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On the relevance of molecular diffusion for travel time distributions inferred from different water isotopes

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Abstract: Water isotopes are a tool of choice for assessing travel time distributions of water and chemical species in soils, aquifers and rivers. However, the question of whether different water isotopes tag the same travel time distributions of the water molecule, or whether the inferred travel time distribution is specific to the chosen water isotope, remains under debate. Here we conjecture that the latter is correct. We state that (a) travel time distributions of water and any tracer reflect the spectrum of fluid velocities and diffusive/dispersive mixing between the flow lines connecting the system in- and outlet, and (b) the self-diffusion coefficients of deuterium, tritium and ^{18}O differ by as much as 10%. Using particle tracking simulations, we show that these differences do indeed affect the variance of the travel time distribution – as one would expect for well-mixed advective-dispersive transport. Moreover, our simulations suggest that in the case of imperfect mixing, also the average travel time becomes sensitive to the differences in self-diffusion coefficients. We find that when advective trapping occurs in low conductive zones, an isotope with a smaller diffusion coefficient remains there for longer times compared to a substance exhibiting faster diffusion. This implies that for imperfectly mixed transport, average transit times ultimately increase with a decreasing self-diffusion coefficient: deuterium has the longest average travel time, followed by tritium, followed by ^{18}O. Depending on the type of simulated system, we find differences in average travel times ranging from 10 days to more than 2 years. As these differences are in relative terms of order 5-10%, one could be tempted to erroneously explain them as measurement errors. Our findings suggest instead that these differences are physics based. These differences persist and even grow with increasing space and time scales, rather than being averaged out. We thus conclude that travel time distributions inferred from O-H isotopes of the water molecule are conditioned by the chosen water isotope.

1 INTRODUCTION

Travel or transit time distributions play a key role in contaminant leaching from the partially saturated zone into groundwater (Sternagel et al., 2021; Klaus et al., 2013; Klaus et al., 2014) and stream flow chemistry in general (Kirchner et al., 2000). As early as 1982, Simmons (1982) and Jury (1982) introduced the concept of travel time and travel distance distributions into soil physics, to acknowledge that field observations of solute transport were frequently inconsistent with predictions of the advection-dispersion model. When injecting a tracer pulse into the soil, the normalized concentration as function of depth characterizes the distribution of travel

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distances at a fixed time, while the time series of the normalized concentration observed at a constant depth yields the distribution of times the molecules need to travel to this depth (TTD). Recalling the theory of linear systems, Simmons (1982) and Jury (1982) advocated the TTD, also often referred to as solute breakthrough curve (BTC), as the transfer function for simulating solute breakthrough to a given depth.

The charm of this approach is that by using alternative transfer functions, one can step beyond the limitations of advective-dispersive transport. The latter is also called Fickian transport and reflects the case of perfect mixing, wherein chemical species visit the entire domain and thus experience the entire spectrum of fluid velocities "many" times. In this case, the central limit theorem applies, and normally distributed transport distances emerge and the variance in travel distances grows linearly with time (Roth and Hammel, 1996). Simmons et al. (1982) showed that a stochastic convective transfer function is well suited to simulate solute transport in the yet imperfectly mixed near field, where the variance in travel distance grows with the squared transport time. The general drawback here is that transfer function approaches require linearity and thus a time invariant velocity field. However, water flow velocities do change nonlinearly with soil water content, which means that TTD are conditional to (changing) soil water contents and rainfall forcings. This explains notably why transfer function approaches are (despite their mathematical appeal) of low practical relevance to predict solute leaching in soils.

Naturally, the concept of travel time distributions has been generalized to groundwater systems. Berkowitz and Scher (1995) introduced the continuous time domain random walk to simulate Fickian and non-Fickian transport of chemical species, which essentially uses transfer functions characterizing travel time distributions of solutes inferred from observed BTC; see Berkowitz et al. (2006) for a detailed introduction. A closer look reveals that travel or transit time distributions can also be defined for entire river basins (McGlynn et al., 2002; McGlynn et al., 2003; Weiler et al., 2003; Hrachowitz et al., 2009; Hrachowitz et al., 2016; Benettin et al., 2015; Benettin et al., 2018; Rodriguez et al., 2018; Rodriguez et al., 2021), because catchments or watersheds drain the collected precipitation to their stream outlet or release it via evapotranspiration. The defined "inlet" for rainfall and tracers is hence the catchment surface/soil surface, while the defined outlet is either the riparian zone or the vegetation. As flow velocities in the stream are several orders of magnitude larger relative to those prevailing in the subsurface domain, tracer observations at the catchment outlet yield a very good (lumped)

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approximation of the transit time distribution of water and chemical species through the catchment system into the stream.

Early attempts to predict stream flow chemistry relied also on transfer functions and naturally faced the same problems of state-dependent and seasonally varying travel time distributions (Hrachowitz et al., 2013; Klaus et al., 2015; Rodriguez et al., 2018). Alternative approaches rely on age ranked storage in combination with StoreAgeSelection (SAS) functions for, e.g., stream flow to infer the respective travel time distributions (Harmann et al. 2015; Rinaldo et al., 2015). This requires the numerical solution of the Master Equation, i.e., the catchment water balance for each time and each age (Rodriguez and Klaus, 2019) and an appropriate selection of the SAS-function, e.g., as a gamma or beta distribution (Hrachowitz et al., 2010; Klaus et al., 2015; Rodriguez and Klaus, 2019; van der Velde et al., 2012). Recent work reveals that this approach is even suited to capture fingerprints of preferential flow in the partially saturated zone (Türk et al, 2025).

