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The nature and extent of bomb tritium remaining in deep vadose zone: A synthesis and prognosis

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Abstract

Tritium present in deep vadose zones is a useful tracer for estimating groundwater recharge, but its full utility is constrained by not knowing where and for how long the tritium tracing method remains applicable. We obtained 44 tritium profiles from 17 globally distributed sites with vadose zone thicknesses of 12–624 m and used transport models to estimate the number of years that tritium may still be useful. Results show that the method may still be usable for 26 of 44 soil profiles surveyed, mainly in China, Australia, the United States, South Africa, and Senegal, with a remaining useful period of between 6 and 83 years. We also developed a statistical model that uses outputs from a hydrological model to predict the applicability of the tritium tracing method. Global implementation of the statistical model showed that the method remains usable at 20% of Earth's land mass (excluding Antarctica and Greenland) over the next few decades.

Abbreviations: ADRE, advection-dispersion reaction equation; AET, actual evapotranspiration; DWT, depth to water table; IQR, interquartile range; MAP, mean annual precipitation; PET, potential evapotranspiration; TU, tritium unit.

1 | INTRODUCTION

The global presence and extent of bomb tritium signals, widely used as indicators of flow and transport processes, remain poorly understood in deep vadose zones. Early work by Begemann and Libby (1957) showed that tritium injected into the atmosphere by nuclear weapons can be used to quantify continental water balance and groundwater recharge rates. Back then, the task was an easy one: tritium was everywhere, and atmospheric concentrations only started to decline in 1963 with the comprehensive test ban treaty. Today, elevated tritium concentrations in shallow soils and nearby streamflow have been largely washed out (Scanlon et al., 2002), although recent work suggests that background tritium can remain a useful tracer, particularly in the southern hemisphere (Morgenstern et al., 2010). Still, important questions to answer are as follows: Where is the bomb tritium peak still evident in soils around the world? How long can the tritium method still be used to assess groundwater recharge rates? Answering these questions may revitalize research that seeks to integrate process understanding and statistical modeling of water flow in deep vadose zones to inform the sustainable management of water resources (Gleeson et al., 2016).

Deep vadose zones cover over 50% of the Earth's land surface (Fan et al., 2013). In this study, we define deep vadose zones as soils thicker than 13 m, well within the 10–40 m consensus of a typical regolith thickness (Pelletier et al., 2016; Rempe & Dietrich, 2014). Deep vadose zones act as "recorders" of the bomb tritium signal over long time scales, thereby providing useful information for understanding water flow in the subsurface (Phillips, 1994). Modeling water movement in deep vadose zones remains challenging because subsurface heterogeneity amplifies the complexity of the processes, dynamics, and feedback at various scales in space and time (Camacho Suarez et al., 2015). Furthermore, the opaque nature of the subsurface means that groundwater recharge can only be indirectly observed and quantified (Phillips, 1995).

It has been shown that water-stable isotopes can yield biased estimates of transit times longer than a few months or years (Kirchner, 2016; Seeger & Weiler, 2014). This suggests that water-stable isotopes are unlikely to be useful for estimating the long timescales that characterize infiltration into deep vadose zones. However, tritium (^{3}H), a radiogenic and radioactive isotope with a half-life of 12.32 ± 0.02 years (Lucas & Unterweger, 2000), can be used to estimate water ages ranging between 1 and roughly 100 years (Morgenstern et al., 2010). Tritium is found in the global environment as tritiated water ($^3H^1HO$) and is therefore a potentially powerful and direct tracer of water, including for deep vadose zones. Tritium concentrations in water are typically reported in tritium units (TU) (1 TU = 1 ^{3}H in 10^{18} atoms ^{1}H, or 0.118 becquerel per liter; Morgenstern & Taylor, 2009).

Core Ideas

- Soil tritium profiles were compiled to estimate current 1963 bomb peak distributions in deep vadose zones.
- Bomb-peak tritium had migrated by an average of 20 m, depending on each site's soil and climate conditions.
- Climate and vadose zone thickness suggest a narrowing window of time for tritium tracing applicability.

The main global pulse of tritium into the atmosphere, produced by the thermonuclear weapon tests in the 1950s and 1960s, has since fallen close to natural levels that are produced by cosmogenic and geogenic reactions (Lehmann et al., 1993). The correspondence between precipitation tritium time series and soil tritium concentration profiles has been used to study soil water flow and groundwater recharge mechanisms, using either the tritium peak depth method or the tritium storage method (Li & Si, 2018; Li et al., 2019). The tritium peak depth method estimates groundwater recharge as a percentage of mean annual precipitation (MAP) based on soil water movement (Si & de Jong, 2007). The tritium storage method estimates recharge as a ratio of tritium stored in the soil profile to accumulated tritium input from precipitation (Allison et al., 1994).

Little is known about the present and future applicability of tritium-based tracing methods for soil water. It is generally not known where and when tritium methods might still be useful for deep vadose zone research. This knowledge is important, especially in semi-arid and arid settings with deep vadose zones, because of the challenges in inferring recharge rates in these environments from Darcy's law, solutions of the Richards equation, or water balance methods (Phillips, 1994). On the one hand, while recharge rates may be estimated by modeling using the Richards equation, sampling deep vadose zones to determine appropriate model parameters can be expensive and logistically prohibitive. Moreover, parameters inferred at scales that can be sampled are not necessarily transferable to scales at which we need to use them. Small errors in estimates of either precipitation or evapotranspiration can lead to large errors in calculations of downward fluxes when using the water balance method. Tracer-based methods obviate some of these challenges because they "follow the water" directly, thus allowing direct measurement of the movement of a water parcel through the subsurface.

