California GAMA Special Study:
Groundwater Age Simulation and Deconvolution Methods for
Interpretation of $^3$H-$^3$He Data

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GAMA Special Studies Task 9.3:
Combining groundwater age and introduced tracer results to determine contaminant transport rates to drinking water wells
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Methods for Interpretation of $^3$H-$^3$He Data

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Executive Summary

Under the State Water Resources Control Board’s Groundwater Ambient Monitoring and Assessment (GAMA) Program many hundreds of tritium and helium-3 concentrations in drinking water well samples have been measured to derive estimates of $^3$H-$^3$He groundwater age for drinking water supplies in California basins. Calculated groundwater ages provide valuable information about the susceptibility of drinking water wells to contamination.

Using the $^3$H-$^3$He system to constrain groundwater susceptibility and contaminant transport, however, requires understanding how this system deviates from ideal tracer behavior. Water wells capture a distribution of groundwater sources and, hence, groundwater samples from these wells contain a distribution of groundwater ages. Age distribution is of particular importance to understanding susceptibility – certain contaminants (e.g. pathogens) are of concern even at very low concentrations that might result from small contributions of “young” groundwater transported along fast paths. In this study, we further refined our ability to deconvolve $^3$H-$^3$He groundwater age distributions using a generalized method for modeling gas-liquid phase transport of isotopic tracers.

The Gas Liquid Flow–Multi-Component Transport (GLF-MCT) method explicitly considers the gas and liquid phase properties of $^3$H and $^3$He, and simulates their transport in both unsaturated and saturated conditions. The method can replicate previous particle-tracking methods for simulating mean groundwater age, and allows direct comparison of apparent $^3$H-$^3$He groundwater age with advective (piston flow) groundwater age. The new modeling shows that mixing of $^3$H from near the bomb-pulse peak can cause $^3$H-$^3$He ages to converge toward 30+ years with apparently high “pre-modern” fractions. Therefore, groundwater modelers are advised, when calibrating to older $^3$H-$^3$He age data, to use $^3$H-$^3$He properties that account for the bomb pulse, including unsaturated flow with gas-liquid phase equilibrium, macrodispersion, and molecular diffusivity.
Introduction

Isotopic methods for estimation of groundwater age are attractive for estimation of rate-dependent quantities in aquifer systems - flow velocity, residence time, discharge, and recharge. Consequently, there is need to better integrate isotopic groundwater age dating techniques into interpretation of groundwater flow and transport processes. Appendix A discusses the fundamentals utility of groundwater age data for groundwater flow models.

In practice, groundwater age estimates determined from isotopic tracers cannot always be interpreted by an advection-only or a “piston flow” conceptual model (Bethke and Johnson, 2002; Bethke and Johnson, 2008). In particular, isotopic reactions and properties combined with diffusion, hydrodynamic dispersion, and large scale mixing processes lead to non-idealities in translating isotopic data to groundwater age estimates. Large scale mixing processes include flow convergence and flow transients. Flow convergences occur at, for example, well-screens and discharge points such as streams or springs. Flow transients result from, for example, pumping schedules and seasonal and annual variations in recharge.

The $^3$H-$^3$He groundwater age dating method is useful for estimating groundwater residence time within a timeframe of about five tritium half-lives, or 50 years (see Appendix B). The processes and properties that control $^3$H and $^3$He transport have disadvantages and advantages compared to an ideal tracer for mean groundwater age (Goode, 1996).

Disadvantages include:

- Unlike the ingrowth of “age mass”, which accumulates at a rate independent of groundwater chemical or isotopic properties (Goode, 1996), the accumulation of $^3$He is directly proportional to groundwater $^3$H activity.
- The tritium source term varies over time.
- Helium has a different molecular diffusivity than water.

Advantages include:

- Tritium exists mostly as tritiated water (HTO), physically and chemically practically identical to non-tritiated water.
- The phase equilibrium properties of the noble gas helium are much different than water, which enables groundwater residence times to be dated from the water table instead of the ground surface.

While methods for directly simulating mean groundwater age have been developed (Goode, 1996), consideration of the chemical and physical properties of isotopic tracers has not been thoroughly incorporated into groundwater flow and transport models. Likewise, Cook and Bohlke (2000) and Bohlke (2002) use assumed groundwater age distributions (e.g., piston flow, exponential, binary or combinations of piston flow and exponential or binary) in ‘lumped parameter’ models and compare model values to measured tracer concentrations to determine likely age distributions, but do not generate unique age distributions based on tracer properties. In particular, unsaturated flow processes have not been addressed in $^3$H-
$^3$He transport. Our study shows that tritium and helium transport processes can be simulated using a coupled gas-liquid phase flow and multi-component (e.g., water, air, $^3$H, $^3$He) reactive transport model. The reactive transport simulation framework offers direct means to constrain the groundwater flow processes controlling observed $^3$H-$^3$He distributions and, subsequently, a direct method to compare apparent $^3$H-$^3$He age with mean or advective groundwater age.

**Mean Groundwater Age**

The concept of mean groundwater age (Goode, 1996) is a useful starting point for understanding the non-idealities in groundwater age estimation from isotopic data. The mean groundwater age is conceptualized as the arithmetic mean age of mixture groundwater parcels of equal mass but different ages. Goode (1996) shows that mean groundwater age can be directly simulated by applying the advection-dispersion equation to transport of “age mass”, $A$, by Equation (1).

$$\begin{align*}
\frac{\partial A}{\partial t} &= -\nabla \cdot A \frac{q}{\theta} + \nabla \cdot D \cdot \nabla A + 1 + \frac{F}{\theta \rho} \\
\end{align*}$$

where:

$q =$ groundwater flux vector  
$D =$ dispersion tensor  
$\theta =$ moisture content (porosity under saturated conditions)  
$\rho =$ density of the groundwater

The constant rate (zero-order) internal source term of magnitude 1 simulates the linear accumulation of “age mass” with time. Fluxes, $F$, account for exchange with different phases or sources or sinks of water having non-zero age.