Regardless of whether one favours the transfer function or the SAS approach, water isotopes are in both cases used as a continuous source of information for transit time distributions at the pedon (Sprenger et al. 2016) and the catchment scales (McGlynn et al., 2002; McGlynn and Seibert, 2003; Weiler et al., 2003; Klaus et al., 2013; Sprenger et al., 2016). Yet to date, a controversial debate prevails as to whether different water isotopes yield information on the same travel time distribution. Rodriguez et al. (2021) found different median travel times of deuterium (1.77 y) and tritium (2.19 y) in the 42 ha large Weierbach catchment in Luxembourg. However, the authors considered these differences as unphysical, because they refer to two times “the same water molecule” and explained these differences by mere measurement uncertainty. However, Stewart et al. (2010, 2021) report that average travel times inferred from ^{18}O and tritium might differ more than one year and argued that these differences are significant and physics based.

Here we conjecture that travel time distributions are indeed specific to the chosen water isotope. More specifically, we argue that (a) TTDs reflect the spectra of fluid velocities along the flowlines of variable lengths *as well as* diffusive and/or dispersive mixing among them, and (b) the self-diffusion coefficients of deuterium (D_2O or HDO), tritium (HTO) and ^{18}O ($^{18}OH_2$) differ by as much as 10%. At the pore scale, one would thus naturally expect differences, as the

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underlying transport process is essentially advective-diffusive. At larger scales, one can observe either Fickian or non-Fickian transport. Fickian transport reflects, as already stated, the asymptotic case of perfect mixing, characterized by normally distributed transport distances in line with the advection-dispersion equation. However, the dispersion coefficient grows with the inverse of the molecular diffusion coefficient, as detailed in section 2.1. Differences in self-diffusion coefficients of water isotopes should hence affect dispersion and thus the variance of travel times. However, one would not expect differences in average travel times, because for advective-dispersive transport the latter is controlled solely by the average fluid velocity. This in turn does not depend on molecular diffusion or on the dispersion coefficient.

Here we conjecture that in the case of imperfect mixing, the average travel time becomes sensitive to differences in diffusion coefficients, as detailed in section 2.1. Anomalous transport can manifest through skewed travel distance distributions leading to a faster first arrival and/or a longer tailing compared to Fickian transport (Levy and Berkowitz, 2003; Edery et al., 2014; Edery et al., 2015; Dentz et al., 2023). Recent experimental work of Elhanati et al. (2025) investigating the breakthrough of deuterium and Br^- through saturated columns containing uniform and heterogeneous arrangements of porous media revealed very similar behavior of both tracers, and quantitative analysis demonstrated clearly non-Fickian transport with long tailing of breakthrough curves. Motivated by these findings and the discussion between Stewart et al. (2010, 2021) and Rodriguez et al. (2021), we use physically based numerical simulations to test our conjecture. To this aim, we explore the sensitivity of average travel times to the changes in self-diffusion coefficients, comparing transport of tritium, deuterium and ^{18}O through media with different types and levels of heterogeneity.

2 BACKGROUND AND NUMERICAL SIMULATIONS

2.1 Background: Solute transport in porous media in a nutshell

Before detailing the numerical experiments, we briefly revisit the theory of dissolved matter transport, to justify our conceptual and numerical simulation approach. In the simplest case, i.e., dissolved transport of an inert (non-reactive, conservative) substance through a fluid at rest is solely controlled by molecular diffusion. According to Fick's law, the solute flux $\boldsymbol{j}$ (kg s^{-1} m^2) is the product of the molecular diffusion coefficient, D_{mol} (m^2 s^{-1}), and the gradient in solute concentration, C (kg m^{-3}):

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$$\boldsymbol{j} = -D_{mol}\,\nabla C \quad \text{(Eq.1)}.$$

Einstein (1905) showed that molecular diffusion is an effective, macroscopic fingerprint of Brownian motion. Molecular diffusion (D_{mol}) grows with the absolute temperature but decreases with the viscosity of the fluid and the diameter of the molecule. Moreover, it is well known that for a fluid at rest and assuming an initial delta distribution of the substance, the travel distance obeys Gaussian distribution, centered at the origin (Einstein, 1905). The variance of travel distance grows linearly with time t (s), while the molecular diffusion coefficient is the growth factor.

When the fluid moves with constant and spatially homogeneous velocity, $\boldsymbol{v}$ (m s^{-1}), the solute flux is the sum of an advective and a diffusive component:

$$\boldsymbol{j} = \boldsymbol{v}C - D_{mol}\,\nabla C \quad \text{(Eq. 2)}.$$

This is what is meant when loosely stating that the "solute velocity" is not equal to the fluid velocity. The distribution of travel distances still obeys Gaussian behavior, its variance increases proportionally to D_{mol} and t, while the mean travel distance grows with $\boldsymbol{v}\,t$. This is the well-known case of advection-diffusion.

In line with Einstein's argument and Roth and Hammel (1996), we note that dispersion is a macroscopic, effective fingerprint of diffusive mixing of solutes between flowlines of different fluid velocities. Recalling that water flow in an individual soil pore can be characterized by Hagen-Poiseuille law, this can be effectively visualized by discussing the migration of a tracer pulse injected into a pore of radius r (m) and travelling through the parabolic velocity field. Fig. 1 displays the three main states of Taylor-Aris dispersion, which were all inferred from particle tracking simulations (see section 2.2) through a parabolic flow field with mean velocity of v = 10^{-4} m/s. For times t much smaller than the diffusive mixing time scale, $t_{mix} = \frac{\mathbf{2}r^2}{D_{mol}}$, tracer molecules migrate along the same flowline and their displacement mirrors essentially the parabolic flow field (Fig. 1a). In this so-called near field, transport is essentially deterministic and the variance in travel distance scales with t^2, as shown in Figs. 1e and 1f for small transport times. However, the non-uniform displacements in x directions cause a transversal

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concentration gradient between the flowlines, which is gradually depleted by transversal diffusive mixing from fast to slow flowlines and *vice versa* (see Fig. 1b for $t = t_{mix}$). For times much larger than the diffusive mixing time, all molecules experience the entire velocity field many times and the central limit theorem applies (Fig. 1 c).