Our main objective is to broadly determine the applicability of the tritium tracing method in deep vadose zones. Herein, we compile tritium profiles in thick vadose zones from the literature, supplemented by original new data from our study sites. We explore the following research questions: (1) When is the last date that the tritium method may be applicable at an individual site? (2) What controls the applicability of the tritium tracing method? In addressing these questions, we develop a global map of locations where the tritium method may still be applicable.

2 | MATERIALS AND METHODS

2.1 | Data compilation and treatment

We compiled tritium data from the literature for settings with deep (>12 m) vadose zones. This depth threshold is necessary because deep vadose zones make the continued applicability of the tritium method more plausible. This is because the likelihood of finding the characteristic shape of soil water tritium profiles increases with vadose zone depth. The shapes of soil water tritium profiles (TU vs. depth) are almost superimposable on the shapes of precipitation tritium time series (TU versus time). Broadly, these characteristic shapes have three regions: natural background tritium concentrations prior to about 1950, a substantial rise to a tritium peak in 1963, and a decline after 1963 (Figure 1A). Since the similarity in the shapes of precipitation tritium time series and soil water tritium profiles can be used to quantify the age of water taken up by trees (Zhang et al., 2017) or to investigate the parameters of groundwater recharge (Scanlon et al., 2002), we only considered soil water tritium profiles that resemble the shapes of the precipitation tritium time series, restricting our analysis to soil water tritium profiles in which a peak is apparent (Figure 1A). This criterion is consistent with our objective to assess the applicability of the "tritium peak method" (Li et al., 2019), with implications for groundwater recharge. Including only soil profiles with clear tritium peaks is necessary because the absence of a tritium peak suggests complicated recharge mechanisms such as preferential flow. In such cases, an approach called the "tritium mass balance" method is more appropriate. The tritium mass balance method, however, is challenging because it depends on accurate reconstructions of long-term precipitation tritium time series, which are difficult to obtain.

The two criteria above form the basis for our prognosis of the applicability of the second tritium method (see next section). Including data from our own field sites at the Loess Plateau of China, we obtained a total of 44 soil water tritium profiles from 17 sites that satisfied the soil profile-precipitation time series criterion. The final dataset represented 17 geographical settings (Figure 1B, inset), with MAP ranging from 150 to 804 mm, actual evapotranspiration (AET) ranging from 129 to 620 mm, potential evapotranspiration (PET) ranging from 645 to 1753 mm, and depth to water table (DWT) ranging from 12 to 624 m (Figure 1B).

2.2 | Inverse and forward modeling

The study's main objective was to identify the last date that the tritium method still may be applicable at an individual site. To achieve this objective, we estimated the solute transport parameters from observed tritium concentrations (the inverse problem) and then predicted future tritium concentrations (the forward problem) using the one-dimensional advection-dispersion reaction equation (ADRE) with first-order decay given by van Genuchten (1981):

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - \mu C \tag{1}$$

where C is the tritium concentration (TU), v is the pore water velocity (m year^{-1}), D is the dispersion coefficient (m^2 year^{-1}), μ is the first-order decay constant of tritium (0.0565 year^{-1}), R is the retardation factor, z is depth from the soil surface (m), and t is time (years). In the case of tritium, we assume $R = 1$ (i.e., no adsorption onto the vadose zone solid phase).

Tritium concentrations versus depth or time were described using the analytical solution of Equation (1) for a semi-infinite profile subject to a third-type Dirac delta solute input boundary condition at the soil surface (van Genuchten & Parker, 1984). Details are provided in the Supporting Information. The inverse and forward calculations were carried out using the CXTFIT computer program (Toride et al., 1999) within the STANMOD software (Simunek et al., 2000; van Genuchten et al., 2012; Mahmoodlu et al., 2021). To independently test the goodness-of-fit of the ADRE model, we calculated the pore water velocity v also by fitting a Lorentzian peak growth model to each soil tritium profile (Figure S1, also see Table S4).

For the inverse problem, CXTFIT implements a Marquardt–Levenberg type nonlinear least-squares fitting algorithm to optimize the fit with the data. We used CXTFIT to estimate the transport parameters v and D (see the Supporting Information for details).

For the forward problem, we used the estimated parameters from the inverse problem to predict future tritium distributions and to determine the time when the tritium tracing method may still be applicable at a site and for a given profile. We defined the applicability τ^* of the tritium tracing method as the smallest value of the year τ_z^* when Z_{peak} (the depth of the peak concentration) reaches the water table (DWT), or the year τ_c^* when the peak concentration becomes too small to