Under the simple case of $q = 0$ (no advection), $D = 0$ (no dispersion), and $F = 0$ (no external sources), Equation (1) reduces to a zero-order (constant) rate equation where $A$ accumulates at a constant rate over time by

$$\frac{\partial A}{\partial t} = 1. \quad (2)$$

Equation (2) can be applied directly to the reference frame of an isolated packet of migrating groundwater, where advection, dispersion, and external sources remain zero (Figure 1).
Groundwater age within the isolated packet can be modeled by zero-order (constant rate) “reaction” process that accumulates “age mass” at a constant rate over time. By setting the constant to “1”, the magnitude of $A$ scales directly to the residence time of the packet. The mean groundwater age, $\overline{A}$, for mixtures of groundwater packets of mass, $m_i$, is equivalent to the mass-weighted mean of ages, $A_i$, for the multiple ($N$) packets of groundwater.

$$\overline{A} = \sum_{i=1}^{N} \frac{A_i m_i}{\sum_{i=1}^{N} m_i} .$$  \hspace{1cm} (3)

**Comparison of $^3\text{H}$-$^3\text{He}$ Age Date to Mean Groundwater Age**

Tritium ($^3\text{H}$) is a very low abundance radioactive isotope of hydrogen (around 1 part in $10^{17}$ of total hydrogen) with a half-life of 12.3 years (Lucas and Unterweger, 2000). Measurement of both tritium and its daughter product helium-3 ($^3\text{He}$) allows calculation of apparent groundwater age by assuming a “piston flow” conceptual model (Figure 1, Appendix B), which is identical to the assumption of $^3\text{H}$ and $^3\text{He}$ transport by pure advection. Goode (1996) shows that mean groundwater age is identical to advective age only if dispersion and diffusion are zero. Once mixing processes are present, the distribution of a tracer, even an ideal tracer, in groundwater will deviate from the distribution predicted by a “piston flow” model. Additionally, there are three major differences in $^3\text{H}$-$^3\text{He}$ properties compared to an ideal tracer of mean groundwater age:

**Figure 1.** Conceptual model of a “piston flow” or isolated packet of groundwater migrating through an aquifer from recharge to discharge points along a streamline "l". From Bethke and Johnson (2008).
1. **First Order Decay Process**: Tritium decay and $^3$He accumulation are first-order processes with respect to groundwater tritium activity, unlike the zero-order process of age mass accumulation described in Equation (2). The rate at which age mass accumulates is zero order because age mass accumulates at a constant rate independent of groundwater chemical or isotopic composition. The absolute rates at which $^3$He accumulates and $^3$H decays are first-order because they are directly proportional to the groundwater activity of $^3$H through the radioactive decay of $^3$H to $^3$He. Even if the source concentration of $^3$H is constant (i.e. the initial activity of $^3$H in recharging water is not a function of recharge year), the first-order radioactive decay process causes a non-constant rate of $^3$He accumulation in the migrating packet of groundwater. As a result, the mean of $^3$H-$^3$He ages of individual packets of groundwater will not equal the $^3$H-$^3$He age measured for the collective packet (Tompson et al., 1999).

2. **Time Variation of Tritium Source**: Natural tritium is produced in the earth’s atmosphere by cosmic radiation. Atmospheric nuclear weapons testing in the 1950’s and early 1960’s released tritium to the atmosphere at levels several orders of magnitude above the background concentration, so that the source mass of $^3$H introduced into to the groundwater system varies over time and, therefore, the mass of $^3$H and $^3$He in groundwater tends to be weighted toward the origin of peak input of $^3$H.

3. **Variably-Saturated Conditions**: Equation (1) can account for variably saturated conditions. However, typical groundwater flow and transport models restricted to single-phase flow processes cannot address $^3$H and $^3$He transport processes in the vadose zone and, consequently, will initiate groundwater age and $^3$H source concentration at the ground surface and not at the water table. The standard model for $^3$H-$^3$He groundwater age, however, assumes that the clock is set (i.e. $^3$He accumulation begins) at or immediately below the water table, not at the ground surface. A gas-liquid phase flow and transport model is needed to simulate $^3$H-$^3$He transport processes with consideration of the vadose zone.

**FIRST ORDER DECAY PROCESS**

In $^3$H to $^3$He decay assuming a 12.32 year half-life, $^3$He is formed from $^3$H in a first-order process

$$\frac{\partial [^3He]}{\partial t} = -\frac{\partial [^3H]}{\partial t} = \alpha [^3H]. \quad (4)$$

where

$$\alpha = \frac{\ln(2)}{12.32 \text{ years}} = \frac{1}{17.8 \text{ years}}$$

The difference between Equation (4) and Equation (2) is the first fundamental non-ideality between the $^3$H-$^3$He age dating and mean groundwater age transport processes.
In $^3$H-$^3$He apparent age interpretation, $^3$H and $^3$He concentrations derived from a tritium source concentration, $[^3H_0]$, vary over time as

\[
[^3H] =[^3H_0] e^{-\alpha t}
\]

\[
[^3He] =[^3H_0] -[^3H] =[^3H_0][1 - e^{-\alpha t}]
\]

where

\[
[^3H_0] =\text{concentration of } ^3\text{H at the initiation of recharge to the saturated zone.}
\]

As $^3$H decays to $^3$He over time, $t$, the $^3$H-$^3$He ratio evolves as

\[
\frac{[^3He]}{[^3H]} = \frac{1 - e^{-\alpha t}}{e^{-\alpha t}} = e^{\alpha t} - 1.
\]

The $^3$H-$^3$He apparent age, $\tilde{A}$, in years is derived from

\[
\tilde{A} = 17.8 \ln \left(1 + \frac{[^3He]}{[^3H]}\right). \quad (5)
\]

The first order decay process of Equation (4) leads to non-linearity of $\tilde{A}$ for mixtures of groundwater packets. For example, consider a mixture of two packets with equivalent mass and $[^3H_0]$

- Packet 1: $[^3He] = 0$ and $[^3H] = [^3H_0]$ resulting in $\tilde{A} = 0$, and
- Packet 2: $[^3He] = [^3H_0]$ and $[^3H] = 0$ resulting in $\tilde{A} > 50$ years.

Using Equation (3), Equation (5) applied to the mixture will yield an apparent groundwater age $\tilde{A} = 12.32$ years, while the mean groundwater age for the two parcels is greater than 25 years. Any mixing process will lead to difference between a $^3$H-$^3$He groundwater age, $\tilde{A}$, and the mean groundwater age, $\bar{A}$, because the $^3$H-$^3$He decay process in Equation (4) differs from the zero-order mass accumulation process of Equation (2) for the mean groundwater age tracer.

**TIME VARIATION OF $^3$H SOURCE**

Tritium is produced through cosmic ray reactions in the upper atmosphere at a relatively constant rate. Atmospheric nuclear weapons testing released large quantities of tritium into the atmosphere, resulting in precipitation with tritium levels up to three orders of magnitude
above the cosmogenic background for a short period of time centered on 1963 and known as the “bomb pulse” (see Appendix B). As a result, the concentration of tritium in recharging surface waters will be variable in time, and the tritium concentration in groundwaters will be a function of the recharge year, residence time in the vadose zone, and groundwater age.

Assuming piston flow with no dispersion or mixing, the use of Equation (5) circumvents the problem of time variability of bomb-pulse $^3$H by formulating the age of a groundwater parcel in terms of the $^3$H-$^3$He ratio only. Since tritiogenic $^3$He in groundwater refers is determined by subtracting out the atmospheric $^3$He component, the ratio of tritiogenic $^3$He to $^3$H is effectively zero in atmospherically-equilibrated recharging waters and the ratio in groundwater is only a function of age or residence time.