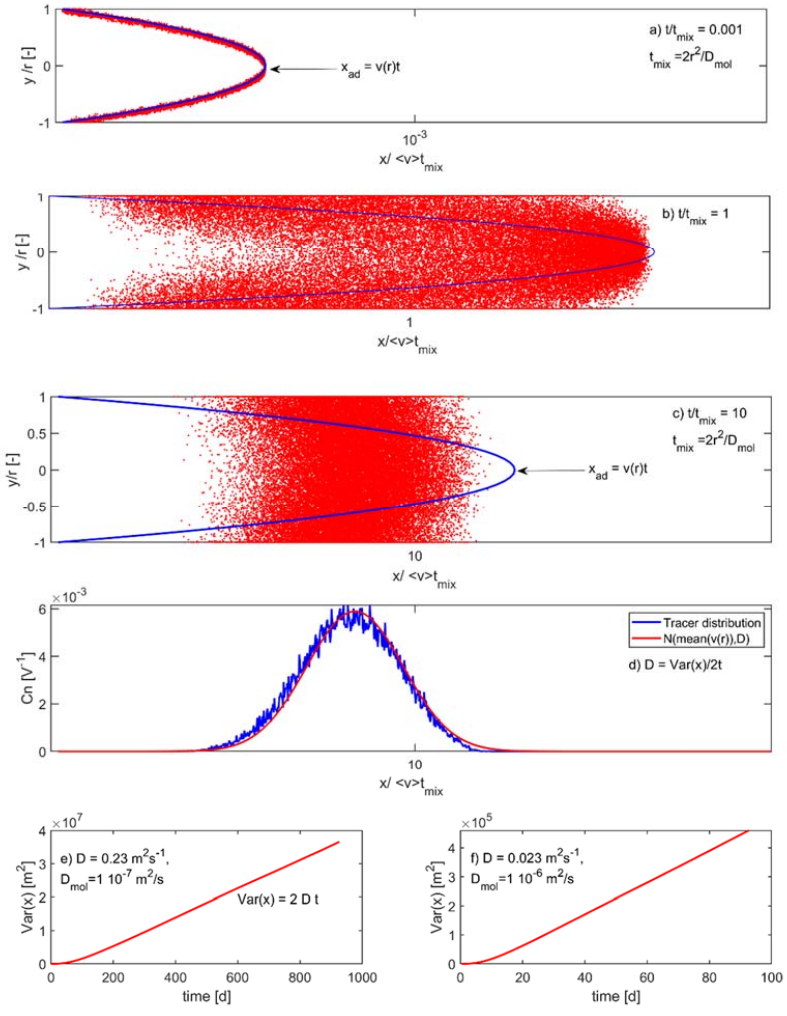

Figure 1: The three stages of Taylor-Aris dispersion in a capillary tube pore with radius r (m) as a function of the diffusive mixing time scale t_{mix}= 2r/D_{mol}: (a) near field for $t << t_{mix}$, intermediate state for $t=t_{mix}$ (b) and well mixed far field for $t >> t_{mix}$ (c). Variance of particle transport distances as a function of time for D_{mol} = 1 × 10^{-6} m^2/s(e) and D_{mol} = 1 × 10^{-7} m^2/s (f). All graphs were inferred from transport simulations based on particle tracking.

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The comparison of the travel distance distribution inferred from the particles to the Gaussian distribution in Fig. 1c corroborates that indeed a Gaussian travel time distribution eventually emerges. The mean travel distance grows with the spatially averaged fluid velocity, $\overline{\boldsymbol{v}}$, and t (Fig. 1d). The variance of travel times now grows linearly with t and the slope is the macro-dispersion coefficient D (Fig. 1e,f). For Taylor-Aris dispersion in a cylindrical pore with radius r, the dispersion coefficient is determined as:

$$D = \frac{\overline{\boldsymbol{v}}^2 r^2}{D_{mol}} \quad \text{(Eq. 3)}.$$

The key point is that D grows linearly with D_{mol}^{-1}. Fig. 1 corroborates for the simulated transport of two different tracers with D_{mol} of 1×10^{-7} (Fig. 1e) and 1×10^{-6} m^2/s (Fig. 1f). Diffusion that is slower by a factor of 10 causes not only a ten times larger dispersion coefficient. It also implies that it takes ten times longer to reach the well-mixed advective-dispersive case and that the variance in travel distances increases ten times faster with time. We can thus state that the macro-dispersion coefficient is an effective, macroscopic fingerprint of subscale diffusive mixing between streamlines of variable of fluid velocities.

Of course, we acknowledge that dispersion in a real-world porous medium relates to the variability in pore sizes and that the geometry and tortuosity of soil pores is clearly more complex than the above example. Yet we argue that Taylor dispersion and Hagen-Poiseuille flow occur in each individual soil pore. This implies the lateral diffusive mixing time for isotopic tracers will be due to their different diffusion coefficients, in each individual soil pore, meaning that the tracer with lower diffusion coefficient will experience a stronger longitudinal dispersion. When a well-defined advective-dispersive transport process emerges, we expect that the variance of travel distances will, hence, still grow with the decreasing molecular diffusion coefficient. However, we do not expect that they will show different mean travel times, simply because advective-dispersion transport relies on a linear superposition of advective and dispersive solute flux, and the average flow velocity $\overline{\boldsymbol{v}}$ is not affected by changes in the diffusion coefficient.

$$\boldsymbol{j} = \overbrace{\widetilde{\boldsymbol{v}}\widetilde{C}}^{advective\ solute\ flux} - \overbrace{\widetilde{D}\widetilde{\nabla C}}^{dispersive\ solute\ flux} \quad \text{(Eq. 4)}.$$

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Instead, we propose that the independence of the average transit time from the diffusion coefficient no longer holds when non-Fickian transport occurs. The latter breaks the symmetry of perfect mixing (Bloschl and Zehe, 2005), either because molecules are trapped in low conductive bottlenecks for very long times, and/or because molecules traveling along rapid preferential flow paths leave the system after very short times (Berkowitz and Zehe, 2020; Wienhöfer et al., 2009). As an important implication, the travel time distribution becomes skewed and in the case of advective trapping in low conductive bottlenecks, one might expect that an isotope with a smaller diffusion coefficient stays in the bottlenecks for longer times compared to an isotope which exhibits faster diffusion. This could imply that in case of as for non-Fickian transport average transit times grow with a decreasing diffusion coefficient.