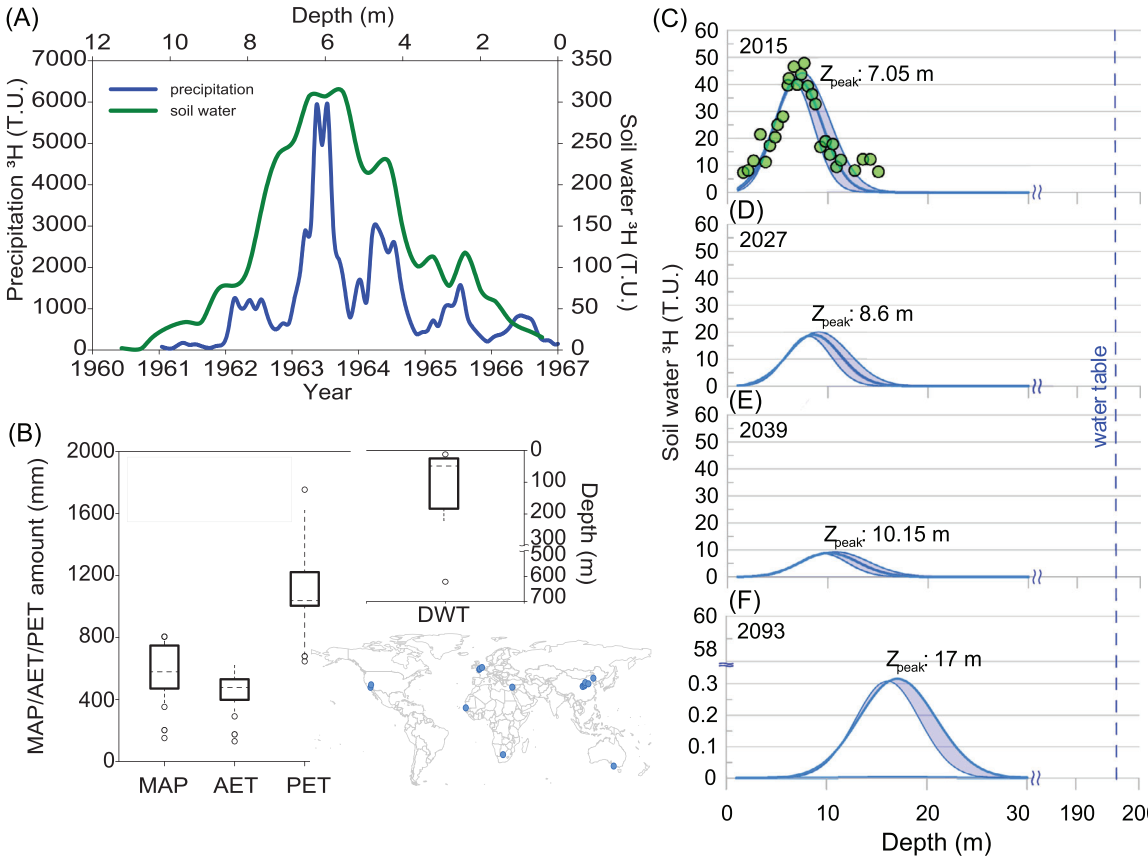

FIGURE 1 Panel A shows examples of tritium concentrations (smoothed splines tritium unit [TU]) in precipitation (Vienna, Austria; LHS) and soil water (Shaanxi, China; RHS), scaled such that the peak in soil water tritium corresponds to the peak in precipitation tritium. Panel B shows box plots of mean annual precipitation (MAP), actual evapotranspiration (AET), potential evapotranspiration (PET) (LHS), and depth to water table (DWT) (RHS), with the inset showing the 17 locations of the compiled soil water tritium profiles. Panel C shows the fit of the advection-dispersion reaction equation (ADRE) to data for one profile (Changwu 5, CN) sampled in 2015. Panels D and E show forward modeling results for periods of approximately one and two half-lives. Panel F shows the 0.3 threshold below which the tritium method would no longer be usable. Also shown in panels C–F are lower and upper 95% confidence limits (light blue shaded areas), depths corresponding to the peak concentrations (Z_{peak}), and water table depths (blue dashed line) beyond which the tritium method would no longer be applicable. The lower and upper 95% confidence intervals were derived from the 95% confidence limits of the parameter estimates obtained when solving the inverse problem.

measure. The minimum of these two values will set the last date (τ^*) that the tritium tracing method is still usable at a given site, that is.:

$$\tau^* = \min\left(\tau_c^*, \tau_z^*\right) \tag{2}$$

We further use:

$$\tau = \tau^* - 2022 \tag{3}$$

such that τ represents the number of years, before or after the year 2022, that the tritium method may still be applicable. We set the threshold of the peak concentration at 0.3 TU, assuming that any peak below this value is too small to measure. Note that this threshold is 15 times higher than the state-of-the-art 0.02 TU detection limit at the GNS Science Water Dating Laboratory (Lower Hutt, New Zealand) (Morgenstern & Taylor, 2009). For this reason, we also ran the ADRE model with the threshold set at 0.02 TU (Table S1). The 0.3 TU threshold may be regarded as conservative, considering that analytical methods are likely to become more sensitive over time. A comparison of the two thresholds is represented in Figure S2.

2.3 | Geospatial modeling

We identified site-specific long-term AET, PET, and MAP values as surrogates for climate and hydrology. Specifically, we determined site-specific AET/MAP and PET/MAP values. We also identified site-specific long-term DWT values as surrogates for geomorphology and geology. We then developed a statistical model that best explains τ. The model is composed of a site's dryness index (PET/P) and vadose zone thickness

(DWT). This model was constructed to test the hypothesis that PET/P, DWT, and their interactions are the important predictors of τ.

The model was found to provide a plausible explanation for the movement of tritium in the vadose zone, both conceptually and statistically. Conceptually, the dryness index (PET/P) and the DWT provide a parsimonious explanation for τ; warmer and drier places (i.e., high PET/P) tend to be characterized by slower movement of water (i.e., low pore water velocities) in the vadose zone, and the time it takes for water to reach the water table tends to increase with vadose zone thickness, which is related to DWT.

We implemented the statistical model to predict τ at over 2,000,000 globally distributed 5-arcmin grid points where depths to the water table have been modeled with a global groundwater flow model (De Graaf et al., 2017). We adopted a conservative extrapolation approach in that we only considered grid points with PET/P, DWT, and τ values bounded by the respective values in the dataset (Figure 1B): PET/P between 0.90 and 9.8, DWT between 12 and 624 m, and τ between −42 and 83 years. We also considered only the grid points that were consistent with the ecoregions represented in our dataset: temperate broadleaf and mixed forests, tropical and subtropical grasslands, savannas and shrublands, temperate grasslands, savannas and shrublands, montane grasslands and shrublands, mediterranean forests, woodlands and scrubs, and deserts and xeric shrublands, as delineated by Dinersten et al. (2017) and Linke et al. (2019). Consequently, our geospatial model consisted of about 518,000 5-arcmin grid points, representing 28% of the global land mass (excluding Antarctica and Greenland).