Mixing between “bomb pulse” groundwater and younger groundwater, however, will enrich the mixed groundwater with $^3$H and $^3$He derived from the bomb pulse peak, and skew the apparent $^3$H-$^3$He age, $\tilde{\tau}$, toward the bomb pulse in the early 1960s. For example, mixing of equal masses of a zero-age groundwater with the tritium activity of modern precipitation ($\sim 10$ pCi/L) and a 45-year old groundwater with the initial tritium activity of the 1963 precipitation in Ottawa, Canada, produces a groundwater with a $^3$H-$^3$He apparent age of 43 years.

**VARIABLY SATURATED CONDITIONS**

The properties of helium favor much higher partitioning (compared to water) of $^3$He into the gas phase relative to the liquid phase, while $^3$H (mostly as HTO) behaves much like water. Within the vadose zone, tritiogenic $^3$He will largely partition and subsequently dissipate into the gas phase. As a result, a $^3$H-$^3$He groundwater age pertains to residence time in the saturated zone because tritiogenic $^3$He concentration in the vadose zone is effectively zero. Tritiogenic liquid phase $^3$He concentrations in the vadose zone will yield $\tilde{\tau} \cong 0$ from Equation (4) unless $^3$He is anomalously present under variably saturated conditions.

The relationship of $^3$H-$^3$He groundwater apparent age to groundwater residence time in the saturated zone differs from the single-phase flow formulation of mean groundwater age in Equation (1) as given by Goode (1996). Age mass as described in Equation (1) will accumulate at any location, saturated or unsaturated, unless additional sinks of age mass are introduced to account for phase exchange. Goode (1996) proposes that sources or sinks of age mass and multi-phase processes can be coupled through the “$F$” term in Equation (1). However, no quantitative examples were given in the literature involving phase exchange processes using Equation (1).

**PROPERTIES OF AN "IDEAL TRACER" FOR MEAN GROUNDWATER AGE**

An “ideal tracer” for mean groundwater age would have the following properties:
• Density equal to water or very low concentrations that do not affect groundwater density;
• High ratio of gas-liquid phase partitioning (like $^3$H);
• Zero or constant surface concentration (no concentration variation as with $^3$H); and
• Constant accumulation rate in the liquid phase (e.g., by zero-order reaction or first-order reaction of water to a very low concentration of the ideal tracer).
• Identical molecular diffusivity to water.

In regard to molecular diffusivity, Labolle et al. (2006) show that the higher molecular diffusivity for $^3$He relative to H$_2$O can lead to non-dispersive secondary effects on $^3$H-$^3$He age estimates. These diffusive effects on $^3$H-$^3$He age are referred to as “diffusive fractionation,” and are most apparent in fine-grained materials where groundwater ages are not normally acquired. The most significant effect of diffusive fractionation in coarser-grained aquifer materials is caused by the bomb pulse and affects groundwaters with calculated ages of over 40 years. Over time, as groundwater tritium from atmospheric testing decays away, the combined effect of the bomb pulse and diffusive fractionation will be of lesser impact.

Hypothetically, an isotope with $^3$He properties could fit the “ideal tracer” description if either of the following two transport processes actually existed:

• $^3$H surface concentration was constant and $^3$He was generated without loss of $^3$H (zero-order decay and ingrowth)
• $^3$He was generated by water at a constant rate (zero-order ingrowth).

Note that as the “bomb pulse” dissipates over time, and tritium in the atmosphere and in precipitation returns to natural levels that are relatively constant on a decadal scale, the $^3$H-$^3$He system becomes closer to an ideal tracer for groundwater transport.

**Groundwater Age Deconvolution**

To address the non-idealities of isotopic age tracers, Bethke and Johnson (2008) recommend use of reactive transport models for interpretation of isotopic data. Gas-liquid phase processes will be involved with $^3$H-$^3$He transport from surface recharge to groundwater if the recharge process is exposed to air in the subsurface. Consequently, understanding of how $^3$H-$^3$He data relate to actual ages in aquifers and wells - “groundwater age deconvolution” - will require modeling of gas-liquid phase flow and multi-component transport (GLF-MCT) processes. The GLF-MCT models are designed to bridge the gap between the distribution of $^3$H and $^3$He in the subsurface and the distribution of actual mean groundwater ages. The GLF-MCT model is used as tool to explain how groundwater flow processes can affect $^3$H-$^3$He ages and, conversely, to help integrate use of $^3$H-$^3$He data into groundwater models. Importantly, a flow model calibrated to the actual $^3$H-$^3$He data can be used to infer mean groundwater age with correction for mixing processes.
Consideration of reactive transport processes is a major advantage of using a GLF-MCT model over purely advection-based model for interpreting $^3$H-$^3$He or other isotopic data. In particular, the GLF-MCT model can account for non-ideal processes such as gas-liquid phase partitioning, differences in component diffusivity, and hydrodynamic dispersion.

To implement a GLF-MCT model, we use the NUFT code developed at Lawrence Livermore National Laboratory (Nitao, 1999). The NUFT code enables thermal multi-phase and multi-component transport simulation. At this juncture we are assuming isothermal conditions in the flow and transport simulations. Future simulations could include thermal effects because our gas-liquid phase equilibrium models include temperature dependence.

**Figure 2.** Example of mean groundwater age simulation by Goode (1996) with (a) flow velocity vectors, (b) stream lines, (c) mean age in years for zero diffusion and zero dispersivity case, and (d) mean age in years for case with dispersivity of 6 years and diffusion coefficient of $1.16 \times 10^{-9}$ m²/s.

**DIRECT SIMULATION OF MEAN GROUNDWATER AGE**

Figure 2 shows a two-dimensional flow field example of mean groundwater age simulation by Goode (1996). The flow field is fully saturated assuming constant fluid density and viscosity. The example uses two hydraulic conductivities: $1 \times 10^{-5}$ m/s above a depth of 70
meters, and $1 \times 10^{-4}$ m/s below a depth of 70 meters. Recharge is input on the left side with variable flux over distance. Discharge conditions on the right side are implemented by constant head conditions at the top of the domain between the distance of 900-1000 meters. The resulting flow field produces higher flow velocities in the high-permeability layer below 70 meters depth (Figure 2a). Much of the recharge is transmitted down to the high-permeability layer, as evident by concentration of stream lines into the lower layer (Figure 2b). For the case with no diffusion or dispersion (Figure 2c), Goode (1996) verified that simulated mean groundwater age reflects an “advection only” or “plug flow” process. With molecular diffusion and moderate dispersivity values (Figure 2d), however, the mean groundwater ages become dispersed relative to an advective age (Figure 2c).

