

Matrix Diffusion as a Mechanism Contributing to Fractal Stream Chemistry

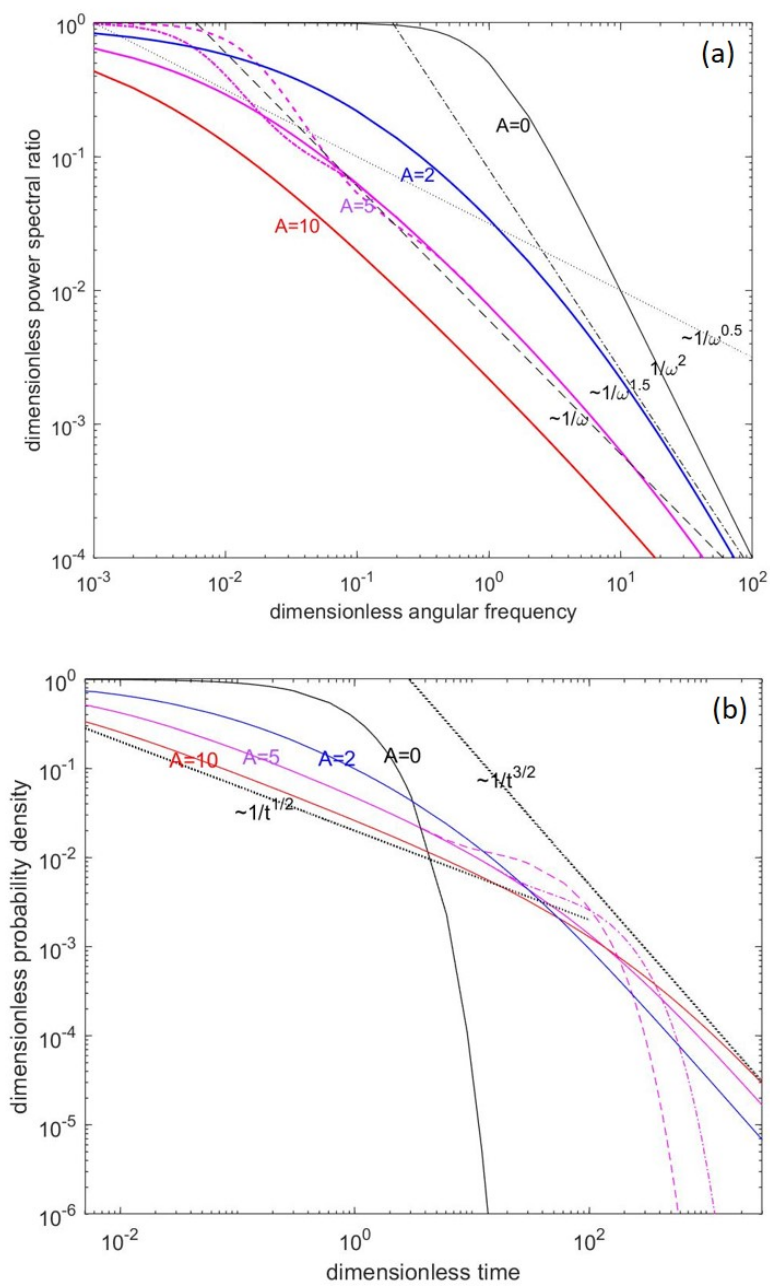
Harihar Rajaram¹

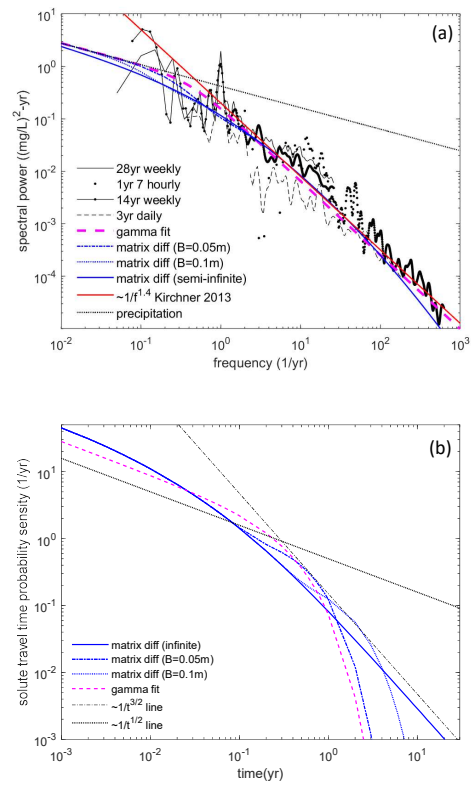
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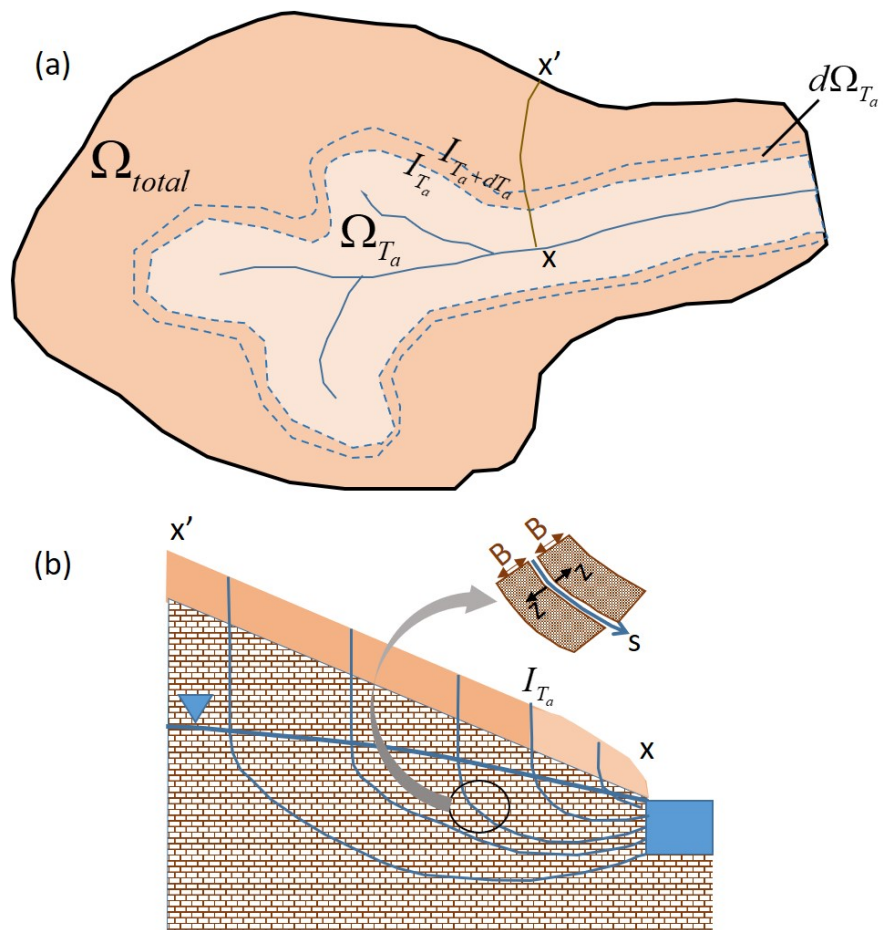
November 30, 2022