2.2 Transport simulations and numerical experiments

To shed light on the role of the different self-diffusion coefficients of deuterium, tritium and O^{18} for the average transit time distributions, we simulated advective-diffusive transport through steady-state flow fields in 2d saturated domains of increasing heterogeneity, comparing the transport of the three different water isotopes. The respective self-diffusion coefficients at a temperature of 25 °C are, according to Devel (1962) and Wang (1952), $D_{HDO} = 2.25 \times 10^{-9}\ m^2\ s^{-1}$, $D_{HTO} = 2.44 \times 10^{-9}\ m^2\ s^{-1}$ and $D_{18OH2} = 2.66 \times 10^{-9}\ m^2\ s^{-1}$. For the case of HTO we chose to ignore its radioactive decay, to assure that optional differences in average travel times stem only from the differences in self-diffusion coefficients.

In all cases we used particle tracking, the particle advancement, $\Delta \boldsymbol{s}$ (m), being characterized by the Langevin equation, starting from a given particle location at time t_i:

$$\Delta \mathbf{s}(x, y) = \boldsymbol{v}[\mathbf{s}(t_i)]\Delta t + \xi\sqrt{2\, D_{mol}\, \Delta t} \quad \text{(Eq. 5)}$$

The first term characterizes advective displacement, depending on the 2d fluid velocity vector $\boldsymbol{v}$, and the time step Δt. The second term denotes the diffusive displacement, which scales with a modulus of $\sqrt{2\, D_{mol}\, \mathrm{d}t}$ times a standard normally distributed random number ξ.

Three different model scenarios, A, B, and C, are examined, accounting for different types of hydraulic conductivity fields. Scenario A was inspired by the experimental work of Elhanati et

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al. (2025) investigating the breakthrough of deuterium and Br- through homogeneous (uniformly packed) and heterogeneous sand columns (Fig. 2, Scenario A). We simulated steady flow through a 1 m by 10 m block, containing either a sandy or a silty saturated soil, which surrounds a less conductive lens (Fig. 2). The surrounding medium had a hydraulic conductivity of either K_s=1×10^{-5} m/s or K_s=1×10^{-7} m/s and porosity of 0.4 or 0.44, respectively. The low conductive lens had a hydraulic conductivity of either K_s=10^{-8} m/s or K_s=10^{-9} m/s. We used a discretization of 0.2 m by 0.2 m, a permeameter type of boundary condition with a head gradient of 0.05 m/m, and calculated the flow field using the model CATLFOW (Zehe et al. 2001). We considered no-flow boundary conditions on the horizontal domain boundaries. We simulated advective diffusive transport by using particle tracking according to Eq. 5. As scenario A is an upscaled version of the medium that Elhanati et al. (2025) used in their experiments, we expect that non-Fickian transport will emerge in line with their experimental findings.

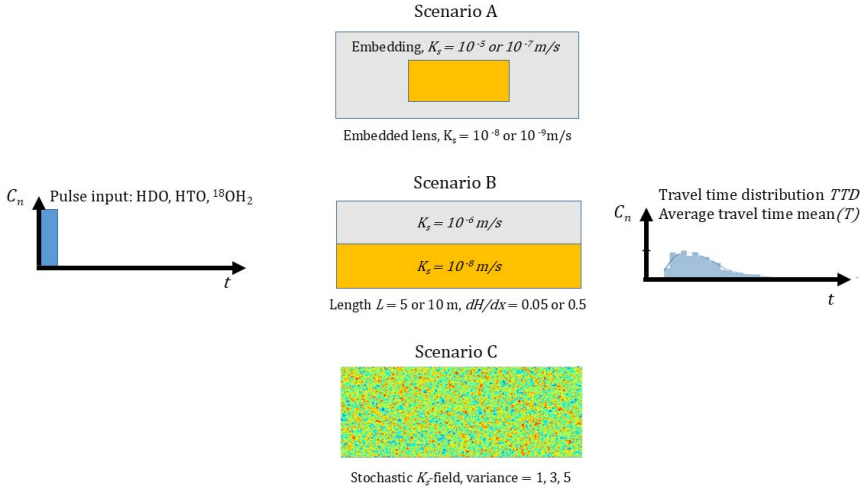

Figure 2: Scheme of model scenarios.

In scenario B, we simulated advective-diffusive solute transport in a simple two-layer aquifer system of 2 m total height and a length of either 5 or 10 m (Fig. 2, Scenario B). The layers with a height of 1m are homogeneous but differ by their saturated hydraulic conductivity K_s=10^{-6} m/s and 10^{-8} m/s. Both layers were exposed to the same head gradient, which was first set to dH/dx = 0.05 and then to dH/dx = 0.5 to compare two different Peclet numbers. Transport of deuterium, tritium and ^{18}O with the diffusion coefficients was simulated using a pulse input of

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100,000 particles through the left upstream domain, while no-flow conditions were assigned to the two horizontal domain boundaries.