3 | RESULTS

3.1 | Applicability of the tritium tracing method

Forward modeling results show that the tritium tracing method is potentially applicable to 26 of our 44 profiles for the next 6–83 years (median 71 years, interquartile range [IQR] 53), representing 13 of 17 locations in the compiled dataset (Figure 2A). The locations where the method is applicable are in Australia (n = 1), China (n = 16), Senegal (n = 1), South Africa (n = 4), and the United States (n = 4). In the United States, the method is possibly applicable at Yucca Mountain, Nevada (UZ#4 and UZ#5) over the next ∼40 years, at Amargosa Desert, Nevada (UZB-1) over the next 74 years, and at Mojave Desert, California (LOGW-1) over the next 12 years. Conversely, the tritium method may no longer be applicable to 18 of 44 profiles (median −22 years, IQR 25), representing six of 17 locations in our dataset (Figure 2A). The locations where the method is no longer applicable are in Australia (n = 9), Cyprus (n = 1), South Africa (n = 1), and United Kingdom (n = 7; all UK profiles in the dataset). Overall, τ tends to be longer in the northern hemisphere (median 68 years, IQR 78) than in the southern hemisphere (median 10 years, IQR 26).

Figure 2B–D shows the corresponding values of the pore water velocity v, dispersion coefficient D, and the vadose zone thickness DWT. Broad patterns suggest that soil profiles with high v and shallow DWT values tend to correspond with low τ values. Considering only soil profiles with ADRE model R^2 values larger than 0.6 (n = 39; 15 of 17 locations) shows that τ is a nonlinear function of DWT (Figure 2E, blue-dashed curve). Considering all soil profiles regardless of the ADRE R^2 values yields the same relationship (Figure 2E, red-dotted curve).

3.2 | Model-based inventory of applicability of the tritium tracing method

Our global implementation of the statistical model for grid points over the ecoregions with explanatory variables within the ranges of the observations shows that the tritium method may be applicable up to 83 years (median 27 years, IQR 38 years) at 20% of the land mass (excluding Antarctica and Greenland) (Figure 3A). Note that τ may also be longer in deserts and xeric shrublands (median 47 years, IQR 25), Mediterranean forests and woodlands (median 28 years, IQR 23), and montane grasslands (median 23 years, IQR 24) than in tropical and subtropical grasslands (19 years, 22), and temperate grasslands and savannas (median 17 years, IQR 23).

In the conterminous United States (CONUS), the method may still be applicable over 34% of the land area, with a median of 24 years (IQR 37 years). In northeastern United States, the method may be applicable for a median of 18 years (IQR 16 years). In the western United States, the method may be applicable for a median of 40 years (IQR 40 years).

4 | DISCUSSION

4.1 | The interplay between transport, vadose zone thickness, and model applicability

The search for places with low groundwater recharge rates sustained much of the historical interest in the tritium method for deep vadose zone research (Rockhold et al., 1995; Scanlon et al., 2002). Identifying low recharge areas in turn was important for radioactive and hazardous waste disposal (Scanlon et al., 1997; Tyler et al., 1996). Although the 5 arc-minute resolution (approximately 10 × 10 km at the equator) of our geospatial model is too low for focused recharge studies, it is high enough to estimate diffuse recharge for groundwater resource assessments (Döll & Fiedler, 2008).

Applicability of the tritium tracing method relative to the unsaturated zone thickness depends, unsurprisingly, on the