Abstract

Solute travel time distributions (TTDs) in catchments are relevant to both hydrochemical response and inference of hydrologic mechanisms. Time and frequency domain methods have been employed to estimate solute TTDs and associated power spectra. Stream concentration power spectra in some catchments exhibit fractal scaling ($\sim 1/\text{frequency}$, or generally, $1/\text{frequency}$ to a power < 2). Various mechanisms have been proposed previously for fractal scaling. In several catchments, a significant fraction of streamflow is derived from groundwater in shallow fractured bedrock, where matrix diffusion significantly influences solute transport. I present frequency and time domain theoretical analyses of solute transport to quantify the influence of matrix diffusion on solute TTDs in catchment groundwater systems. The theoretical concentration power spectra exhibit fractal scaling, and the corresponding TTDs resemble a gamma distribution. An application to the Lower Hafren catchment using site-specific parameters shows that theoretical spectra match previously reported power spectral estimates derived from concentration measurements.







Matrix Diffusion as a Mechanism Contributing to Fractal Stream Chemistry

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Key Points:

- Influence of matrix diffusion on concentration power spectra and catchment solute travel time distributions is quantified theoretically
- Matrix diffusion is shown to produce fractal scaling in stream concentration power spectra when combined with variable advective travel times long streamlines
- 1/frequency spectral filtering identified in stream chloride power spectrum at Lower Haverhill is reproduced by matrix diffusion model

Abstract

Solute travel time distributions (TTDs) in catchments are relevant to both hydrochemical response and inference of hydrologic mechanisms. Time and frequency domain methods have been employed to estimate solute TTDs and associated power spectra. Stream concentration power spectra in some catchments exhibit fractal scaling ($\sim 1/\text{frequency}$, or generally, $1/\text{frequency}$ to a power < 2). Various mechanisms have been proposed previously for fractal scaling. In several catchments, a significant fraction of streamflow is derived from groundwater in shallow fractured bedrock, where matrix diffusion significantly influences solute transport. I present frequency and time domain theoretical analyses of solute transport to quantify the influence of matrix diffusion on solute TTDs in catchment groundwater systems. The theoretical concentration power spectra exhibit fractal scaling, and the corresponding TTDs resemble a gamma distribution. An application to the Lower Hafren catchment using site-specific parameters shows that theoretical spectra match previously reported power spectral estimates derived from concentration measurements.

Plain Language Summary

A significant fraction of rainfall on catchments flows as groundwater before discharging to a river. Groundwater in catchments is often hosted in shallow fractured bedrock. In these systems, solutes dissolved in rainfall are transported relatively rapidly by water flowing in rock fractures. However, some of the solute diffuses from fractures into the tiny pores of the rock matrix where water is stagnant. This phenomenon is referred to as matrix diffusion and leads to retention and slow long-term release of solutes. Solute transport and retention in catchments is relevant to understanding their response to contamination (e.g. by atmospheric deposition, agricultural chemicals) and inference of flow processes. This paper develops theoretical equations to

describe the transport and retention of solutes in catchments underlain by fractured bedrock, and the delivery of solutes to rivers. These theoretical equations explain interesting features of observed solute concentration variations in rivers and can be used to model catchment response to contamination.

1. Introduction

The transport and retention of solutes in catchments is influenced by both hydrologic and biogeochemical processes. Solute travel time distributions (TTDs) provide insights on integrated behavior of hydrologic and biogeochemical processes within catchments, although the distinction between the processes and time scales involved in hydrologic/hydraulic versus hydrochemical response should be emphasized (Maloszewski and Zuber, 1993; McGuire and McDonnell, 2006; Fiori and Russo, 2008; Botter et al. 2010; Birkel et al. 2011; Hrachowitz et al. 2013). There is a large body of research on TTDs in catchments, which has been synthesized in review papers (e.g. Maloszewski and Zuber, 1993; McGuire and McDonnell, 2006; Hrachowitz et al. 2016; Sprenger et al. 2019). Although TTDs were historically associated with steady flow systems, they have been generalized to unsteady flow using cumulative discharge transformation (Niemi, 1977; Rodhe et al. 1996), time variable travel/transit time distributions and storage selection functions (Sayama and McDonnell, 2009; Hrachowitz et al. 2010; Botter et al. 2011; van der velde et al. 2012; Harman, 2015).