In scenario C (Fig. 2, Scenario C; Fig. 3), we considered steady-state fluid flow within two-dimensional, stochastic heterogeneous media with moderate, intermediate and strong variance in the hydraulic conductivity (Zehe et al., 2021). The 60 m long and 20 m wide domain was discretized into 0.2 m by 0.2 m elements. Flow was driven by a head gradient of dH/dx = 1/6, from the left upstream boundary to the right downstream boundary, while no-flow conditions were assigned to the two horizontal domain boundaries. We used random and yet statistically homogeneous, isotropic Gaussian fields of three different variance of ln(K), namely 1, 3 and 5 generated with the sequential Gaussian simulator GCOSIM3D (Gómez-Hernández et al,. 1997) and a correlation length of 1 m. Advective diffusive transport was again simulated using particle tracking according to Eq. 5. Previous work showed that these media were highly susceptible to preferential flow and transport (Edery et al. 2014; Zehe et al. 2021). We compared simulations for an average hydraulic conductivity of K_s = 10^{-7} m/s or K_s =10^{-6} m/s to account for different Peclet numbers. Fig. 3 shows the hydraulic conductivity fields and the cumulative number of particles that visited a grid cell in the simulation domain for small, medium and large variance for the lower average hydraulic conductivity.

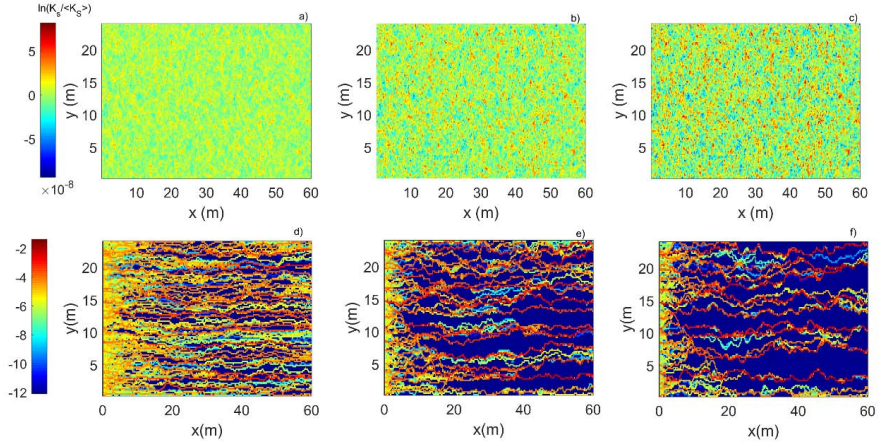

Figure 3: The normalized hydraulic conductivity fields for three randomly selected realizations of small, medium and large variance (a, b, c). Cumulative number of particles (Np) that visited a grid cell in the simulation domain for small, medium and large variance (d, e, f) for HDO.

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3 RESULTS

3.1 Travel time distributions inferred from scenario A

Fig. 4 shows the normalized breakthrough curves of deuterium for the heterogeneous case with the low conductive embedding, containing either a lower conductive or a higher conductive clay lens. This reveals, in line with the experimental evidence of Elhanati et al. (2025), a clearly non-Fickian breakthrough with an earlier first arrival and a significantly longer tailing compared to the breakthrough curve of the homogeneous system (green dots, Fig. 4). In addition, Fig. 4 provides average travel times, named *mean(T)* hereafter, which correspond to the first central moment of the normalized breakthrough curve. We find that the average travel times through the heterogeneous media are, with *mean(T)* = 509.4, 510.3 and 515.4 d, larger than the average travel time through the homogeneous medium, which is *mean(T)*= 508.4 d. Interestingly, we observe that the average travel time declines slightly when the hydraulic conductivity of the clay lens is increased from 10^{-9} to 10^{-8} m/s. The latter can be explained by a stronger advective transport of the tracer into the lens, due to the smaller drop in conductivity. Consistently, we observe an even larger *mean(T)* of 515.4 d, when elongating the clay lens with $K_s = 10^{-8}$ m/s by 30%.

For convenience, we compared the average travel times, *mean(T)*, to the average hydraulic retention time, RT_{hyd}, which was calculated by dividing the total pore volume of the domain by the averaged flow rate. RT_{hyd} and *mean(T)* match, as expected, very well for the case of Fickian transport through the homogeneous domain. In the case of non-Fickian transport, however, we observe that the average travel times inferred from the BTCs are slightly larger than suggested by the hydraulic retention time RT_{hyd}. This underestimate grows clearly with the length and thickness of the BTC tails.

We generally acknowledge that one can *a priori* expect deviations from Fickian transport in this setup, as the transport distance is only twice as large as the length of the embedded clay lens. Yet, the long tail reflects diffusion of molecules into the low conductive lens, which evidently reside there over considerably long times. The channeling of the flow around the lens and the enlarged transport velocities explain in turn the earlier arrival of the solutes compared to the homogeneous case. However, we did not find variations in any of the average travel times that related to the different self-diffusion coefficients of the isotopic tracers.

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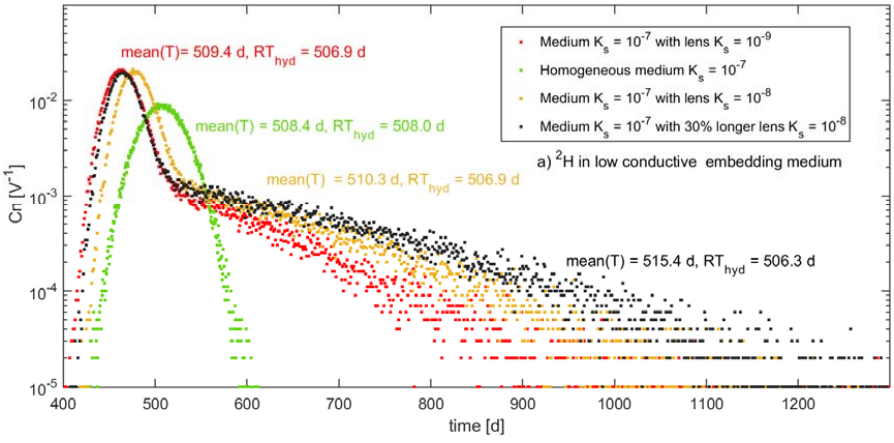

Figure 4: Normalized breakthrough curves of HDO and related average travel times TTD and hydraulic retention times for scenario A for the low conductive embedding medium with K_s =10^{-7} m s^{-1}.

