, where $t_{\mathrm{BT}} > t_c$. For values of the dummy integration variable greater than or equal to this root, $\nu \ge t_{\mathrm{BT}}$, 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 (13b) of the main text, where the root t_{BT} is a function solely of $t - T$:

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

0.2.4. Solution for $t > t_c$ and $0 \le T < T_{m1}(t)$

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 (20). 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 (20) 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 (13b) of the main text:

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

Text S4. Graphical Interpretation of Solution for Tank 2 A graphical interpretation of the Tank 2 age-ranked storage function is presented in Figure S2. Prior to the critical time, $t \leq t_c$, water in Tank 2 consists solely of original water of age $T = T_0 + t$ (Figure S2a). This original water can be divided into the portion that was initially present in Tank 2 at time $t = 0$, $S_{0,2}(t)$, and the portion that was initially present in Tank 1 but transferred to Tank 2 over time t, $S_{0,1}(t)$.

A solution for the function, $S_{0,2}(t)$, can be derived by noting that, under uniform sampling, the discharge rate of original water initially present in Tank 2 is proportional to both the total discharge rate, $Q(t)$, and the fraction of Tank 2 storage still occupied by that original water (Figure S2a):

$$\frac{dS_{0,2}}{dt} = \frac{S_{0,2}(t)}{(1-p)S(t)}Q(t) \tag{21}$$

Applying the initial condition, $S_{0,2}(t=0) = (1-p)S_0$, equation (21) can be integrated to yield the first term on the right hand side of the upper solution in equation (13a) of the main text: $S_{0,2}(t) = (1-p)S_0 e^{-\bar{\tau}(t)}$ (see lower portion of age-ranked storage in Figure S2a). Thus, the portion of original water that was initially present in Tank 2 at time $t = 0$ decays exponentially with discharge-weighted time.

A solution for the function, $S_{0,1}(t)$, can be derived by noting that the product $Q_\Delta(\nu)d\nu$ represents the differential volume of water transferred from Tank 1 to 2 over the time increment $d\nu$. Furthermore, by reference to the above solution for $S_{0,2}(t)$, following its introduction to Tank 2 at time ν, the portion of this differential volume of water remaining in Tank 2 will decay exponentially with discharge-weighted time, $dS_{0,1} = Q_\Delta(\nu)d\nu e^{-\bar{\tau}(t,\nu)}$. Integrating over all differential volumes of original water entering Tank 2 up to time t, we arrive at the second term on the right hand side of the upper solution in equation (13a) in the main text: $S_{0,1}(t) = \int_0^t e^{-\bar{\tau}(t,\nu)} Q_\Delta(\nu)\, d\nu$. The boundary between $S_{0,1}(t)$ and $S_{0,2}(t)$ in Figure (S2a) marks the location, in age-ranked storage, of the first parcel of original water that was transferred from Tank 1 to Tank 2 at time $t = 0$.

The bottom solution in equation (13a) of the main text, $S_T(T < T_0 + t, t) = 0$ can be understood as follows. Prior to the critical time, all water in Tank 2 is original water. Therefore, by definition the age-ranked storage in Tank 2 is zero for any choice of the age variable less than the age of original water, $0 \leq T < T_0 + t$.

A similar line of reasoning can be used to derive the four separate solutions for age-ranked storage in Tank 2 after the critical time, $t > t_c$ (equation (13b) in the main text and Figure S2b above).

The top solution in equation (13b) of the main text applies when the age variable is set equal to the maximum age of water in the vadose zone, $T = T_0 + t$. In this case, the age-ranked storage for Tank 2 includes all water in Tank 2 ($S_2(t)$ in Figure (S2b)), including contributions from original water initially present in Tank 2 and all original and new water transferred into Tank 2 from Tank 1 up to time t.

The second solution in equation (13b) of the main text applies when the age variable falls in the range $t \leq T < T_0 + t$. In this case the age-ranked storage function excludes all original water (of age $T = T_0 + t$) but includes all new water transferred into Tank 2 from Tank 1 of age $T \leq t$. The lower integration limit is therefore the critical time, t_c, when new water first entered Tank 2 from Tank 1 (Figure (S2b)).