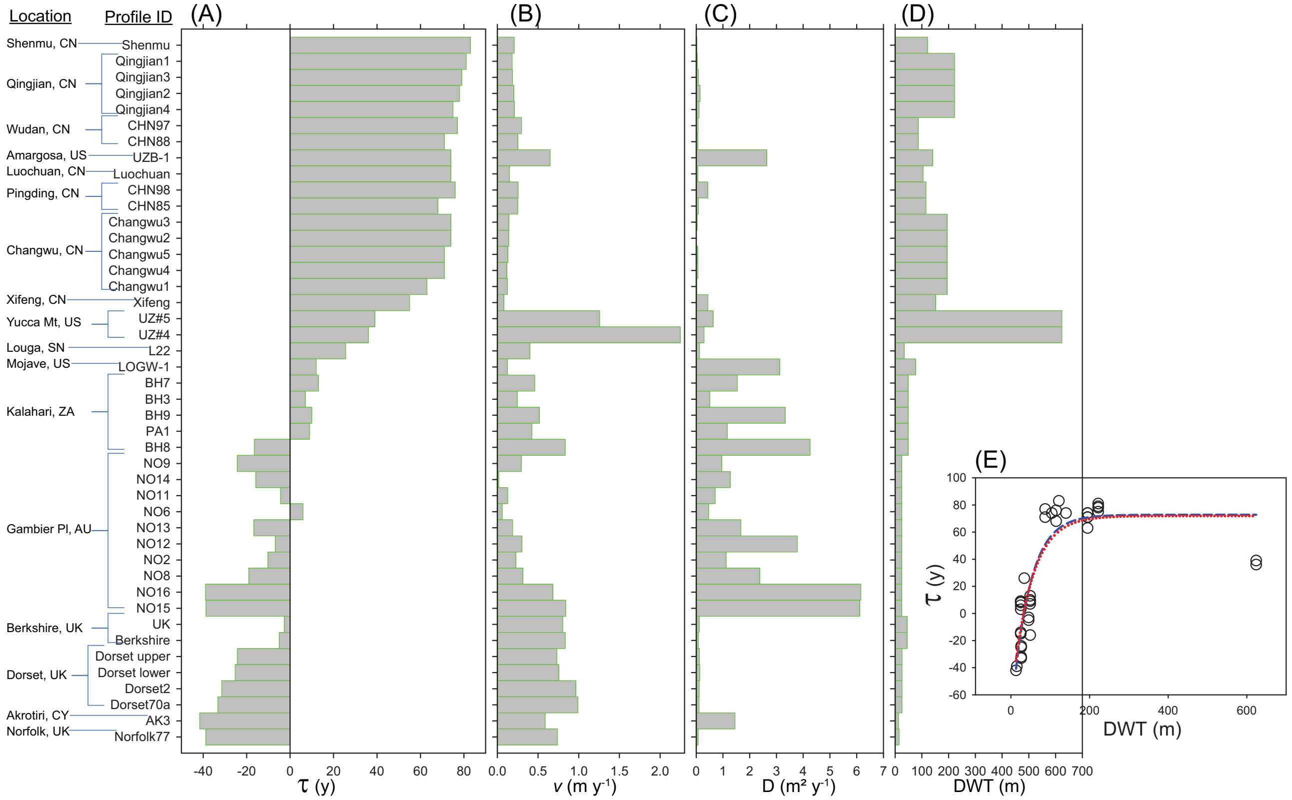

FIGURE 2 Panel A shows applicability τ of the tritium tracing method in years (zero represents 2022) per soil profile ($n = 44$) in the compiled dataset, arranged in decreasing average τ per location; soil profiles from the same location are nested together. Panels B, C, and D show corresponding values of the pore water velocity v (m year^{-1}), dispersion coefficient D (m^2 year^{-1}), and depth-to-water table DWT (m). Panel E shows the relationship between DWT and τ; the blue-dashed (root mean qquare error [RMSE] 18.69) and red-dotted (RMSE 19.38) curves are exponential best fits through the data for profiles with advection-dispersion reaction equation (ADRE) $R^2 \geq 0.6$ ($n = 39$; 15 of 17 locations) and for all soil profiles, respectively.

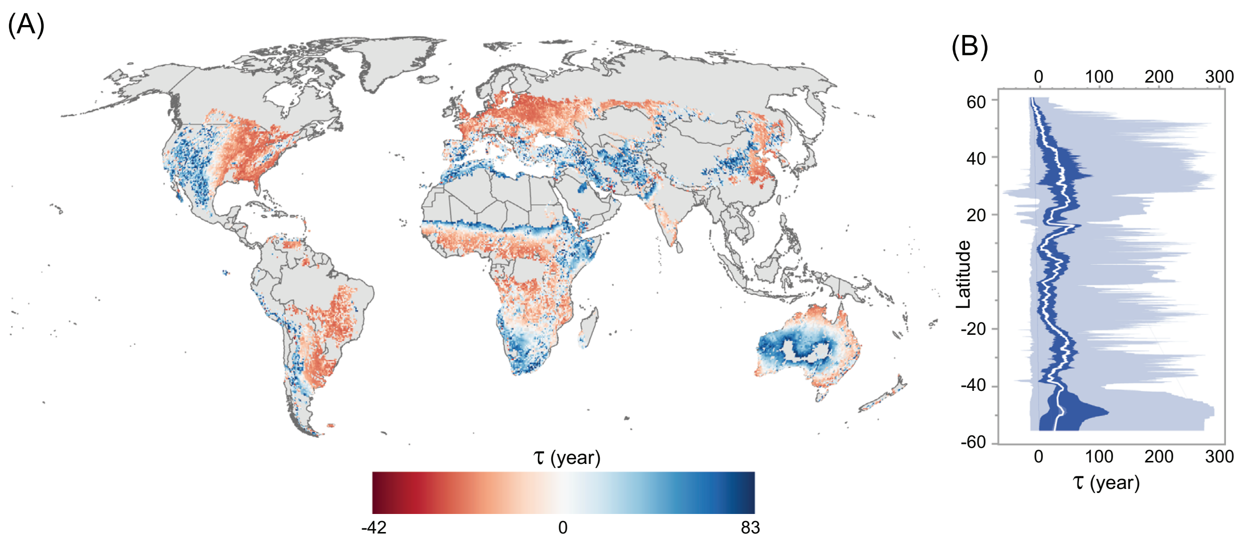

FIGURE 3 Panel A shows a mean annual precipitation (MAP) of predicted applicability (τ) of the tritium tracing method using the statistical model (also see Table S3). Grey areas indicate locations where actual evapotranspiration (AET)/P, potential evapotranspiration (PET)/P, depth to water table (DWT), τ, and the ecoregions lie outside the values found in the calibration dataset and thus are not considered in the geospatial model (i.e., values outside PET/P between 0.90 and 9.8, DWT between 12 and 624 m, and τ between −42 and 83 years). Panel B shows the latitudinal distributions of τ represented as a continuous version of a wandering schematic plot or "moving box" (Tukey, 1977); the white line is a moving median, the dark-blue shaded region represents the extents of the box plots, and the light-blue shaded region the extents of the whiskers.

prevailing pore water velocity (v). For example, the estimated mean v of 0.13 m year^{-1} at Changwu5 in China's Loess Plateau (CLP) corresponds to a reported characteristic peak depth of 7 m in sampling year 2015 (Li et al., 2018). The thick loess deposits at CLP, extending to over 200 m, ensure a sufficiently thick unsaturated zone, whereas the high 1963 atmospheric tritium levels guarantee a clear characteristic peak (Figure 1C). Assuming the same v, the ADRE predicts a peak depth of 17.1 m, which corresponds to a τ of 71 years. This suggests that at this location, τ is mainly limited by transport and radioactive decay, not by the vadose zone thickness. Conversely, the estimated mean v of 0.84 m year^{-1} at Berkshire, UK, corresponds to a reported characteristic peak depth of 4 m in sampling year 1968 (Smith et al., 1970). Assuming the same v, the ADRE predicts a peak depth of 45.4 m, which corresponds to a τ of −5 years. The relatively high v and shallow DWT (45 m) values at this location mean that τ is mainly limited by the thickness of the unsaturated zone.