3.2 Travel time distributions inferred from scenario B

Fig. 5 provides the normalized breakthrough curves for case B through the 10 (Fig. 5a, c) and 5 m long layered aquifer (Fig. 5b, d), as a function of the two different head gradients. Average travel times range from the order of 700 d to the short aquifer at the high Peclet (Fig. 5b) to the order of 5300 d for the longer aquifer and the smaller Peclet (Fig. 5c). A closer look reveals that while the breakthrough curves of the three tracers look similar, their corresponding first central moments are indeed different, as shown in the legend of Fig. 5. One can see a clear increase of the average travel time with a declining diffusion coefficient of the isotopic tracers. Deuterium has the smallest self-diffusion coefficient but generally the longest average travel time, while it is *vice versa* for ^{18}O. For a better comparison we focus on the difference between the average travel time of deuterium and ^{18}O, defined as:

$$\mathrm{dTT} = \mathrm{mean}(\mathrm{T}_{HDO}) - \mathrm{mean}(\mathrm{T}_{18OH2}) \text{ (Eq. 6)},$$

and the relative difference thereof, defined as:

$$dTT_{rel} = \mathrm{dTT}/\mathrm{mean}(\mathrm{T}_{18OH2}) \text{ (Eq. 7)}.$$

dTT increases with the length of the system but declines with the Peclet number. Differences in mean travel times, dTT, range from 51 d for the short aquifer and the high Peclet number of

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11.1 (Fig. 5b) up to 207 days for the longer aquifer and the small Peclet number of 2.2 (Fig. 5c). Note that the relative differences dTT_{rel} are small: app. 5% for the small Peclet and they increase to ~10% when increasing the Peclet number.

For both aquifers, we calculated again the hydraulic retention times, using the arithmetic and the geometric means of the hydraulic conductivities of the layers, respectively. The latter was, for the hydraulic gradient of the small Peclet number with RT_{hyd} = 1557 d (4.2 y), more than three times smaller than the average travel times inferred from the tracer breakthrough curves, which was of order 5300 d (Fig. 5c).

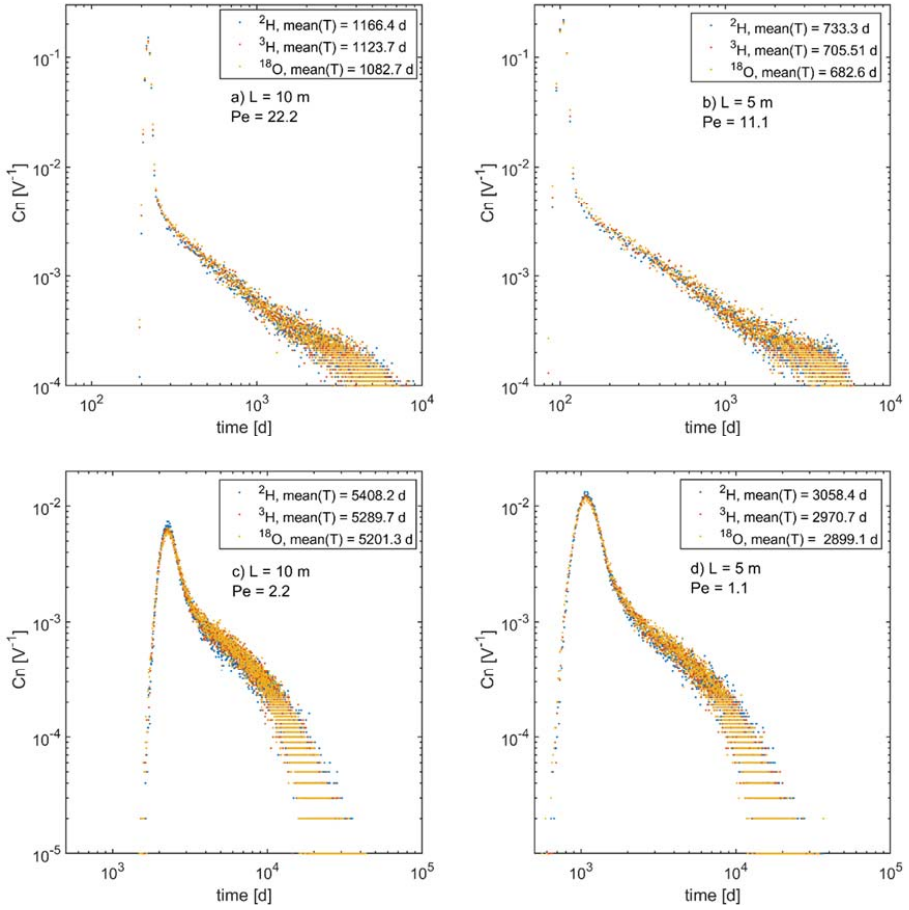

Figure 5: Normalized breakthrough curves of deuterium (^{2}H blue dots), tritium (^{3}H red dots) and ^{18}O (yellow dots) and the corresponding average travel times, *mean(T),* for scenario B. Simulations for the 10 m (a, c) and 5 m (b, d) long layered aquifer, for the two head gradients and the corresponding Peclet numbers (Pe). Note that for better visibility panels a and b, as well as c and d, have different scales.

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The corresponding difference for the shorter aquifer and the high Peclet number is smaller but still remarkable: RT_{hyd} is with 578.5 d more than a 100 d smaller than the average travel times inferred from the particle transport simulations. This underpins that even in the case of simple layered systems, the analysis of hydraulic retention times may, due to the difference between fluid and tracer velocities, yield error prone estimates of average tracer travel times.