**GLF-MCT SIMULATION OF MEAN GROUNDWATER AGE USING A ZERO-ORDER REACTION**

To verify and benchmark the reactive transport age simulation framework in fully saturated conditions, the GLF-MCT model is first applied to replicate the mean groundwater age simulations by Goode (1996). In the implementation of mean groundwater age simulation in the GLF-MCT model, a constant-rate source of age mass, the “1” term in Equations (1) and (3), is implemented as a first-order reaction from the water component to a water tracer component, $C$, with a reaction rate, $R$, given in units of moles/kg-s:

$$\text{water} \xrightarrow{R} C$$

Because $C$ is treated as a dilute component with $[C] < [\text{water}]$, accumulation of $C$ over time is effectively a zero-order reaction:

$$\frac{\partial [C]}{\partial t} = R m_c$$

(6)

Where $m_c$ is the molecular weight of component $C$. The estimate of the mean groundwater age is obtained from the GLF-MCT model by

$$\bar{A} = \frac{[C]}{R m_c}$$

(7)

Equation (6) and (7) represent the properties of an “ideal tracer” for mean groundwater age – the tracer would accumulate at a constant rate within the saturated zone. Consequently, mean groundwater age is inferred by the tracer concentration divided by the product of tracer’s accumulation rate (moles/kg-s) and molecular weight.

In this implementation, values of $R = 5.5556 \times 10^{-8}$ moles/kg-year and $m_c = 0.018$ kg/mole ($R m_c = 1 \times 10^{-9}$ year$^{-1}$) were assigned. The $[C]$ mole fraction units scale to mean groundwater age by $\bar{A} = [C] \times 10^9$ year. The assignment of $m_c = 18.0$ g (near molecular
weight of water) to the mean age tracer component was implemented to avoid density-driven flow.

Figure 3 compares the mean groundwater age simulation between the advection-only (i.e. zero dispersion and zero molecular diffusion) case from Goode (1996) to the GLF-MCT simulation result. The simulated ages fields are nearly identical. The small differences are mostly attributable to numerical dispersion fields from the Eulerian scheme in the GLF-MCT model. The Lagrangian scheme used by Goode (1996) avoids numerical dispersion. Small differences can also result from pressure-dependence of density and viscosity considered in the GLF-MCT model, discretization, and contouring. Nonetheless, the close comparison between the two simulation results provides validation of the GLF-MCT model for simulating advective groundwater age using the more detailed physical and chemical processes of the reactive transport model.

![Image](image.png)

**Figure 3.** For the advection-only case, a Lagrangian simulation of mean groundwater age from Goode (1996) (top panel) is compared to an Eulerian reactive transport simulation of mean groundwater age using the GLF-MCT model (bottom panel).

Figure 4 compares the mean groundwater age simulation between Goode’s 1996 dispersion-diffusion case (with $D_L=6.0 \text{ m}$ and $D_T=0.6 \text{ m}$) to a GLF-MCT simulation result that includes a 30-m thick vadose zone. Importantly, the GLF-MCT model simulates the gas-liquid phase equilibrium properties of the age tracer, resulting in initiation of groundwater age at the water table and not at ground surface. This capability is necessary to implement age tracer source boundary conditions at the ground surface where $^3\text{H}$ concentrations are known. The strong agreement of simulated age fields in the saturated zone shows that the GLF-MCT modeling framework can account for effects of unsaturated flow processes on groundwater age by including coupled gas-liquid phase flow and transport.
The power of the GLF-MCT model is its flexibility in handling non-ideal properties of isotopic age tracers. As discussed above, $^3$H-$^3$He age data involve several non-ideal properties. As a benchmark comparison to the same two-dimensional layered case developed by Goode (1996) and examined in Figures 2 and 3, the GLF-MCT model was implemented with $^3$H and $^3$He properties including the following realistic factors in $^3$H-$^3$He age dating:

- A $^3$H source influenced by the bomb pulse.
- $^3$H and $^3$He diffusion coefficients.
- $^3$H-$^3$He decay implemented as a first-order reaction.
- All concentrations implemented in realistic units.
- $^3$He concentrations contain both background and tritiogenic fractions.

Figure 5 shows GLF-MCT simulation results for mean groundwater age compared to $^3$H-$^3$He age, in both cases with zero hydrodynamic dispersion. The $^3$H-$^3$He ages include molecular diffusion processes, while the mean groundwater ages do not. This comparison provides insight into the accuracy of $^3$H-$^3$He age for the best-case scenario of no hydrodynamic dispersion. The simulation comparison indicates that $^3$H-$^3$He ages less than 30 years are accurate. The distribution of $^3$H-$^3$He ages less than 30 years old largely coincides with diverging flow paths that dampen mixing (see Figure 2b). The simulation comparison indicates $^3$H-$^3$He ages less than 30 years old will be more accurate for recharge.
areas or other portions of flow systems not impacted greatly by mixing and convergence of groundwater sources with multi-decadal age ranges.

Figure 5. Comparison of simulations of mean groundwater age (top) to \(^3\text{H}-\text{He}\) age for identical flow conditions (bottom).

Differences between mean and \(^3\text{H}-\text{He}\) age are more evident at ages greater than 30 years. Remarkably, the simulation shows that without dispersion, the \(^3\text{H}-\text{He}\) could resolve ages over 50 years to an accuracy of within 20%. The simulated \(^3\text{H}-\text{He}\) ages over 30 years are the most heavily skewed by bomb-pulse peak \(^3\text{H}\). The simulated \(^3\text{H}-\text{He}\) ages between 30 and 50 years old span a mean groundwater age of about 25 to 60 years. Numerical dispersion and diffusion of the bomb-pulse peak \(^3\text{H}\) causes \(^3\text{H}-\text{He}\) ages to skew toward the age of the bomb-pulse peak.
SIMULATION OF FRACTION PRE-MODERN

$^3$H-$^3$He data can also be used to estimate the percentage of “pre-modern” groundwater present in a sampled groundwater (see Appendix B). “Pre-modern” groundwater is water that recharged before atmospheric weapons testing released large quantities of anthropogenic tritium into the atmosphere. Such groundwater recharged more than 50 years ago (about 5 tritium half lives) and contained low tritium activities (on the order of 10 pCi/L) at the time of recharge. Today, pre-modern groundwater is essentially “tritium-dead” with undetectably low tritium activity. In contrast, “modern” groundwater recharged during or after the bomb pulse and will still contain detectable activities of tritium. Initial tritium activities for “modern” groundwater recharge can be estimated using historical precipitation tritium activity data archived by the International Atomic Energy Agency (IAEA, 2010). Figure 6 illustrates the calculation of the fraction pre-modern, and Figure A.3 in Appendix B gives an example from a GAMA study in the Los Angeles Basin.