The third solution in equation (13b) of the main text applies when the age variable falls in the range $T_{m1}(t) \leq T < t$. In this case, age-ranked storage for Tank 2, $S_{T2}(T, t)$, includes only the portion of new water in Tank 2 that is of age T or younger at time t (i.e., the portion of age-ranked storage above the grey horizontal dashed line, Figure (S2b)). The lower integration limit is therefore the Tank 2 entrance time, $t_{\mathrm{BT}}(t_i)$, of a water parcel that entered Tank 1 at time $t_i = t - T$. As outlined in the main text (see equation (15b) in the main text and discussion thereof), this initial "breakthrough time" can be estimated from the following implicit equation:

$$t_{\mathrm{BT}} - T_{m1}(t_{\mathrm{BT}}) = t - T = t_i,\ t > t_c,\ T_{m1}(t) \leq T < t \tag{22}$$

Finally, at time t all water in Tank 2 will be older than the maximum age of water in Tank 1, $T_{m1}(t)$. Therefore the Tank 2 age-ranked storage function is equal to zero for any choice of the age variable less than the maximum age of water in Tank 1 (fourth solution in equation (13b) in the main text).

Practical implementation of the age-ranked storage solution for Tank 2 entails four steps: (1) integrate equation (14a) to obtain a time series of discharge-weighted time, $\bar{\tau}(t)$, over the elapsed time interval [0,t]; (2) using the result from step (1), calculate the discharge-weighted time over any elapsed time interval [ν,t] (equation (14b)); (3) if the elapsed time of interest is past the critical time, find the root of equation (22) to obtain the elapsed time a water parcel breakthrough to Tank 2, $t_{\mathrm{BT}}(t_i)$, conditioned on the same water parcel entering Tank 1 at elapsed time, $t_i = t - T$; and (4) given the results from steps (1) through (3), numerically evaluate the appropriate solution for age-ranked storage depending on whether the elapsed time is before or after the critical time (equations (13a) or (13b), main text), and the choice of the age variable T.

Text S5. PDF form of the Age Distribution in Outflow In this section we derive the PDF form of the age distribution of water leaving the control volume 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:

$$p_{Q2}(T,t) = \frac{1}{(1-p)S(t)} \frac{\partial S_{T2}}{\partial T} \tag{23}$$

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 (15)), its derivative with respect to age can be written as follows where $\delta(\cdot)$ is the Dirac Delta function:

$$\begin{aligned}\frac{\partial S_{T2}}{\partial T} &= (1-p)S_0\delta(T-t-T_0)e^{-\bar{\tau}(t)} \\ &\quad + \int_0^t \delta(T-t+\nu-T_{m1}(\nu))e^{-\bar{\tau}(t,\nu)}Q_\Delta(\nu)\,d\nu\end{aligned} \tag{24}$$

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 (11) 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 $t_{\mathrm{BT}}(t-T)$ is the single root of the equation, $t_{\mathrm{BT}} - T_{m1}(t_{\mathrm{BT}}) = t - T$ for times greater than the critical time, $t > t_c$, and the maximum age is bounded as follows, $0 \le T_{m1}(\nu) \le \nu$ (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):

$$\delta(T - t + \nu - T_{m1}(\nu)) = \frac{\delta(\nu - t_{\mathrm{BT}}(t-T)}{1 - T'_{m1}(t_{\mathrm{BT}}(t-T))} \tag{25}$$

As noted in the main text, the function $t_{\mathrm{BT}}(t-T)$ 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 $1 - T'_{m1}(t_{\mathrm{BT}})$ 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 (11) 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 control volume) 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 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 (26), 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 (7) in the main text).

$$1 - T'_{m1}(t_{\mathrm{BT}}(t-T)) = \frac{Q_\Delta(t_{\mathrm{BT}}(t-T))}{J(t_{\mathrm{BT}}(t-T) - T_{m1}(t_{\mathrm{BT}}(t-T))} \tag{26}$$