3.3 Travel time distributions inferred from scenario C

Fig. 6 presents the normalized breakthrough and average travel times *mean(T)* for scenario C for all isotopic tracers at transport distances of L = 60 m (a, c, e) and 30 m (b, d, f). The variance of the hydraulic conductivity field decreases from top to bottom panels, the average K_s is 10^{-7} m/s. The strength of the "transport anomaly," i.e., its deviation from Gaussian behavior, clearly increases with the variance of the hydraulic conductivity field and increasing transport distance. The larger the variance, the longer the tail of the breakthrough curve. The average travel time to L = 30 m increases from approximately 1310 days for variance 1, up to approximately 1810 days for variance 5. Note that for L = 60 m the corresponding difference is of the order of 1000 days. Consequently, the average travel time of a tracer for a given transport distance L increases strongly with the variance of the hydraulic conductivity field.

Again, we find that the average travel times of the different tracers increase with smaller diffusion coefficients of the water isotopes. Deuterium has the smallest self-diffusion coefficient, but in all cases the largest average travel time, due a longer trapping in low conductive bottlenecks. The related differences between average travel times of deuterium and ^{18}O rise clearly with increasing variance of the hydraulic conductivity field up to values of a 110 days for the length of 60 m, compared to 50 days for L = 30 m.

However, the average travel times at a given variance grow for each tracer almost proportionally to the transport distance. This implies that differences in *mean(T)* between the tracers will not average out but grow with increasing transport distance and thus increasing average travel time. To corroborate this statement, we re-simulated tracer migration through the conductivity field with the variance 5 while lowering the average K_s to 1×10^{-8} m/s (Fig. 7). The differences between the average travel time of deuterium and ^{18}O are in the order of 2 years for the long and 1 year for the shorter system.

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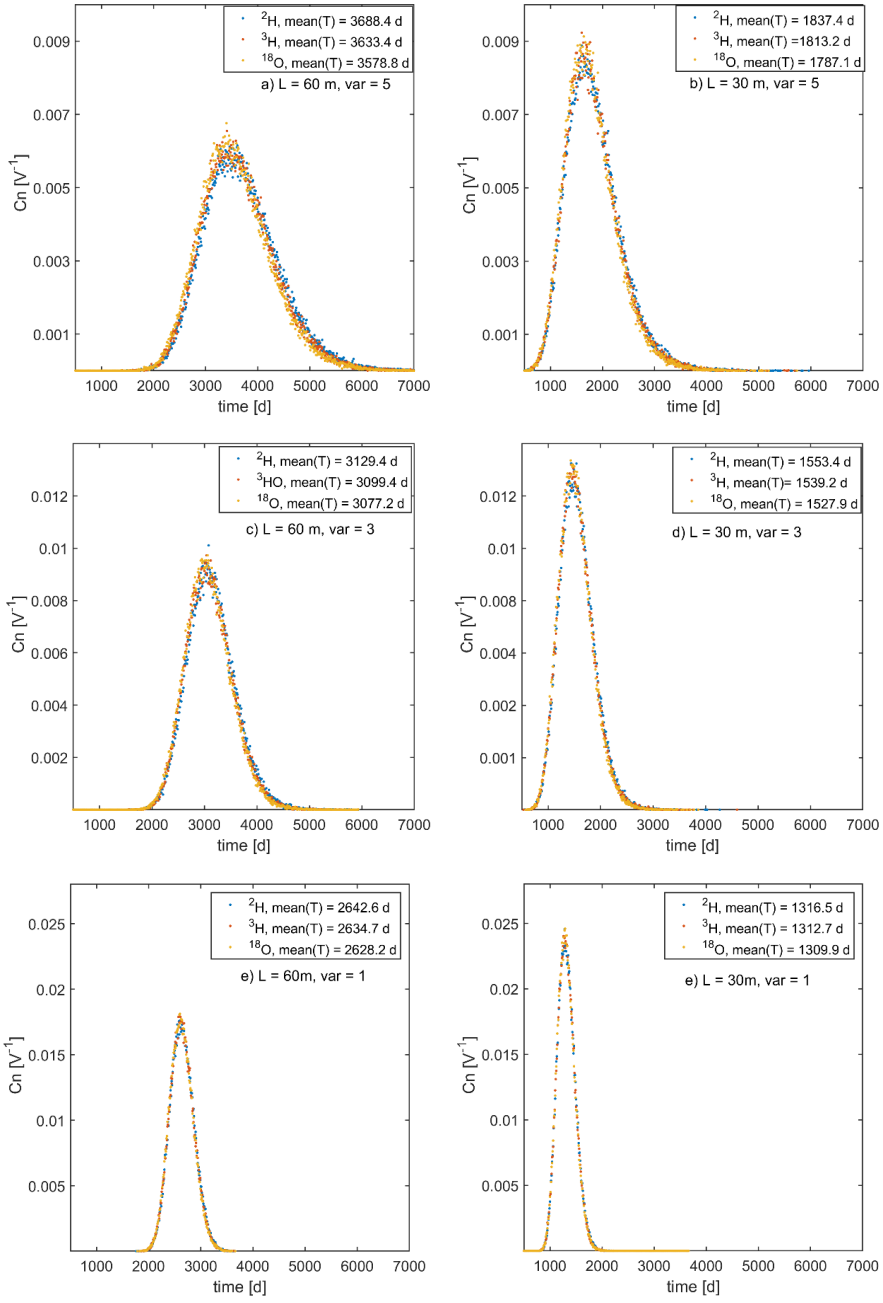

Figure 6: Normalized breakthrough and average travel time for scenario C for deuterium (^{2}H, blue dots), tritium (^{3}H, red dots) and ^{18}O (yellow dots) and corresponding average travel times *mean(T)* after transport distances of 60 m (a, c, e) and 30 m (b, d, f). The variance of the hydraulic conductivity field decreases from top to bottom panels; the average K_s is 10^{-7} m/s.