Figure 6. Calculation of the fraction of tritium-dead or pre-modern water in a collected groundwater sample. In this example, a sample collected and analyzed in 2010 has a calculated $^3$H-$^3$He groundwater age of 20 years equating to a recharge year of 2010 – 20 = 1990. Comparison of initial tritium (= residual tritium + tritiogenic $^3$He) to IAEA precipitation data for the recharge year 1990 results in a calculated pre-modern component of 33%.
The fraction of pre-modern groundwater in a collected groundwater sample can be estimated by comparing the initial tritium activity calculated for the sample (from the sum of measured residual tritium and tritiogenic helium-3) to the tritium activity in precipitation in the calculated recharge year (determined from the sample’s tritium/helium-3 groundwater age and the IAEA Global Network of Isotopes in Precipitation data bank) (Figure 6 and Appendix B). Calculated initial tritium activities less than precipitation tritium activities in the calculated recharge year are interpreted as resulting from dilution with “pre-modern” water. The fraction pre-modern – the proportion of $^3$H source concentration unaccounted for as inferred from the $^3$H-$^3$He age - represents “tritium-dead” water effectively more than 50 years old.

![Image of Figure 7](image-url)

**Figure 7.** Comparison a direct simulation of mean groundwater age (top) to the fraction pre-modern estimated from $^3$H-$^3$He age simulation (bottom) for the year 2002.

The distribution of pre-modern water in an aquifer can be simulated using the same method used to simulate the distribution of $^3$H and $^3$He described above. The simulation framework offers a means to test the concept of estimating fraction pre-modern from $^3$H-$^3$He data. In
particular, the simulation framework enabled testing of a practical time cutoff for “pre-
modern” water. It was found that the year of maximum tritium concentration, 1962, is the most suitable year to define a cutoff between modern and pre-modern water. If earlier years are used, such as 1950, estimation of the pre-modern fraction becomes erratic.

Figure 7 compares a direct simulation of mean groundwater age (top) to the fraction pre-
modern estimated from $^3$H-$^3$He age simulation (bottom) at the year 2002. The $^3$H-$^3$He age simulation was terminated at the year 2002 so that the 40-year age contour coincides with the source year of 1962. If 100% pre-modern is defined at a cutoff source year of 1962, delineation of “modern” and “pre-modern” groundwater is most distinct. If a year older than 1962 is used to delineate “modern” and “pre-modern” groundwater, the clear distinction is lost. Importantly, the zone of 100% pre-modern defined by $^3$H-$^3$He transport closely coincides with the 40-year mean age or 1962 source contour based on the 2002 year of the $^3$H-$^3$He age simulation.

**Effects of Dispersion**

As demonstrated by Goode (1996) from comparison of Figure 1c and 1d, dispersion will cause spreading of the mean groundwater age transport process with respect to the advective age. $^3$H-$^3$He ages will be more affected by dispersion than mean groundwater ages because of the dispersal of the bomb-pulse peak $^3$H source and mixing of packets of groundwater subject to the first-order decay process.

To more closely examine effects of groundwater pumping, we developed another recharge and discharge scenario. The recharge pattern remains the same as illustrated in Figure 1a but scaled up by a factor of 1.5. The permeability structure is reconfigured to two high permeability layers in the depth range of 60-75 m and 85-100 m. Discharge is changed to groundwater extraction at a constant rate on the right boundary within the high-permeability layers.

Figure 8 shows simulated $^3$H-$^3$He ages for a case with no dispersion and for case with coefficients of longitudinal dispersivity, $D_L=50$ m, and transverse dispersivity, $D_T=5$ m. While these dispersivity coefficients are nearly an order of magnitude higher than those used by Goode (1996), they are within the range for data for observational scales of 100-1000 meters (Gelhar et al., 1985). The $^3$H-$^3$He age simulation with no dispersion indicates that even though the wells are located at different depths, the $^3$H-$^3$He ages could be very similar, particularly if the $^3$H-$^3$He content is dominated by the bomb peak, as typical for the 30-40 year age range in year 2002. The case with dispersion indicates that over length scales of 100-1000 meters or more, dispersion could erase much of the true age stratification in the aquifer system.

Figure 9 compares simulation of the fraction pre-modern (based on 1962 cutoff) for cases of no dispersion and of dispersivities $D_L=50$ m and $D_T=5$ m. The “no dispersion case” illustrates a scenario where the shallow pumping is extracting 0% “pre-modern”
groundwater, and the deeper pumping is extracting 100% “pre-modern” groundwater. With dispersion, both pumping intervals are extracting an estimated 75-80% “pre-modern.”

**Figure 8.** Comparison of simulated $^3$H-$^3$He ages in 2002 for a scenario of pumping in two high-permeability layers for cases of zero dispersivity (top) and dispersivities of $D_L=50m$ and $D_T=5m$ (bottom). The symbols labeled “Pumping” indicate screen depths for pumping wells in “High K” (high-permeability) layers.

**Figure 9.** Comparison of simulated $^3$H-$^3$He fraction pre-modern (based on 1962 cutoff) in 2002 for scenario of pumping in two high-permeability layers for cases of zero dispersivity (top) and dispersivities $D_L=50m$ and $D_T=5m$ (bottom). The pumping regime is the same as illustrated in Figure 8.
The simple comparisons with and without dispersion suggest that in some aquifer systems, dispersion could cause $^3$H-$^3$He transport properties to deviate significantly from the “piston flow” model. $^3$H-$^3$He age and %pre-modern estimates will deviate from ideal tracer properties and the “piston flow” conceptual model primarily where residence times are over 20 to 30 years or where a convergent groundwater flow field mixes a wide range of groundwater ages.

**Gas-Liquid Phase $^3$H-$^3$He Age Simulation**

As discussed previously, $^3$H-$^3$He age simulation needs to address coupled gas-liquid phase flow and transport processes. The NUFT code can simulate $^3$H and $^3$He transport for gas-liquid flow using the distinct physical and chemical properties of $^3$H and $^3$He.

Figure 10 shows a two dimensional (2-D) simulation of the liquid phase concentration of $^3$H and $^3$He for a variably-saturated flow and transport simulation. Recharge occurs on the left by a constant head condition and on the top by a constant flux condition. The bomb pulse can be seen migrating through the saturated zone. The concentration of $^3$He in the vadose zone is near equilibrium with the atmosphere as a result of the high gas-to-liquid ratio of the $^3$He phase equilibrium. The $^3$H and $^3$He liquid phase concentrations at year 1980 are applied to Equation (5) to infer the $^3$H and $^3$He apparent groundwater age at year 1980.