One feature of catchment solute TTDs that has received much interest is that they often exhibit longer tails than the exponential distribution, a commonly used model for TTDs. Kirchner et al. (2000; 2001) analyzed the relationship between stream and precipitation concentration fluctuations of chloride in catchments at Plynlimon, U.K. They suggested that a gamma

distribution, $h(t) = (t^{\alpha-1} e^{-t/\beta}) / (\beta^\alpha \Gamma(\alpha))$, with scale parameter $\alpha = 0.5$ (more generally $\alpha < 1$), captures short-term responsiveness and long-tailed behavior and is hence a better model for solute TTDs than the exponential distribution ($\alpha = 1$). Correspondingly, stream concentration power spectra were observed to exhibit 1/frequency behavior (more generally 1/frequency to a power < 2), which they referred to as “fractal stream chemistry”. Similar behavior has been documented at other catchments (Godsey et al. 2010), and for a variety of solutes (Kirchner et al. 2013), although some catchments do exhibit exponential baseflow TTDs (e.g. McGuire et al. 2005).

Various mechanisms have been proposed to explain fractal stream chemistry. Kirchner (2001) showed that a model of advection-dispersion along a one-dimensional flowpath with distributed solute inputs and a very large dispersivity (on the order of the hillslope length, equivalently Peclet number (Pe) ~ 1), produces a solute TTD similar to a gamma distribution with $\alpha = 0.5$. Lindgren et al. (2004) proposed that for moderate heterogeneity and dispersion, first-order mobile-immobile exchange can explain fractal scaling. Both the above models assume uniform mean flow and neglect nonuniform flow commonly associated with hillslope hydrologic systems. Cardenas (2007) demonstrated that advection-dispersion in a nonuniform Tothian hillslope groundwater flow (with significant variation in advective travel times across streamlines) produces power-law solute TTDs. Kollett and Maxwell (2008) employed particle-tracking in simulated flow fields for a real catchment to demonstrate that power-law stream concentration spectra result even with very small dispersivities ($Pe \sim 10^4$), due to variations in advective travel time across streamlines. They showed that transient vadose zone processes influence the stream concentration spectra at higher frequencies. Fiori and Russo’s (2008) simulations of transient flow and solute transport in a hillslope produced TTDs resembling gamma distributions with $\alpha <$

1. Haitjema (1995) and Fiori and Russo (2008) showed that transient effects and heterogeneity have a minor influence on TTDs compared to variations in travel times across streamlines in steady flow representations. Ameli et al. (2016) showed that decreasing permeability with depth, either exponential or due to macroscopic layering, produced a gamma TTD with α close to 0.5. They also showed that in the absence of such heterogeneity, α is closer to 1. Harman (2015) showed that a time-variable uniform TTD with a range parameter that increases with decreasing storage (inverse storage effect) reproduces 1/frequency spectra. Lumped parameter hydrochemical models with multiple compartments have also reproduced gamma TTDs with $\alpha < 1$ (Hrachowitz et al. 2013; Benettin et al. 2014).

The contribution of shallow groundwater flow through fractured bedrock to streamflow and solute export in mountain catchments has long been recognized, including at Plynlimon (Neal et al. 1997; Kirchner et al. 2001) and other recent studies (Godsey et al. 2010, Frisbee et al. 2013; Manning et al. 2014; Herndon et al. 2015; Hale et al. 2016; Tokunaga et al. 2019; Carroll et al. 2019; 2020). It is well established that matrix diffusion, a phenomenon first invoked to explain anomalous tracer ages (Foster, 1975; Neretnieks, 1981), significantly influences the travel time of tracers in fractured rock. The potential influence of matrix diffusion on catchment hydrochemical response and tracer ages was further highlighted by Maloszewski and Zuber (1993) and Shapiro (2011). However, few models of catchment-scale solute TTDs explicitly incorporate the influence of matrix diffusion. In this paper, I present frequency domain and time domain analyses of the combined influence of variable advective travel times and matrix diffusion on solute transport in a catchment/hillslope groundwater system hosted in fractured bedrock. I show that the theoretical power spectrum of stream concentration variations inherently exhibits fractal scaling, and that the solute TTD strongly resembles a gamma

distribution with $\alpha < 1$. I also present an application to the Lower Hafren catchment at Plynlimon.

2. Conceptual Model and Transport Equations

The catchment-scale groundwater flow system is represented as a steady saturated flow in fractured bedrock, receiving spatially uniform recharge. Figure 1 shows a schematic representation (adapted from Haitjema, 1995). Fluid flow is assumed to occur only in fractures with stagnant water in the rock matrix. Solutes undergo rapid advection along streamlines through permeable fractures, while simultaneously diffusing in and out of the rock matrix. The fracture density is assumed to be high so that an equivalent porous medium representation is employed for flow (but not for transport). Thus, the water table and hydraulic head field are assumed to be well defined and smooth. Isochrones I_{T_a} denote contours of equal advective travel time T_a from the water table to the outflow at the stream, and Ω_{T_a} denotes the surface area contained within I_{T_a} . Advective travel times T_a along streamlines (streamsurfaces) from the water table to the stream are assumed to increase monotonically with Ω_{T_a} . The streamtube originating from the surface element $d\Omega_{T_a}$ in Figure 1a is bounded by isochrones I_{T_a} and $I_{T_a+dT_a}$, comprising streamlines along which advective travel times to the stream range from T_a to $T_a + dT_a$. It is important to emphasize the distinction between advective and total solute travel times: the total travel time along a streamline is also influenced by matrix diffusion and thus much longer than the advective travel time. The catchment-scale solute TTD is derived by considering the distribution of total travel times across all streamlines.