From a mechanistic model standpoint, given known v and D values, the ADRE may be used to constrain site-level estimates of the depths at which the characteristic peak of soil water tritium could become too small to measure. In this study, we report τ for two thresholds: 0.3 (Figure 2) and 0.02 TU (Table S1). In practice, thresholds can vary depending on analytical precision, detection limit, the invoked electrolytic enrichment method, and capability to prevent sample contamination (Morgenstern & Taylor, 2009).

Given known PET/P and DWT values at a site, the statistically robust 3-parameter statistical model may be used to predict the last date that the tritium method may still be applicable (threshold set at 0.3 TU). From the profile estimates alone, we found that τ tends to be longer in the northern hemisphere (median 69 years, IQR 78.5) than in the southern hemisphere (median 8 years, IQR 5). The latitudinal distribution of modeled τ, however, suggests that the bomb tritium signal is preserved as well in the southern as in the northern hemisphere, despite estimates that only about 5% of the atmospheric bomb tritium mixed into the southern hemisphere (Morgenstern et al., 2010).

The explanatory power of PET/P and DWT for τ is a result of slower water flow in the vadose zones of warmer and drier settings. These locations also tend to have thicker vadose zones. Consequently, the time it takes for water to reach the water table tends to be longer with larger vadose zone thicknesses.

4.2 | Limitations and possible sources of uncertainty

It is not clear what fraction of the soil water tritium profiles in the literature satisfies the two inclusion criteria that were adopted in this study. This suggests opportunities for future systematic literature reviews and/or meta-analyses that examine the utility of the "tritium peak" and "tritium mass balance" methods for estimating groundwater recharge. The criteria for including a soil profile in the dataset are limited to the two conditions that satisfy the implementation of the "tritium peak method." We do not (and cannot) claim that the literature review conducted was systematic, sensu stricto, for example, following the PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) guidelines (Evaristo & McDonnell, 2017; Liberati et al., 2009). Thus, more data may be available than what is represented in our dataset.

An ideal, robust approach to quantifying recharge rates is to accurately measure the seasonal, annual, and spatial variations of the input tritium content in precipitation (Plummer et al., 1993). Unfortunately, these approaches were not possible to implement in our study because of the limited data that are available across all study sites. Future studies could possibly consider using input tritium data of precipitation at places where such data are available (e.g., data in Jasechko, 2019). We estimated that the tritium concentrations represented in our compiled soil profiles are, on average, 1087 TU (1σ 1565). This was determined by integrating under the Lorentzian curve fit for each profile. Thus, it is apparent that the tritium concentrations represented in the compiled soil profiles are, on average, 18% of the precipitation input tritium, assuming an atmospheric input of 6000 TU in the northern hemisphere (Zuber & Maloszewski, 2008). This suggests that a considerable proportion of the precipitation input tritium, and by extension, the infiltrating water, might have bypassed much of the soil profile via preferential flowpaths (Scanlon, 2000), extracted by vegetation (Phillips, 1994), or intercepted by the canopy or litter layer. This estimate, however, does not account for radioactive decay, a process that our study attempts to consider. Other factors may influence not only the rate of displacement but also the mass that is integrated under the characteristic shape of the soil tritium profile. For example, land cover and land use have been shown to influence the displacement of the tritium peak at neighboring sites (Huang et al., 2019). While a finer scale understanding of the factors that control the retention and movement of soil tritium in deep soils is crucial, this is presently beyond the scope of this study. We note, however, that the PCR-GLOBWB's (PCRaster Global Water Balance) (De Graaf et al., 2017) recharge rate and vadose zone thickness already consider the spatial variation of soil and land use, as well as spatial variations in the climate and precipitation rate.

5 | CONCLUSIONS

There has been renewed interest in the use of tritium for groundwater recharge and vadose zone studies, mostly from the Loess Plateau of China. This prompted us to identify the locations, globally, where the tritium tracing method may still be applicable and for how long. Building on compiled soil water tritium profiles from the literature, we applied a statistical model—informed by hydroclimate and unsaturated zone thickness—to globally distributed grid points. Our findings show that the tritium method may still be applicable in about 20% of the global land mass (excluding Antarctica and Greenland) where the model was applied. Our results are useful as first-order approximations of where the tritium peak method may still work, preferably in combination with other tracers (e.g., Jasechko, 2019). For sensitive applications of contaminant transport, hazardous waste disposal and storage, and water resources management, the tritium method should ideally be used in conjunction with mechanistic analyses of subsurface water flow and contaminant transport.

AUTHOR CONTRIBUTIONS

Yanan Huang: Data curation; formal analysis; methodology; software. **Jaivime Evaristo**: Conceptualization; formal analysis; methodology; software; validation; visualization; writing—original draft; writing—review and editing. **Zhi Li**: Conceptualization; data curation; funding acquisition; methodology; writing—original draft. **Kwok P. Chun**: Methodology; software; validation; visualization; writing—review and editing. **Edwin H. Sutanudjaja**: Formal analysis; methodology; software; validation; visualization; writing—review and editing. **M. Bayani Cardenas**: Methodology; software; supervision; validation; visualization; writing—review and editing. **Marc F. P. Bierkens**: Methodology; supervision; validation; visualization; writing—review and editing. **James W. Kirchner**: Formal analysis; methodology; supervision; validation; visualization; writing—review and editing. **Martinus Th. van Genuchten**: Formal analysis; methodology; software; supervision; validation; visualization; writing—review and editing.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

The data used in the study can be obtained from Dryad (https://datadryad.org/stash/share/sXW1d6pAMNAPazSD5ojs2E9OwGLV34mYyv-nq0quc6o). The R codes used in the study can be obtained from GitHub (https://github.com/edwinkost/tritium). Other information regarding the invoked statistical analysis and geospatial modeling methods are detailed in the Supporting Information.