Combining equations (25) and (26) we arrive at the following result for the Dirac Delta function, where the functional dependence of the variable t_{BT} on $t-T$ has been dropped for clarity:

$$\delta(T - t + \nu - T_{m1}(\nu)) = \frac{\delta(\nu - t_{\mathrm{BT}})J(t_{\mathrm{BT}} - T_{m1}(t_{\mathrm{BT}}))}{Q_\Delta(t_{\mathrm{BT}})} \tag{27}$$

Substituting this last result into the integral appearing on the right hand side of equation (24) we obtain the following:

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

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, $t_{\mathrm{BT}} - T_{m1}(t_{\mathrm{BT}}) = t - T$, for the function $t_{\mathrm{BT}}(t-T)$. Substituting this last result into equation (24) we can write the derivative of the age-ranked storage for Tank 2 in the following compact form:

$$\frac{\partial S_{T2}}{\partial T} = (1-p)S_0\delta(T - t - T_0)e^{-\bar{\tau}(t)} + J(t-T)e^{-\bar{\tau}(t,t_{\mathrm{BT}}(t-T))} \tag{28}$$

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 control volume. Dropping the first term (for old water) and substituting the result into equation

(23) we obtain the PDF form of the transit time distribution of new water exiting the vadose zone (equation (16) in the main text).

Text S6. Age Ranked Storage and Solute Transport in the Plug Flow Sampling Limit In this section we derive an expression for age-ranked storage and 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 equations (7a) and (7b) in Section 1: $p \to 1$, $Q_\Delta(t) \to Q(t)$, $T_{m1}(t) \to T_m^{\mathrm{PF}}(t)$ and $t \to t_c^{\mathrm{PF}}$:

$$S_T^{\mathrm{PF}}(T,t) = \begin{cases} S_0 - \bar{Q}(t) + \bar{J}(t), \; T = T_0 + t \\ \bar{J}(t), \; t \le T < T_0 + t \\ \bar{J}(t) - \bar{J}(t-T), \; 0 \le T < t \end{cases} \quad 0 \le t \le t_c^{\mathrm{PF}} \tag{29a}$$

$$S_T^{\mathrm{PF}}(T,t) = \bar{J}(t) - \bar{J}(t-T), \quad t > t_c^{\mathrm{PF}}, \quad 0 \le T \le T_m^{\mathrm{PF}}(t) \tag{29b}$$

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:

$$S_0 = \bar{Q}(t_c^{\mathrm{PF}}) \tag{30a}$$

$$S(t) = \bar{J}(t) - \bar{J}(t - T_m^{\mathrm{PF}}(t)) \tag{30b}$$

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 (equations (22a)-(22c) in the main text):

$$C_Q^{\mathrm{PF}}(t) = \begin{cases} 0, \; 0 \le t \le t_c^{\mathrm{PF}} \\ C_J(t - T_m^{\mathrm{PF}}(t)), \; 0 \le T_m^{\mathrm{PF}} < t, \; t > t_c^{\mathrm{PF}} \end{cases} \tag{31}$$

Text S7. Age Ranked Storage and Solute Transport in the Uniform Sampling Limit In this section we derive the expression for solute breakthrough under uniform sampling in the main text (equations (23a) and (23b)). In this case, the ACE and associated initial and boundary conditions takes the form:

$$\frac{\partial S_T^{\mathrm{U}}}{\partial t} = J(t) - \frac{S_T^{\mathrm{U}}(T,t)}{S(t)}Q(t) - \frac{\partial S_T^{\mathrm{U}}}{\partial T} \tag{32a}$$

$$S_T^{\mathrm{U}}(T=0,t) = 0 \tag{32b}$$

$$S_T^{\mathrm{U}}(T,t=0) = S_0 H(T-T_0) \tag{32c}$$

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:

$$\frac{d\widetilde{S_T^{\mathrm{U}}}}{dt} = \frac{J(t)}{r} - \widetilde{S_T^{\mathrm{U}}}(r,t)\Big(\frac{Q(t)}{S(t)} + r\Big) \tag{33a}$$

$$\widetilde{S_T^{\mathrm{U}}}(r,t=0) = S_0\frac{e^{-rT_0}}{r} \tag{33b}$$

Equations (33a) and (33b) 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:

$$\widetilde{S_T^{\mathrm{U}}}(r,t) = S_0\frac{e^{-r(t+T_0)}}{r}e^{-\bar{\tau}^{\mathrm{U}}(t)} + \int_0^t \frac{e^{-r(t-t_i)}}{r}e^{-(\bar{\tau}^{\mathrm{U}}(t)-\bar{\tau}^{\mathrm{U}}(t_i))}J(t_i)\,dt_i \tag{34a}$$

$$\bar{\tau}^{\mathrm{U}}(t) = \int_0^t \frac{Q(\nu)}{S(\nu)}d\,\nu \tag{34b}$$

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:

$$S_T^{\mathrm{U}}(T,t) = S_0 H(T-t-T_0)e^{-\bar{\tau}^{\mathrm{U}}(t)} + \int_0^t H(T-t+t_i)e^{-(\bar{\tau}^{\mathrm{U}}(t)-\bar{\tau}^{\mathrm{U}}(t_i))}J(t_i)\,dt_i \tag{35}$$

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:

$$p_Q^{\mathrm{U}}(T,t) = \frac{1}{S(t)}\frac{\partial S_T^{\mathrm{U}}}{\partial T} \tag{36}$$

Taking the derivative of equation (35) and substituting it into equation (36) we arrive at the following expression for the PDF form of the age distribution of water in outflow:

$$p_Q^{\mathrm{U}}(T,t) = \frac{S_0\delta(T-t-T_0)}{S(t)}e^{-\bar{\tau}^{\mathrm{U}}(t)} + \frac{J(t-T)}{S(t)}e^{-(\bar{\tau}^{\mathrm{U}}(t)-\bar{\tau}^{\mathrm{U}}(t-T))} \tag{37}$$

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 (23a)) for solute breakthrough concentration in outflow from the vadose zone under uniform sampling.