Previous studies suggest that when advective travel times across streamlines vary over a large range, the influence of heterogeneity and dispersion is secondary (Gelhar, 1993; Duffy and Gelhar, 1986; Haitjema, 1995; Fiori and Russo, 2008). I therefore neglect streamline tortuosity and dispersion in the analysis presented below. Heterogeneity will lead to additional random variations in advective travel times and may be incorporated using modified advective travel time distributions as in the Lagrangian stochastic frameworks of Cvetkovic et al. (1999), Simic and Destouni (1999) and Cvetkovic et al. (2012). I assume one-dimensional diffusion with an effective matrix width B (Figure 1b), which may either be related to the block size or an accessible weathered matrix thickness adjacent to fractures. Although matrix blocks in fractured rock exhibit complex geometries, simplified solutions that assume one-dimensional matrix diffusion (e.g. Tang et al. 1981; Maloszewski and Zuber, 1985) and various effective models (Carrera et al. 1998; Cvetkovic et al. 1999; Haggerty et al. 2000; Berkowitz et al. 2006) are widely used and have provided useful insights. Multi-dimensional diffusion in matrix blocks is similar to one-dimensional diffusion with modified parameters, as discussed by Barker et al. (1985).

For the above flow system, solute transport equations along a streamline and the stagnant matrix domain adjacent to it are presented below, following Grisak and Pickens, (1980), Tang et al. (1981), and Maloszewski and Zuber (1985). The fracture concentration at time t , at location s along a streamline that originated at isochrone I_{T_a} (Figure 1) is denoted by $C_f(s, t; I_{T_a})$; and the concentration in the adjacent rock matrix is denoted by $C_m(s, z, t; I_{T_a})$, where z is the distance from the fracture matrix interface (see Figure 1b). The fracture transport equation is:

$$\frac{\partial C_f}{\partial t} + u_s \frac{\partial C_f}{\partial s} = \frac{2\phi_m D_e}{b} \frac{\partial C_m}{\partial z} \bigg|_{s, z=0, t} \quad (1)$$

148 where u_s is the solute velocity along the streamline, b is the fracture aperture; ϕ_m and D_e are the
 149 matrix porosity and effective diffusivity respectively. The parameters b , ϕ_m and D_e are
 150 assumed as constant catchment-scale average values, while u_s varies across the flow system.
 151 The diffusion equation in the rock matrix is:

$$152 \quad (\phi_m + \rho_b K_d) \frac{\partial C_m}{\partial t} - \phi_m D_e \frac{\partial^2 C_m}{\partial z^2} = 0 \quad (2)$$

153 where ρ_b and K_d are respectively the bulk density of solids and the distribution coefficient in the
 154 rock matrix. The lateral boundary conditions for (2) are:

$$155 \quad C_m(s, z = 0, t; I_{T_a}) = C_f(s, t; I_{T_a}), \quad \frac{\partial C_m}{\partial z}(s, z = B, t; I_{T_a}) = 0 \quad (3)$$

156 The streamline coordinate s in (1) may be replaced with an advective travel time coordinate
 157 (Gelhar and Collins, 1971; Duffy and Gelhar, 1986; Cvetkovic et al. 1999):

$$158 \quad \tau_a = \int_{s'=0}^s \frac{ds'}{u_s(s')} \quad (4)$$

159 Correspondingly, the fracture and matrix concentrations may be written as functions of τ_a , i.e.

160 $C_f(\tau_a, t; I_{T_a})$ and $C_m(\tau_a, z, t; I_{T_a})$, and (1) can be rewritten as (Cvetkovic et al. 1999):

$$161 \quad \frac{\partial C_f}{\partial t} + \frac{\partial C_f}{\partial \tau_a} = \frac{2\phi_m D_e}{b} \frac{\partial C_m}{\partial z} \bigg|_{\tau_a, z=0, t} \quad (5)$$

162 I use (5), together with (2) and (3) to relate the stream concentration to the input concentration.

163 At the inflow end of a streamline ($s = 0$, $\tau_a = 0$), concentration inputs $C_i(t)$ are assumed to be

164 uniform across the catchment area (i.e. all streamlines), but vary with time:

$$C_f(\tau_a = 0, t; I_{T_a}) = C_i(t) \quad (6)$$

At the outflow boundary, the stream concentration $C_o(t)$ is obtained by mixing of concentrations from all streamlines. The fraction of the total outflow that originates within the streamtube $d\Omega_{T_a}$ is denoted as $w(I_{T_a})d\Omega_{T_a}$, where $w(I_{T_a})$ is a flux-weighting function. If T_a increases monotonically with Ω_{T_a} , the fraction $w(I_{T_a})d\Omega_{T_a}$ may also be represented using the advective travel time probability density function across streamlines, $P(T_a)$, as $P(T_a)dT_a$. Thus $C_o(t)$ may be written in terms of an integral over either Ω_{T_a} or T_a :

$$C_o(t) = \int_{\Omega_{total}} C_f(T_a, t; I_{T_a}) w(I_{T_a}) d\Omega_{T_a} = \int_{T_a=0}^{\infty} C_f(T_a, t; I_{T_a}) P(T_a) dT_a \quad (7)$$