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4 DISCUSSION AND CONCLUSIONS

Our study provides clear evidence that the sensitivity of average TTDs to small changes in diffusion coefficients is – albeit relatively small – not a question of measurement error but a question of transport physics. Particularly, for the case of heterogeneous media and anomalous transport we demonstrate that differences in average travel times of different water isotopes (HTO, H2O18, HDO) can deviate by as much as two years, which corresponds to 3% of the average travel time. We found the strongest relative differences of the order of 10% for a simple two-layered system, consisting of a mobile layer overlying a relatively immobile water storage compartment.

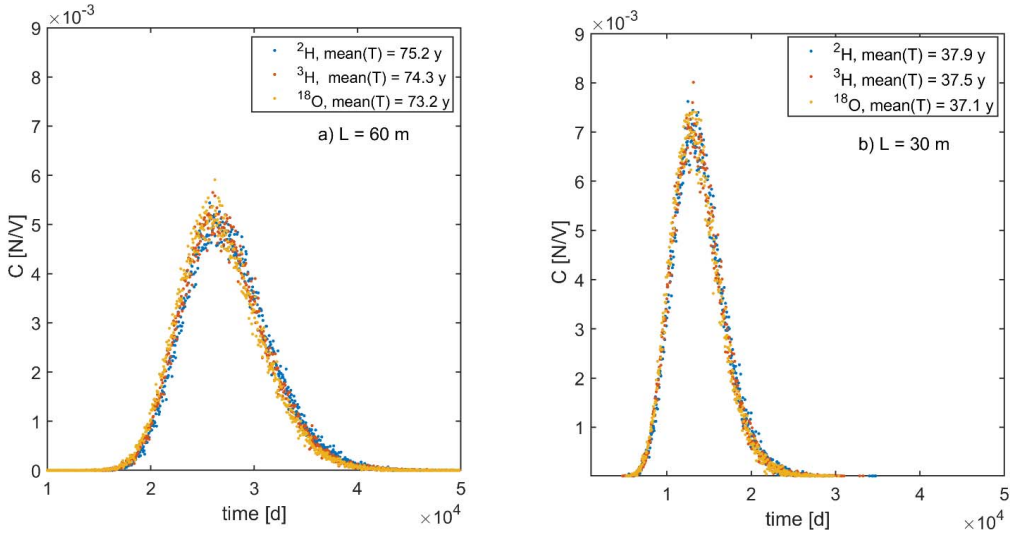

Figure 7: Normalized breakthrough and average travel time for scenario C for deuterium (^{2}H, blue dots), tritium (^{3}H, red dots) and ^{18}O (yellow dots) and corresponding average travel times *mean(T)* after transport distances of 60 m (a) and 30 m (b). The variance of the hydraulic conductivity field is 5, while the average K_s is 10^{-8}.

We found smaller differences of the order of 3 to 5% for strongly stochastically heterogeneous media. Given their size, one could be inclined to erroneously interpret these differences as measurement errors. However, these differences are indeed physical and reflect tracers with smaller diffusion coefficients that eventually remain over longer times in low conductive bottlenecks, which enlarges the tails and average travel times. Thus, these effects do not average out, but persist when doubling the transport distances – even despite the total travel distances being 100 times larger than the short correlation length of the hydraulic conductivity field.

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Our findings are in line with the experiments of Elhanati et al. (2025) and corroborate that water isotopes show similar behaviors to Br-. The molecular diffusion coefficient of bromide is 2.01×10^{-9} m^2/s, indeed close to that of HDO (2.22×10^{-9} m^2/s). Our study corroborates furthermore the argument of Stewart et al. (2010, 2021), namely that averaged travel times inferred from ^{18}O might in the case of two-layered mobile and immobile storage regions, or of a strongly heterogeneous subsurface, be systematically shorter than those inferred from tritium. The maximum differences we found ranged between 90 d to 1.1 y. The latter corresponds to the difference Stewart et al. (2010) reported for the Brugga catchment, which has an average travel time of order 3-6 y for deep groundwater. Stewart et al. (2010) reported an even larger difference between mean(T_{18OH2}) = 3.4 y to mean(T_{THO}) = 9.6 y for the Pukemanga catchment. We cannot expect to detect similarly large differences here, because we did not account for radioactive decay of tritium (half-life of 12.32 years). Based on this decay one might detect contributions of rather old water, that typically cannot be resolved based on differences in ^{18}O.

A comparison between the hydraulic retention times, inferred by dividing the storage volume by the flow, and average travel times, was in accord with the case of well-mixed advective-diffusive transport. The hydraulic retention times, however, systematically underestimated the average tracer travel times of the isotopic tracers, when transport was not well-mixed. This discrepancy can again be explained by diffusive trapping of tracers in rather immobile storage components: relatively long residence time cause the long tail in the breakthrough curve, which shifts the average travel time to the right.

We thus conclude that travel time distributions of isotopic tracers reflect the spectrum of fluid velocities and diffusive/dispersive mixing between the flow lines connecting inputs and outputs to the system. Travel time distributions of isotopic tracers might thus reflect the differences in their diffusion coefficients, which are of order 10%, and in the case of non-Fickian transport this eventually also affects the mean travel time.

Author contributions: Erwin Zehe conducted most of the analysis and wrote the paper. Laurent Pfister worked on the part explaining the role of water isotopes for inferring transit times, provided evidence on their self-diffusion coefficients and contributed to the writing. Brian Berkowitz contributed to the theory and writing, particularly parts related to non-Fickian transport and critically overlooked the study.

Competing interests. At least one of the (co-)authors is a member of the editorial board of Hydrology and Earth System Sciences.

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