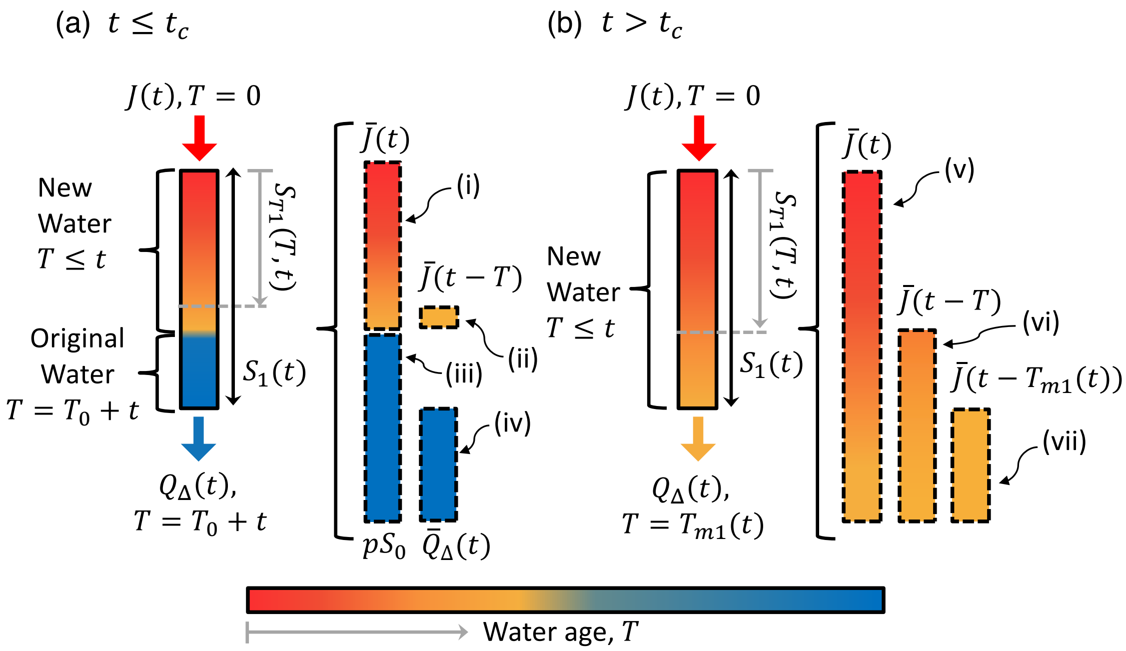

Figure S1. A graphical representation of the Tank 1 solution for age-ranked storage under plug flow sampling. The vertical columns with a solid border represent the total volume of water (per unit area) present in Tank 1 at any time t, $S_1(t) = pS(t)$. Age-ranked storage in Tank 1, $S_{T1}(T, t)$, is defined as the volume of water (per unit area) in Tank 1 storage of age T or younger at time, t (grey arrow). Cumulative and instantaneous flows are represented, respectively, with and without an overbar. (a) Prior to the critical time, $t \leq t_c$, the storage in Tank 1 consists of both original water (of age $T = T_0 + t$) and new water (of age $T \leq t$) that entered the vadose zone as inflow. The solution for age-ranked storage in this time range (equation (7a)) depends on four separate cumulative volumes represented graphically by vertical columns with dashed borders (labeled (i), (ii), (iii) and (iv)). (b) After the critical time, $t > t_c$, the storage in Tank 1 consists only of new water (of age $T \leq t$). The solution for age-ranked storage (equation (7b)) and implicit relationship for the maximum age (equation (10)) depend on three cumulative volumes (vertical columns with dashed borders labeled (v), (vi) and (vii)).

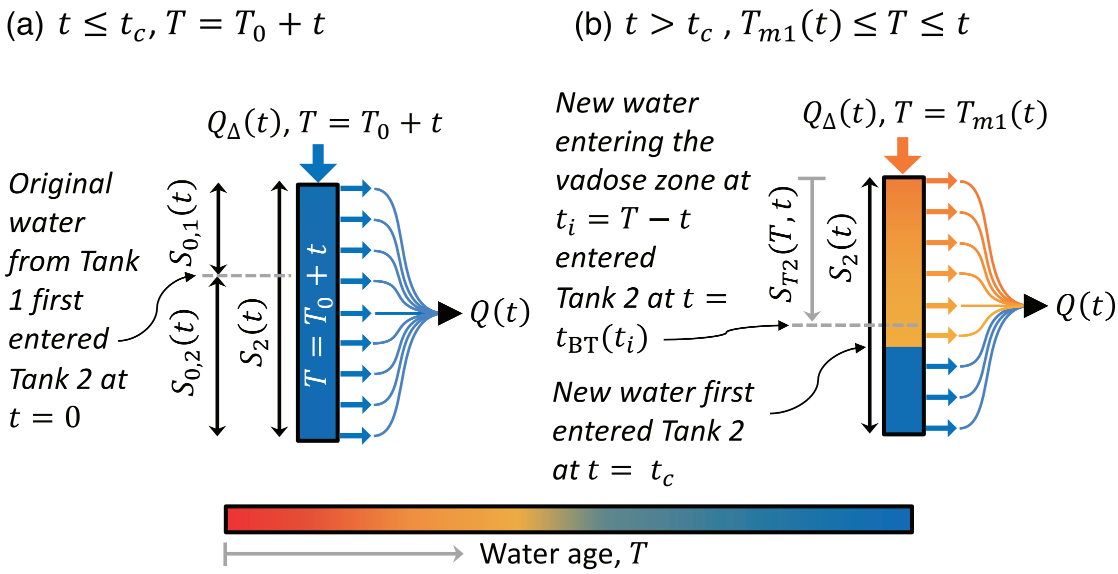

Figure S2. A graphical representation of the Tank 2 solution for age-ranked storage. (a) Before the critical time, only original water of age $T = T_0 + t$ is present in Tank 2 storage, including original water initially present in Tank 1 ($S_{0,1}(t)$) and original water that was initially present in Tank 2 ($S_{0,2}(t)$). (b) After the critical time, age-ranked storage in Tank 2 will always include some original water of age $T = T_0 + t$ (dark blue) plus new water that entered Tank 2 after elapsed time $t = t_c$. The time $t_{\mathrm{BT}}(t_i)$, which represents the Tank 2 entrance time of a water parcel that entered Tank 1 at time $t_i = t - T$, can be estimated by solving for the root of equation (22).