**Figure 10.** A 2-D simulation of the liquid phase concentration of $^3$H and $^3$He for a variably-saturated flow and transport simulation. The simulated apparent age is computed from the Equation (5). The red dashed line indicates the water table.
Conclusions

A generalized Eulerian method for modeling gas-liquid phase transport of isotopic tracers has been developed. The method name is abbreviated to GLF-MCT for “gas liquid flow-multi-component transport.” We show that the GLF-MCT method can replicate previous Lagrangian-based results for simulating the mean groundwater age. The general applicability of GLF-MCT enables modeling of $^3$H-$^3$He ages with a direct accounting of gas and liquid phase properties for $^3$H and $^3$He. Moreover, the GLF-MCT method enables direct comparison of $^3$H-$^3$He age with the actual mean groundwater age. As $^3$H-$^3$He ages approach 30 years or older, the $^3$H-$^3$He apparent age become very susceptible to mixing of the bomb-pulse peak source of $^3$H. Considering that longitudinal macrodispersivity may increase to values of tens of meters or more in heterogeneous aquifer systems at scales of kilometers or more, widespread mixing of bomb-pulse peak source $^3$H can cause $^3$H-$^3$He ages to converge toward 30+ years with apparently high “pre-modern” fractions. Therefore, groundwater models are advised to calibrate to older $^3$H-$^3$He age data using $^3$H-$^3$He properties that account for surface concentration, unsaturated flow with gas-liquid phase equilibrium, macrodispersion, and molecular diffusivity.
Appendix A – Utility of Groundwater Age Data in Flow Modeling

Consider the Darcy’s Law concept of steady-state groundwater flow:

\[ \mathbf{v} = \frac{-K \nabla \phi}{n} \]  

(A.1)

where:
\( \mathbf{v} \) = groundwater velocity (length/time),
\( K \) = hydraulic conductivity (length/time),
\( \nabla \phi \) = gradient of hydraulic head (unitless),
\( n \) = porosity (unitless).

In practice, the hydraulic gradient and porosity are usually more thoroughly characterized spatially compared to velocity and hydraulic conductivity. Rewriting Equation (A.1) with lesser known quantities of \( \mathbf{v} \) and \( K \) on the left-hand-side yields

\[ \frac{\mathbf{v}}{K} = -\frac{\nabla \phi}{n}. \]  

(A.2)

The quantity \( \frac{\mathbf{v}}{K} \) is often well-constrained by water level and porosity data. Assuming water level and porosity data are accurate, steady-state groundwater interpretations and models cannot constrain prediction of a hydraulic conductivity without constraints on groundwater velocity or flux.

A spatial map of groundwater residence time, \( A \), or “age” would provide a direct method to infer a groundwater flow velocity field

\[ \mathbf{v} = \frac{1}{\nabla T} \]

Combined with hydraulic gradient and porosity constraints and Darcy’s Law, a spatial map of groundwater age under steady-state flow conditions could conceivably be used to map the hydraulic conductivity field as

\[ K = \frac{n}{-\nabla \phi \nabla A}. \]
Appendix B – The Traditional Approach to $^3$H-$^3$He Groundwater Age Dating

Tritium/Helium-3 Groundwater Age

Tritium ($^3$H) is a very low abundance (around 1 part in $10^{17}$ of total hydrogen), radioactive isotope of hydrogen with a half-life of 12.34 years. Natural tritium is produced in the earth’s atmosphere by cosmic radiation. Atmospheric nuclear weapons testing in the 1950’s and early 1960’s released tritium to the atmosphere at levels several orders of magnitude above the background concentration (Figure A.2). This atmospheric tritium enters groundwater (as HTO, with one hydrogen atom as tritium) during recharge. Tritium concentration in groundwater is reported in units of picoCuries per liter, and has a regulatory limit (Maximum Contaminant Level or MCL) of 20,000 pCi/L. Its concentration in groundwater decreases by radioactive decay, dilution with non-tritiated groundwater, and dispersion. While the presence of tritium is an excellent indicator of water that recharged less than about 50 years ago, age dating groundwater using tritium alone results in large uncertainties due to spatial and temporal variation in the initial tritium at recharge.

Measurement of both tritium and its daughter product helium-3 ($^3$He) allows calculation of the initial tritium present at the time of recharge (Figure A.1), and ages can be determined from the following relationship:

$$\text{Groundwater Age (years)} = -17.8 \times \ln \left(1 + \frac{^3\text{He}}{^3\text{H}}\right)$$

Figure A.1. Solid line shows the decay of tritium, with a half-life of 12.34 years, while the dashed line shows the growth of the daughter product, $^3$He. The sum of tritium and $^3$He is the same at any time, and equal to the initial tritium value. This is the basis for the groundwater age-dating technique used in this study.
Groundwater age measures the time since the water sample was last in contact with the atmosphere. The $^3$He_{nmt} indicated in the equation is the component of $^3$He that is due to the decay of tritium. Methodologies have been developed for correcting for other sources of $^3$He, such as the earth’s atmosphere and potential small contributions from thorium and uranium decay (Aeschbach-Hertig et al., 1999; Ekwurzel et al., 1994).

Figure A.2. The tritium concentration measured in precipitation at three North American locations (International Atomic Energy Agency, 2010). Nuclear weapons testing introduced a large amount of tritium into the atmosphere in the 1960’s, peaking in 1963.

Well water samples are always a mixture of water molecules with an age distribution that may span a wide range. The reported groundwater age is the mean age of the mixed sample, and furthermore, is the age only of the portion of the water that contains measurable tritium. Groundwater age dating has been applied in several studies of basin-wide flow and transport (Ekwurzel et al., 1994; Poreda et al., 1988; Schlosser et al., 1988; Solomon et al., 1992; Szabo et al., 1996). The basic premise for using groundwater age to establish vulnerability is that young groundwater has been transported to a well capture zone relatively rapidly from the earth’s surface. Most contaminants have been introduced in shallow zones, by human activity in the past 100 years, so younger groundwater is more likely to have intercepted contaminants. On the other hand, old groundwater is likely to be isolated from the contaminating activities that are ubiquitous in modern urban environments.

**Fraction Pre-modern**

A groundwater sample has an age distribution that is a result of groundwater mixing both during transport and in the well’s borehole. Useful information about the groundwater age distribution in a well water sample comes from comparing a sample’s measured tritium to
the tritium expected in the original recharge water. This data analysis technique is illustrated on a plot of initial tritium versus calculated mean age or recharge year (Figure A.3). The tritium that was present at the time of recharge is known from measurements of tritium in precipitation at several sites in North America. The calculated tritium-helium groundwater age is plotted along the x-axis position on Figure A.3, against the corresponding expected initial tritium value, on the y-axis. Water that recharged before about 1955 now contains extremely low levels of tritium. Samples that fall below the ‘initial tritium’ curve thus contain a fraction of water that recharged before 1955 (‘pre-modern’). In contrast, a groundwater sample for which the measured age gives a decay-corrected tritium value that falls on or near the curve, is not significantly diluted with a component of pre-1955 water. A coarse estimate of the fraction of pre-modern water that is drawn from a well comes from calculation of the difference between the measured tritium and the ‘initial’ tritium. Most long-screened drinking water wells produce a combination of post-modern and pre-modern groundwater. This technique can be complicated by: scatter in $^3$H concentrations in precipitation, poor retention of $^3$He in the vadose zone, and mixing of post-modern aged waters in the modern fraction, especially for waters with ages near the tritium bomb-pulse peak.