If the fluid flux and velocity are assumed to be constant across the depth of the flow system at the outflow as in a Dupuit model, $w(I_{T_a}) = 1/\Omega_{total}$, a constant. Additionally assuming spatially uniform recharge and an approximately constant saturated thickness (H), $P(T_a)$ is an exponential distribution (Gelhar and Wilson, 1974; Maloszewski and Zuber, 1982; Haitjema, 1995):

$$P(T_a) = \frac{1}{\bar{T}_a} \exp\left(-\frac{T_a}{\bar{T}_a}\right) \quad (8)$$

In (8), \bar{T}_a is the mean advective travel time, given by $\phi_a H/r$, where ϕ_a is the active porosity corresponding to the hydrologically responsive fracture flow system and r is the recharge rate. The exponential advective travel time distribution is also applicable to hillslope flow systems with a sloping base, under the assumption of uniform recharge and constant saturated thickness. The relationship for Ω_{T_a} corresponding to (8) is (Haitjema, 1995):

$$\Omega_{T_a} = \Omega_{total} \left(1 - \exp\left(-T_a/\bar{T}_a\right) \right) \quad (9)$$

3. Frequency Domain Analysis: Stream Concentration Power Spectrum

To relate the power spectra of stream and precipitation concentrations, the transport equations are solved in the frequency domain (SI, Sections S.1-2). The Fourier transforms of $C_i(t), C_o(t), C_f(\tau_a, t; I_{T_a})$ and $C_m(\tau_a, z, t; I_{T_a})$ are denoted by $\tilde{C}_i(\omega), \tilde{C}_o(\omega), \tilde{C}_f(\tau_a, \omega; I_{T_a})$ and $\tilde{C}_m(\tau_a, z, \omega; I_{T_a})$ respectively, where ω is the angular frequency. For random concentration variations, the Fourier-Stieltjes spectral representation (Duffy and Gelhar, 1985, 1986; Gelhar, 1993), is more rigorous than the Fourier transform (Kirchner, 2000). However, both interpretations involve the same mathematical manipulations and lead to identical concentration power spectra. The Fourier transforms of (2-3) are solved to express $\tilde{C}_m(\tau_a, z, \omega; I_{T_a})$ in terms of $\tilde{C}_f(\tau_a, \omega; I_{T_a})$ (S7 in SI). Using this relationship in the Fourier transform of (5) produces a differential equation (S8 in SI) for $\tilde{C}_f(\tau_a, \omega; I_{T_a})$:

$$\frac{d\tilde{C}_f}{d\tau_a} + k(\omega)\tilde{C}_f = 0 \quad (10)$$

where (S10-11 in SI):

$$k(\omega) = i\omega + \frac{2\phi_m\sqrt{RD_e\omega}}{b}\sqrt{i} - \frac{\frac{4\phi_m\sqrt{RD_e\omega}}{b}\sqrt{i}}{\left(1 + \exp\left(2\sqrt{\frac{R\omega}{D_e}}B\sqrt{i}\right)\right)} \quad (11)$$

In (11), $i = \sqrt{-1}$ and $R = (1 + \rho_b K_d / \phi_m)$ denotes the retardation factor in the rock matrix.

199 Solving (10) and using the transform of (6), the Fourier transform of the fracture concentration at
 200 the outflow end of a streamline ($\tau_a = T_a$) is:

$$201 \quad \tilde{C}_f(T_a, \omega; I_{T_a}) = \tilde{C}_i(\omega) \exp\{-k(\omega)T_a\} \quad (12)$$

202 The Fourier transform of the stream concentration is then obtained from (7):

$$203 \quad \tilde{C}_o(\omega) = \tilde{C}_i(\omega) \int_0^{\infty} \exp\{-k(\omega)T_a\} P(T_a) dT_a \quad (13)$$

204 Correspondingly, the stream ($S_{C_o C_o}(\omega)$) and precipitation ($S_{C_i C_i}(\omega)$) concentration power spectra
 205 are related by:

$$206 \quad S_{C_o C_o}(\omega) = S_{C_i C_i}(\omega) \left| \int_0^{\infty} \exp\{-k(\omega)T_a\} P(T_a) dT_a \right|^2 \quad (14)$$

207 Equation (14) generalizes a relationship presented by Duffy and Gelhar (1985) and Gelhar
 208 (1993) for pure advection ($k(\omega) = i\omega$), by incorporating matrix diffusion and reformulating the
 209 integral in terms of $P(T_a)$. In general, any appropriate advective travel time distribution
 210 (obtained from an analytical or numerical groundwater flow model) can be employed in (14).