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REFERENCES

Allison, G. B., Gee, G. W., & Tyler, S. W. (1994). Vadose-zone techniques for estimating groundwater recharge in arid and semiarid regions. *Soil Science Society of America Journal*, *58*(1), 6–14. https://doi.org/10.2136/sssaj1994.03615995005800010002x

Begemann, F., & Libby, W. F. (1957). Continental water balance, ground water inventory and storage times, surface ocean mixing rates and world-wide water circulation patterns from cosmic-ray and bomb tritium. *Geochimica et Cosmochimica Acta*, *12*(4), 277–296. https://doi.org/10.1016/0016-7037(57)90040-6

Camacho Suarez, V. V., Saraiva Okello, A. M. L., Wenninger, J. W., & Uhlenbrook, S. (2015). Understanding runoff processes in a semi-arid environment through isotope and hydrochemical hydrograph separations. *Hydrology and Earth System Sciences*, *19*(10), 4183–4199. https://doi.org/10.5194/hess-19-4183-2015

de Graaf, I. E. M., van Beek, R. L. P. H., Gleeson, T., Moosdorf, N., Schmitz, O., Sutanudjaja, E. H., & Bierkens, M. F. P. (2017). A global-scale two-layer transient groundwater model: Development and application to groundwater depletion. *Advances in Water Resources*, *102*, 53–67. https://doi.org/10.1016/j.advwatres.2017.01.011

Dinerstein, E., Olson, D., Joshi, A., Vynne, C., Burgess, N. D., & Wikramanayake, E. (2017). An ecoregion-based approach to protecting half the terrestrial realm. *Bioscience*, *67*(6), 534–545. https://doi.org/10.1093/BIOSCI/BIX014

Döll, P., & Fiedler, K. (2008). Global-scale modeling of groundwater recharge. *Hydrology and Earth System Sciences*, *12*(3), 863–885. https://doi.org/10.5194/HESS-12-863-2008

Evaristo, J., & McDonnell, J. J. (2017). A role for meta-analysis in hydrology. *Hydrological Processes*, *31*(20), 3588–3591. https://doi.org/10.1002/hyp.11253

Fan, Y., Li, H., & Miguez-Macho, G. (2013). Global patterns of groundwater table depth. *Science*, *339*(6122), 940–943. https://doi.org/10.1126/science.1229881

Gleeson, T., Befus, K. M., Jasechko, S., Luijendijk, E., & Cardenas, M. B. (2016). The global volume and distribution of modern groundwater. *Nature Geoscience*, *9*, 161–167. https://doi.org/10.1038/ngeo2590

Huang, Y., Evaristo, J., & Li, Z. (2019). Multiple tracers reveal different groundwater recharge mechanisms in deep loess deposits. *Geoderma*, *353*, 204–212. https://doi.org/10.1016/J.GEODERMA.2019.06.041

Jasechko, S. (2019). Global isotope hydrogeology——review. *Reviews of Geophysics*, *57*(3), 835–965. https://doi.org/10.1029/2018RG000627

Kirchner, J. W. (2016). Aggregation in environmental systems-Part 1: Seasonal tracer cycles quantify young water fractions, but not mean transit times, in spatially heterogeneous catchments. *Hydrology and Earth System Sciences*, *20*(1), 279–297. https://doi.org/10.5194/HESS-20-279-2016

Lehmann, B. E., Davis, S. N., & Fabryka-Martin, J. T. (1993). Atmospheric and subsurface sources of stable and radioactive nuclides used for groundwater dating. *Water Resources Research*, *29*(7), 2027–2040. https://doi.org/10.1029/93WR00543

Li, H., Si, B., & Li, M. (2018). Rooting depth controls potential groundwater recharge on hillslopes. *Journal of Hydrology*, *564*, 164–174. https://doi.org/10.1016/J.JHYDROL.2018.07.002

Li, Z., & Si, B. (2018). Reconstructed precipitation tritium leads to overestimated groundwater recharge. *Journal of Geophysical Research: Atmospheres*, *123*(17), 9858–9867. https://doi.org/10.1029/2018JD028405

Li, Z., Jasechko, S., & Si, B. (2019). Uncertainties in tritium mass balance models for groundwater recharge estimation. *Journal of Hydrology*, *571*, 150–158. https://doi.org/10.1016/j.jhydrol.2019.01.030

Liberati, A., Altman, D. G., Tetzlaff, J., Mulrow, C., Gøtzsche, P. C., & Ioannidis, J. P. A. (2009). The PRISMA statement for reporting systematic reviews and meta-analyses of studies that evaluate healthcare interventions: Explanation and elaboration. *BMJ*, *339*, b2700 https://doi.org/10.1136/BMJ.B2700

Linke, S., & Lehner, B., Ouellet Dallaire, C., Ariwi, J., Grill, G., & Anand, M. (2019). Global hydro-environmental sub-basin and river reach characteristics at high spatial resolution. *Scientific Data*, *6*(1), 1–15. https://doi.org/10.1038/s41597-019-0300-6

Lucas, L. L., & Unterweger, M. P. (2000). Comprehensive review and critical evaluation of the half-life of tritium. *Journal of Research of the National Institute of Standards and Technology*, *105*, Article 541. https://doi.org/10.6028/jres.105.043

Mahmoodlu, M. G., Raoof, A., & Van Genuchten, M. T. (2021). Effect of soil textural characteristics on longitudinal dispersion in saturated porous media. *Journal of Hydrology and Hydromechanics*, *69*(2), 161–170. https://doi.org/10.2478/JOHH-2021-0004

Morgenstern, U., & Taylor, C. B. (2009). Ultra low-level tritium measurement using electrolytic enrichment and LSC. *Isotopes in Environmental and Health Studies*, *45*(2), 96–117. https://doi.org/10.1080/10256010902931194