**Figure A.3.** Estimation of the “pre-modern” fraction. Curves show equal fractions of pre-modern water. The line labeled 0% is an approximation of the tritium in precipitation data from IAEA GNIP data. Lines below approximate mixtures of pre-modern and post-modern water. As an example, groundwater samples from southern California coastal basins are shown as points. Most of these groundwater samples have a large component of pre-modern groundwater. (Hudson et al., 2002).
Presentation (Attached)


Cited References


Improved Interpretation of $^3$H-$^3$He Groundwater Age Data Through Modeling of Gas-Liquid Phase Flow and Transport Processes

Steven F. Carle, Bradley K. Esser and Jean E. Moran

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Groundwater Resources Association of California
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Improved Interpretation of $^3$H-$^3$He Groundwater Age Data Through Modeling of Gas-Liquid Phase Flow and Transport Processes

Steven F. Carle$^1$, Bradley K. Esser$^2$, Jean E. Moran$^3$

The State Water Board’s Groundwater Ambient Monitoring and Assessment (GAMA) Program has measured many hundreds of tritium ($^3$H) and helium-3 ($^3$He) concentrations in well water samples to derive estimates of groundwater age at production and monitoring wells in California basins. These $^3$H-$^3$He data are generally recognized as having a groundwater age estimation range of 50 years, with considerably more accuracy within a range of about 30 years. The modern timeframe of $^3$H-$^3$He isotopic groundwater age dating offers direct means to characterize groundwater flow rates, recharge sources, and locations of aquifer vulnerability. In practice, $^3$H-$^3$He data are used to constrain or validate groundwater flow and transport models, assess feasibility of managed aquifer recharge proposals, attribute contaminant timing and source, and evaluate management plans to mitigate contaminant loading to aquifers.

The radioactive decay of tritium to $^3$He, however, differs from an ideal groundwater age tracer in that (1) the accumulation of $^3$He in the system is first-order with respect to tritium content (versus a zero-order age-mass accumulation process), and (2) atmospheric concentrations of tritium and hence of initial tritium contents in recharging water over the last several decades have not been uniform, but rather have been strongly affected by anthropogenic sources of tritium. To better understand how these non-idealities of $^3$H-$^3$He transport processes affect the interpretation of apparent $^3$H-$^3$He ages of groundwater, we are using computer models to improve understanding of coupled gas-liquid phase flow and $^3$H-$^3$He transport processes through the vadose zone and saturated zone in California aquifer systems. Inclusion of coupled gas-liquid phase flow modeling is necessary to assess vadose zone processes affecting $^3$H-$^3$He transport, such as (1) residence time and dispersion of $^3$H within unsaturated conditions, and (2) partitioning of tritiogenic $^3$He to the gas phase and subsequent interaction with atmospheric $^3$He concentration.

The coupled gas-liquid phase modeling framework provides direct means to compare apparent $^3$H-$^3$He age to ideal mean and advective groundwater age for the same groundwater flow conditions. The impacts of mixing processes, particularly from hydrodynamic dispersion and isotope-specific molecular diffusivities, can be compared for both the $^3$H-$^3$He and the ideal age tracer scenarios. The $^3$H-$^3$He transport modeling results show situations where $^3$H-$^3$He ages are accurate and where such ages are systematically offset from ideal mean or advective groundwater ages. In turn, $^3$H-$^3$He gas-liquid phase transport modeling can be used to correct for errors in $^3$H-$^3$He age dates caused by the non-idealities of the $^3$H-$^3$He isotopic properties. Modeling examples are given for test cases in the literature and for interpretation of $^3$H-$^3$He data from aquifer systems in California.

The Groundwater Ambient Monitoring and Assessment program is sponsored by the California State Water Resources Control Board and carried out in cooperation with the U.S. Geological Survey. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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Dr. Esser has a Ph.D. in geochemistry from Yale University, and has worked at LLNL for 17 years. His interest and expertise are in the use of groundwater age-dating, isotope biogeochemistry, and reactive transport modeling to develop better tools for water resource management, especially with regards to groundwater nitrate.

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Dr. Moran recently left LLNL after leading projects in isotope hydrology for 11 years, and has joined the faculty at CSU East Bay. Her expertise is in the chemical evolution of groundwater and groundwater age dating.
Mean Groundwater Age

= Volumetrically averaged advective age of a groundwater parcel

or

= Mean travel time from water table to screened interval
Groundwater age data can map the flow system. 

$^3$H-$^3$He data from Orange County, California

3H-3He groundwater age is a good predictor of contamination vulnerability.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>$\leq 10$ year $^3$H-$^3$He Age</th>
<th>$&gt;50$ year $^3$H-$^3$He Age</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTBE</td>
<td>67%</td>
<td>6%</td>
</tr>
<tr>
<td>Any THM</td>
<td>68%</td>
<td>43%</td>
</tr>
<tr>
<td>Any VOC</td>
<td>82%</td>
<td>43%</td>
</tr>
<tr>
<td>PCE</td>
<td>24%</td>
<td>16%</td>
</tr>
</tbody>
</table>

Results from > 600 wells sampled by Groundwater Ambient Monitoring and Assessment (GAMA) Program
Outline

- \(^{3}\)H-\(^{3}\)He Groundwater Age Interpretation
  - El Verano (Sonoma Valley) example data set
  - \(^{3}\)H-\(^{3}\)He age interpretation concepts

- Groundwater Age Modeling
  - Comparison of mean age to \(^{3}\)H-\(^{3}\)He age
  - Effects of dispersion
  - Effects of vadose zone (considering gas-liquid phase flow and transport)
El Verano Groundwater Age Study Area
Sonoma Valley, California

- Identify recharge sources
- Target relatively shallow wells (<200 feet deep)

El Verano Area Groundwater Age Study Data

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>Screened Interval (ft)</th>
<th>³H-³He Age</th>
<th>% Pre-Modern (&gt;50 yr old)</th>
<th>Recharge Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>City of El Verano</td>
<td>150-175</td>
<td>16 yr</td>
<td>75%</td>
<td>18.3</td>
</tr>
<tr>
<td>City of Sonoma</td>
<td>90</td>
<td>25 yr</td>
<td>94%</td>
<td>17.8</td>
</tr>
<tr>
<td>0-25</td>
<td>24 yr</td>
<td>93%</td>
<td>18.0</td>
<td></td>
</tr>
<tr>
<td>45-105</td>
<td>18 yr</td>
<td>76%</td>
<td>18.2</td>
<td></td>
</tr>
<tr>
<td>40-150</td>
<td>35 yr</td>
<td>98%</td>
<td>17.0</td>
<td></td>
</tr>
<tr>
<td>30-210</td>
<td>24 yr</td>
<td>97%</td>
<td>17.8</td>
<td></td>
</tr>
<tr>
<td>72-100</td>
<td>24 yr</td>
<td>93%</td>
<td>18.0</td>
<td></td>
</tr>
<tr>
<td>70-160</td>
<td>27 yr</td>
<td>96%</td>
<td>17.2</td>
<td></td>
</tr>
<tr>
<td>100-350</td>
<td>43 yr</td>
<td>98%</td>
<td>16.9</td>
<td></td>
</tr>
</tbody>
</table>

Map base by Sonoma County Water Agency
Shallow wells have relatively deep $^3$H-$^3$He signatures. Deep wells have all “pre-modern” (>50 yr) groundwater.