211 For the exponential advective travel time distribution, the stream concentration power spectrum
 212 is obtained by using (11) and (8) in (14) (Section S.2 in SI):

$$213 \quad S_{C_o C_o}(\omega) = S_{C_i C_i}(\omega) \frac{1}{1 + 2\sqrt{2}AM\sqrt{\omega\overline{T}_a} + 2A^2(M^2 + N^2)\omega\overline{T}_a + 2\sqrt{2}AN(\omega\overline{T}_a)^{3/2} + \omega^2\overline{T}_a^2} \quad (15)$$

214 where

$$\begin{aligned}
A &= \frac{\phi_m \sqrt{RD_e \bar{T}_a}}{b}, m = 1 + \exp \left(\sqrt{2\omega \bar{T}_a} \frac{B\sqrt{R}}{\sqrt{D_e \bar{T}_a}} \right) \cos \left(\sqrt{2R\omega \bar{T}_a} \frac{B\sqrt{R}}{\sqrt{D_e \bar{T}_a}} \right) \\
n &= \exp \left(\sqrt{2\omega \bar{T}_a} \frac{B\sqrt{R}}{\sqrt{D_e \bar{T}_a}} \right) \sin \left(\sqrt{2\omega \bar{T}_a} \frac{B\sqrt{R}}{\sqrt{D_e \bar{T}_a}} \right), M = 1 - \frac{2(m+n)}{m^2 + n^2}, N = 1 - \frac{2(m-n)}{m^2 + n^2}
\end{aligned} \tag{16}$$

Equation (15) is written in terms of a dimensionless frequency ($\omega \bar{T}_a$) to highlight the dimensionless parameters that regulate the influence of matrix diffusion. The dimensionless parameter A is a measure of the strength of matrix diffusion. It may also be viewed as a ratio between a characteristic matrix storage over a time scale on the order of the mean advective travel time and the fracture storage. The parameter $B / \sqrt{D_e \bar{T}_a / R}$ represents the influence of matrix thickness. If $B \gg$ the characteristic matrix diffusion length ($\sqrt{D_e \bar{T}_a / R}$), the behavior is identical to that obtained with an infinite rock matrix thickness ($M, N \rightarrow 1$, Section S.2 in SI).

When the influence of matrix diffusion is strong (large A ; M, N close to 1), the catchment spectral filter $S_{C_o C_o} / S_{C_i C_i}$ from (15) exhibits 1/frequency behavior (i.e. the third term in the denominator of (15) dominates). More generally, (15) can produce stream concentration power spectra with a range of apparent decay exponents > -2 (fractal scaling). When $A \rightarrow 0$ (negligible matrix diffusion) or $B \rightarrow 0$ (negligible matrix thickness), (15) reduces to $S_{C_o C_o}(\omega) = S_{C_i C_i}(\omega) / (1 + \omega^2 \bar{T}_a^2)$, which corresponds to pure advection with an exponential advective travel time distribution across streamlines (Gelhar, 1993). The well-mixed reservoir model also produces the same behavior (Gelhar and Wilson, 1974, Duffy and Gelhar, 1985, Gelhar, 1993, Kirchner et al. 2000).

Figure 2a shows the behavior of the spectral ratio $S_{C_o C_o} / S_{C_i C_i}$ for different values of A (0, 2, 5 and 10) and $B / \sqrt{De\bar{T}_a}$ (5, 10 and ∞) for $A = 5$, assuming no sorption ($R = 1$). For context, $A = 5$ would be obtained with $\phi_m = 0.05$, $D_e = 10^{-10}$ m²/s, $b = 10^{-4}$ m, $\bar{T}_a = 12$ days, which are realistic values. The mean total travel time is $\bar{T}_a (1 + 2B\phi_m / b) \approx 612$ and 1212 days for $B / \sqrt{De\bar{T}_a} = 5$ and 10, respectively. For an infinite matrix, the mean total travel time is theoretically unbounded. For $A = 5$ and 10, the slope of the spectral ratio is close to -1 over several orders of magnitude in frequency. For $A = 2$, the spectral ratio exhibits an apparent slope close to -1 at intermediate dimensionless frequencies, approaching -1.5 at higher dimensionless frequencies. In general, the spectral ratio in Figure 2a exhibits curvature and deviates from true linear behavior in a log-log plot. However, the curvature is relatively mild at dimensionless frequencies > 0.1 . The scatter inherent in spectral estimates from noisy real-world data may obscure such curvature and accommodate acceptable straight-line fits. A finite matrix width does not influence the spectral ratio at high frequencies corresponding to time scales smaller than the diffusion time scale across the width. At lower frequencies, spectral ratios for a finite matrix width deviate from that for an infinite matrix and become steeper. This steepening could in fact produce a closer tendency to straight-line behavior when estimating spectra from noisy data (see $1/f$ line plotted in Figure 2a).

A generalization of (15) for a gamma advective travel time distribution (e.g. representing non-Dupuit flow) is presented in SI (S25, Section S.2). With a scale parameter α , the $1 / \omega^{2\alpha}$ scaling in the spectral ratio of the advective travel time distribution is modified to $1 / \omega^\alpha$ by matrix diffusion. For a sorbing solute, (15) predicts that in the frequency range where the third

term in the denominator is dominant, the stream concentration power spectrum is $1/R$ times that for a passive solute. This is consistent with the behavior suggested by Feng et al. (2004).

4. Time Domain Analysis: Solute Travel Time Distribution

The solute TTD $h(t)$ is the solution for $C_o(t)$ corresponding to a unit impulse (Dirac delta) input, i.e. $C_i(t) = \delta(t)$, and can be obtained from (7). The solution for $C_f(T_a, t; I_{T_a})$ at the outflow end of a streamline due to a unit impulse at the inflow, can be expressed in the form $H(t - T_a)g(T_a; t - T_a)$, where $H(t - T_a)$ is the Heaviside function. The function g depends on both the advective travel time T_a and the time since advective breakthrough, $t - T_a$. It has a simple analytical form for an infinite matrix (Maloszewski and Zuber, 1985; Section S.4 in SI):

$$g(T_a; t - T_a) = \frac{aT_a}{\sqrt{\pi}(t - T_a)^{3/2}} \exp\left(-\frac{a^2 T_a^2}{(t - T_a)}\right) \quad (17)$$

where $a = \phi_m \sqrt{RD_e} / b$. However, $g(T_a; t - T_a)$ can only be expressed as an implicit integral or obtained by numerical Laplace transform inversion for finite matrix widths (Maloszewski and Zuber, 1985; Section S.4 in SI). In either case, $h(t)$ can be expressed from (7) as:

$$h(t) = \int_0^\infty H(t - T_a)g(T_a; t - T_a)P(T_a)dT_a = \int_0^t g(T_a; t - T_a)P(T_a)dT_a \quad (18)$$