Morgenstern, U., Stewart, M. K., & Stenger, R. (2010). Dating of streamwater using tritium in a post nuclear bomb pulse world: Continuous variation of mean transit time with streamflow. *Hydrology and Earth System Sciences*, *14*(11), 2289–2301. https://doi.org/10.5194/hess-14-2289-2010

Pelletier, J. D., Broxton, P. D., Hazenberg, P., Zeng, X., Troch, P. A., & Niu, G. Y. (2016). A gridded global data set of soil, intact regolith, and sedimentary deposit thicknesses for regional and global land surface modeling. *Journal of Advances in Modeling Earth Systems*, *8*(1), 41–65. https://doi.org/10.1002/2015MS000526

Phillips, F. M. (1994). Environmental tracers for water movement in desert soils of the American southwest. *Soil Science Society of America Journal*, *58*(1), 15–24. https://doi.org/10.2136/sssaj1994.03615995005800010003x

Phillips, F. M. (1995). The use of isotopes and environmental tracers in subsurface hydrology. *Reviews of Geophysics*, *33*(2S), 1029–1033. https://doi.org/10.1029/95RG00247

Plummer, L. N., Michel, R. L., Thurman, E. M., & Glynn, P. D. (1993). Environmental tracers for age dating young ground water. In W. M. Alley (Ed.), *Regional ground-water quality* (pp. 255–294). VAN Nostrand Reinhold.

Rempe, D. M., & Dietrich, W. E. (2014). A bottom-up control on fresh-bedrock topography under landscapes. *Proceedings of the National Academy of Sciences of the United States of America*, *111*(18), 6576–6581.

Rockhold, M., Fayer, M., Kincaid, C., & Gee, G. (1995). *Estimation of natural ground water recharge for the performance assessment of a low-level waste disposal facility at the Hanford site*. https://doi.org/10.2172/46664

Scanlon, B. R. (2000). Uncertainties in estimating water fluxes and residence times using environmental tracers in an arid unsaturated zone. *Water Resources Research*, *36*(2), 395–409. https://doi.org/10.1029/1999WR900240

Scanlon, B. R., Healy, R. W., & Cook, P. G. (2002). Choosing appropriate techniques for quantifying groundwater recharge. *Hydrogeology Journal*, *10*(1), 18–39. https://doi.org/10.1007/s10040-001-0176-2

Scanlon, B. R., Tyler, S. W., & Wierenga, P. J. (1997). Hydrologic issues in arid, unsaturated systems and implications for contaminant transport. *Reviews of Geophysics*, *35*(4), 461–490. https://doi.org/10.1029/97RG01172

Seeger, S., & Weiler, M. (2014). Reevaluation of transit time distributions, mean transit times and their relation to catchment topography. *Hydrology and Earth System Sciences*, *18*, 4751–4771. https://doi.org/10.5194/hess-18-4751-2014

Si, B. C., & de Jong, E. (2007). Determining long-term (decadal) deep drainage rate using multiple tracers. *Journal of Environmental Quality*, *36*(6), 1686–1694. https://doi.org/10.2134/jeq2007.0029

Šimunek, J., van Genuchten, M. Th., Šejna, M., Toride, N., & Leij, F. J. (2000). *The STANMOD computer software for evaluating solute transport in porous media using analytical solutions of convection-dispersion equation* (Version 2.0, IGWMC-TPS-71). International Ground Water Modeling Center (IGWMC).

Smith, D. B., Wearn, P. L., Richards, H. J., & Rowe, P. C. (1970). Water movement in the unsaturated zone of high and low permeability strata by measuring natural tritium. In *Isotope hydrology 1970: Proceedings of a symposium* (pp. 73–85). International Atomic Energy Agency. https://inis.iaea.org/collection/NCLCollectionStore/_Public/45/025/45025950.pdf?r=1

Tague, C., & Grant, G. E. (2009). Groundwater dynamics mediate low-flow response to global warming in snow-dominated alpine regions. *Water Resources Research*, *45*(7), 7421. https://doi.org/10.1029/2008WR007179

Toride, N., Leij, F. J., & van Genuchten, M. Th. (1999). The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments. (Version 2.1, Research Report 137). U.S. Salinity Laboratory.

Tukey, J. W. (1977). *Exploratory data analysis*. Addison-Wesley Publishing Company.

Tyler, S. W., Chapman, J. B., Conrad, S. H., Hammermeister, D. P., Blout, D. O., & Miller, J. J. (1996). Soil-water flux in the Southern Great Basin, United States: Temporal and spatial variations over the last 120,000 years. *Water Resources Research*, *32*(6), 1481–1499. https://doi.org/10.1029/96WR00564

van Genuchten, M. Th. (1981). Analytical solutions for chemical transport with simultaneous adsorption, zero-order production and first-order decay. *Journal of Hydrology*, *49*, 213–233. https://doi.org/10.1016/0022-1694(81)90214-6

van Genuchten, M. Th., & Parker, J. C. (1984). Boundary conditions for displacement experiments through short laboratory soil columns. *Soil Science Society of America Journal*, *48*, 703–708.

van Genuchten, M. Th., Šimůnek, J., Leij, F. J., Toride, N., & Šejna, M. (2012). STANMOD: Model use, calibration and validation. *American Society of Agricultural and Biological Engineers*, *55*(4), 1353–1366.

Zhang, Z. Q., Evaristo, J., Li, Z., Si, B. C., & McDonnell, J. J. (2017). Tritium analysis shows apple trees may be transpiring water several decades old. *Hydrological Processes*, *31*(5), 1196–1201. https://doi.org/10.1002/hyp.11108

Zuber, A., & Maloszewski, P. (2008). *Lumped parameter models*. (IAEA-TCS–32/F). International Atomic Energy Agency (IAEA).

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