Groundwater Monitoring and Assessment (GAMA) Program
Distribution of $^3$H in California Groundwater Samples

Range of El Verano Study
0.1-6.9 pCi/L
El Verano Area Groundwater Age Study Overall Results:

- Well depths 82-350 (mostly < 200 ft)
- Recharge Temperatures 15.2-19.5 °C
- ³H-He ages 16-43 years
- % Pre-Modern (>50yr) 75-98%

What causes these relatively deep groundwater signatures in relatively shallow wells?

Tritium Helium-3 (³H-³He) Groundwater Age Concepts
\[ ^3\text{H} - ^3\text{He} \text{ Age (years)} = 17.8 \times \ln(1 + \frac{^3\text{He}}{^3\text{H}}) \]

Two non-idealities for mean groundwater age interpretation:
1. \(^3\text{H} - ^3\text{He}\) decay is a first-order (not a zero order) process.
2. \(^3\text{H}\) source is transient because of anthropogenic sources.

First-order decay causes non-linear mixing.

Parcel 1 has a \(^3\text{H} - ^3\text{He}\) age of zero.
First-order decay causes non-linear mixing.

Parcel 2 has a $^3$H-$^3$He Age of 24.6 years.

First-order decay causes non-linear mixing.

The Parcel 1+2 mixture has a mean age of 12.3 years.
First-order decay causes non-linear mixing.

However, the Parcel 1+2 mixture $^3$H-$^3$He age is $\sim$8 years, and is significantly younger than the mean age (12.3 years).

A transient $^3$H source skews $^3$H-$^3$He age toward age of parcels with the larger $^3$H source.

Here, $^3$H-$^3$He age of the mixture is greater than the mean age.
% “Pre-Modern” = 100% \left(1 - \frac{3H_{\text{meas}}}{3H_{\text{source}}} \right)

Three non-idealities in % “Pre-Modern” estimation:
1. $^3$H source originates at surface, not water table ($^3$H decays in VZ).
2. Mixing affects $^3$H-$^3$He transport from source to sample.
3. Tritium source concentration before ~1962 is highly variable.

Direct Simulation of Mean Groundwater Age (Goode, 1996)*
- Provides a benchmark for comparison to $^3$H-$^3$He age.

- Flow Velocity (a)
- Stream Lines (b)
- Mean Age
  - Advective (c)
    - Diffusivity=0
    - Dispersivity=0
  - With Dispersion (d)
    - Diffusivity = $1.16 \times 10^{-8}$ m$^2$/s
    - $D_L=6$ m, $D_T=0.6$ m

*Water Resources Research, v32, n2, p289-296
To improve interpretation of groundwater age isotope data, Bethke and Johnson (2008)* recommend reactive transport modeling.

Modeling indicates “Pre-Modern” (e.g. >50 year) groundwater is best delineated by pre-bomb peak (1962) groundwater.

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*Annu. Rev. Earth Planet Sci., v36, p121-152

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**Direct Mean Groundwater Age Simulation** (Goode, 1996)

**Using LLNL’s NUFT Reactive Transport Modeling Code:**

- Mean Groundwater Age Simulation
  - zero-order kinetic reaction:
    - water $\rightarrow$ water tracer component

- $^3$H-$^3$He Groundwater Age Simulation
  - first-order kinetic reaction:
    - $^3$H $\rightarrow$ $^3$He (12.3 year half-life)
    - Bomb+Cosmogenic $^3$H surface source
    - $^3$H and $^3$He diffusion coefficients
    - No dispersion

---

Modeling indicates “Pre-Modern” (e.g. >50 year) groundwater is best delineated by pre-bomb peak (1962) groundwater.
Effect of Dispersion on $^3$H-$^3$He Groundwater Age:

- **Zero Dispersivity** (Diffusion only)

- $D_L=6\text{m}, D_T=0.6\text{m}$

- $D_L=60\text{m}, D_T=6.0$

Effect of Dispersion on %“Pre-Modern”:

- **Dispersivity** ($D$) = 0
  (Diffusion only)

- $D_L=6\text{m}, D_T=0.6\text{m}$

- $D_L=60\text{m}, D_T=6.0$
Effect of Vadose Zone on $^3$H-$^3$He Groundwater Age: (includes gas-liquid phase flow and $^3$H-$^3$He transport)

| Tritium Source Concentration | All cases $D_{v}=60m$, $D_{w}=6.0$
<table>
<thead>
<tr>
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<tr>
<td>$^3$H-$^3$He Age</td>
<td>Without Vadose Zone</td>
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<tr>
<td>$^3$H-$^3$He Age</td>
<td>With Vadose Zone</td>
</tr>
<tr>
<td>Mean Age</td>
<td>With Vadose Zone</td>
</tr>
</tbody>
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Noble gas solubility depends on temperature and pressure. *Noble gas composition indicates recharge temperature.*
Noble gas recharge temperatures indicate recharge contacts groundwater far below the surface of Carriger Creek Fan.

- Noble gas T lines up with water table T.
- Recharge passes through the vadose zone.
- Sonoma Creek is not the recharge source.

What have we learned about El Verano area groundwater?
- The groundwater is highly mixed from dispersion, transient flow, etc.
- Dispersed recharge passes through the vadose zone (not directly from streams).

<table>
<thead>
<tr>
<th>Sample Location</th>
<th>Screened Interval (ft)</th>
<th>$^3$H-$^3$He Age</th>
<th>% Pre-Modern (&gt;50 yr old)</th>
<th>Recharge Temperature (°C)</th>
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Lawrence Livermore National Laboratory
LLNL-PRES-410499
What have we learned about $^{3}\text{H}-^{3}\text{He}$ age interpretation?

- $^{3}\text{H}-^{3}\text{He}$ transport differs from an ideal mean age tracer.
  - 1st-order decay and variable $^{3}\text{H}$ source cause these differences.
  - Dispersion skews $^{3}\text{H}-^{3}\text{He}$ age toward time of $^{3}\text{H}$ source peak.
  - $^{3}\text{H}-^{3}\text{He}$ ages of 30 years or less are most reliable.

- Recharge passing through the vadose zone will reduce the impact of dispersion and variable $^{3}\text{H}$ source on $^{3}\text{H}-^{3}\text{He}$ age!

- $^{3}\text{H}-^{3}\text{He}$ age and noble gas recharge temperature data constrain the physics of the groundwater system.
  - Quantify flux, estimate dispersivity, locate recharge and discharge,…
  - Identify recharge processes (e.g. stream interaction vs. disperse)

- Models & interpretations of $^{3}\text{H}-^{3}\text{He}$ age data need to consider gas-liquid phase (vadose zone) flow and transport processes.