At any time t after input, the solute TTD (18) only includes contributions from streamlines for which the advective travel time to the stream $T_a \leq t$. The solute TTD in (18) accounts for the combined influence of variable advective travel times across streamlines (with any appropriate form for $P(T_a)$) and matrix diffusion. Cvetkovic et al. (1999), Simic and Destouni (1999), Cvetkovic and Haggerty (2002), Lindgren et al. (2004) and Cvetkovic et al. (2012) employed

similar approaches to combine the influence of retention with advective travel time distributions generated by heterogeneity.

Figure 2b shows the dimensionless solute TTD $h(t/\bar{T}_a)\bar{T}_a$ obtained by numerical integration of (18) with the exponential $P(T_a)$ from (8). Analytical approximations can be derived for large times in the case of infinite matrix widths (SI Section S.4, for exponential and gamma $P(T_a)$).

The TTD for $A = 0$ (no matrix diffusion) is the exponential distribution. For any value of A , at very early times ($t, T_a \rightarrow 0$), $g(T_a; t - T_a) \rightarrow \delta(t - T_a)$ and $h(t) \rightarrow P(t)$, the advective travel time distribution. As A increases, solute breakthrough is attenuated to a greater extent by matrix diffusion. A power-law behavior $h(t) \sim t^{-1/2}$, similar to the gamma distribution with $\alpha = 0.5$, arises in an intermediate time regime for larger values of A (S35, SI Section S.4). For an infinite matrix, the late-time tail behaves as $h(t) \sim t^{-3/2}$ (SI Section S.4) and the mean total travel time is unbounded. For finite matrix widths (shown for $A=5$), the solute TTD coincides with that for an infinite width at times smaller than a characteristic diffusion time scale across the matrix width. It then levels off first, due to back-diffusion of solute from the matrix, and subsequently decreases exponentially as solute is flushed out, thus producing overall behavior resembling a gamma distribution with $\alpha = 0.5$. As noted above, the mean total travel time for finite matrix widths is $\bar{T}_a(1 + 2B\phi_m/b)$. Due to the explicit dependence of g on T_a , flowpaths with shorter T_a are less affected by matrix diffusion than flowpaths with longer T_a . As a result, $h(t)$ exhibits both short-term responsiveness and long-term memory, which are highlighted as salient properties of TTDs at Plynlimon (Krichner et al. 2000).

5. Application to the Lower Hafren Catchment

Neal et al. (1997) describe the hydrology and geology of the Hafren catchment. Storm runoff is dominated by groundwater and interflow, and groundwater levels are highly responsive to rainfall. The shallow groundwater system is hosted in highly fractured shale, mudstone, and greywacke rocks, overlain by relatively thin soils (~0.7m). Typical water table depths are around 5m. Although groundwater is estimated to occur down to 30m below the stream, rapid circulation and significant groundwater storage only occurs down to 9m depth, suggesting a saturated thickness (H) of ~4m for the active portion of the groundwater system. The net recharge rate (r) is about 2 m/year.

Kirchner (2000) and Kirchner et al. (2013) presented stream and precipitation power spectra for chloride at Lower Hafren. The spectra presented by Kirchner et al. (2013) differ from those of Kirchner (2000), due to refined spectral analysis methods and additional and longer datasets. Both analyses suggest that the power spectral ratio $S_{C_oC_o}(\omega)/S_{C_iC_i}(\omega)$ exhibits close to $1/\omega$ behavior. To represent this behavior, Kirchner et al. (2000) proposed a gamma distribution for the solute TTD, for which $S_{C_oC_o}(f)/S_{C_iC_i}(f) = 1/(1 + 4\pi^2 f^2 \beta^2)^\alpha$, where $f = \omega/2\pi$ is the frequency. Kirchner et al. (2000) fitted values of $\alpha = 0.48$, $\beta = 1.9\text{yr}$ to the observed power spectra; which corresponds to a mean total travel time of $\alpha\beta = 0.91\text{yr}$. The power spectra of Kirchner et al. (2013) are better fit with $\alpha = 0.5$, $\beta = 0.4\text{yr}$ (Figure 3a), which corresponds to a shorter mean travel time of 0.2 years. Kirchner et al. (2013) reported that the precipitation chloride spectrum exhibits $1/f^{0.41}$ behavior. From a precipitation spectrum based on a subset of the full dataset (Harman, 2015), I obtained a best fit of $0.38/f^{0.34} (\text{mg/L})^2\text{-yr}$, and with the exponent fixed at 0.41, I obtained a best fit $0.42/f^{0.41} (\text{mg/L})^2\text{-yr}$, which I used in the calculations below. These two alternative forms for the precipitation chloride spectra do not

produce major differences in calculated stream concentration spectra (compare Figure 3a with Figure S4 in SI).

The power spectral ratio (15, 16) depends on two key variables: the mean advective travel time \bar{T}_a and the matrix diffusion parameter A . Because A contains products and ratios of other physical parameters, these parameters cannot be fit uniquely. My intention here is not to produce a “best-fit” parameter set, but rather to present reasonable parameter values that are consistent with the site description and match the spectral estimates of Kirchner et al. (2013). I assume an exponential advective travel time distribution (8). Estimation of \bar{T}_a requires an estimate of the effective fracture porosity ϕ_a associated with the hydrologically responsive flow system at the scale of the watershed, which is a highly uncertain parameter. Assuming a value of $\phi_a = 0.005$, the mean advective travel time is estimated as $\bar{T}_a = \phi_a H / r = 0.01$ years (3.65 days). To put this estimate in context, a regular arrangement of cubic matrix blocks with 0.3m sides, interspersed with $b = 0.5\text{mm}$ wide connected fractures, would produce $\phi_a = 0.005$. The one-dimensional accessible matrix width B in (15,16) could be smaller than the block size for two reasons – first, Barker’s (1985) analysis suggests an effective one-dimensional width equal to 1/6 of the block size for cubical blocks, and secondly, significant matrix diffusion is often restricted to the weathered periphery of matrix blocks. Values for the matrix porosity ($\phi_m = 0.15$), and effective diffusivity for chloride ($D_e = 1.5 \times 10^{-10} \text{ m}^2/\text{s}$), were assigned to fall within the ranges reported for shale and mudstone (Manger, 1963; Barone et al. 1992). These parameter values result in $A = 2.06$.

Figure 3a compares $S_{C_o C_o}(f)$ calculated using $S_{C_i C_i}(f) = 0.42 / f^{0.41}$ and the above parameter values in (15), the gamma model with $\alpha = 0.5$, $\beta = 0.4 \text{ yr}$, and the power spectral estimates from Figure S7 in Kirchner et al. (2013). Both the matrix diffusion and the fitted gamma models produce reasonable matches to the estimated stream concentration spectra and the -1.4 slope estimated by Kirchner et al. (2013). Because of the relatively short \bar{T}_a , even an accessible matrix thickness as small as $B = 0.05 \text{ m}$ ($B / \sqrt{De\bar{T}_a} = 7.27$) produces only a minor deviation of the power spectral ratio from that for the infinite matrix case. All models approach the precipitation concentration spectrum at frequencies $< 0.1 \text{ yr}^{-1}$. At the high frequency end ($> 20 \text{ yr}^{-1}$), the matrix diffusion models underestimate the spectral power slightly. This is likely because the analysis assumes steady flow and will thus miss the influence of hydrologic transients on solute transport. Alternative sets of parameter values that produce reasonable matches with the estimated stream concentration spectra are presented in SI (Figure S3). As noted above, compensatory variations among the physical parameters that occur in A preclude unique parameter estimates.

The solute TTDs corresponding to the power spectral models presented in Figure 3a are shown in Figure 3b. For finite matrix widths ($B = 0.05$ and 0.1 m), the solute TTDs obtained with the matrix diffusion model are comparable to the fitted gamma distribution, which exhibits $t^{-1/2}$ power law behavior at intermediate times. The tails of the solute TTDs are longer for larger B , and for very large B , there is a tendency towards $t^{-3/2}$ behavior at late time. The mean solute travel times corresponding to the finite width matrix diffusion models are 0.31 years ($B=0.05 \text{ m}$) and 0.61 years ($B=0.1 \text{ m}$). Greater differences between the matrix diffusion models and the fitted

gamma model are evident in the TTD tails than in the low frequency behavior of the power spectra.

6. Discussion

Although the role of matrix diffusion in influencing environmental solute ages has been recognized previously, it is seldom explicitly considered in investigations and interpretations of catchment solute TTDs. This paper quantitatively demonstrates that matrix diffusion in fractured bedrock can generate fractal stream chemistry, and power-law behavior and long-term memory in solute TTDs. The general relationships (14) and (18) provide a framework for quantifying catchment-scale stream concentration power spectra and solute TTDs, by superposing the influence of matrix diffusion on any general advective travel time distribution derived from analytical or numerical subsurface flow models (e.g. Ameli et al. 2016; Kollett and Maxwell, 2008; Carroll et al. 2020). Availability of concentration data for multiple solutes will facilitate inverse estimation of catchment-scale matrix diffusion parameters. The matrix diffusion mechanism is physically consistent with the large residual or passive storage component inferred while calibrating compartmental models of catchment hydrochemical response (e.g. Birkel et al. 2011, Benettin et al. 2014). The analysis presented here can be extended to incorporate alternative representations of matrix diffusion and retention (e.g., multi-rate models or memory functions) and heterogeneity within the fracture flow system (Cvetkovic and Haggerty, 2002; Shapiro, 2001; Zhou et al. 2007), and layered hydrostratigraphy. One limitation of the analysis is the neglect of transient flow effects and vadose zone processes, although some previous studies (e.g. Fiori and Russo, 2008; Cvetkovic et al. 2012, Carroll et al. 2020) suggest that steady state approximations are adequate for the dominant subsurface flow paths. Numerical models of unsaturated-saturated flow and transport (e.g. Kollett and Maxwell, 2008; Carroll et al. 2020) can

379 be augmented to include matrix diffusion for more comprehensive evaluation of solute TTDs.
380 Interpretation of solute TTDs, especially in mountain catchments with fractured bedrock, should
381 consider the potential influence of matrix diffusion in addition to other factors.

382

383 **Acknowledgements**

384 This research was supported partially by National Science Foundation award EAR2012264. I
385 am grateful to James Kirchner for providing the power spectral estimates from Lower Hافren,
386 which are available in Figure S7 from Kirchner et al. (2013).

387

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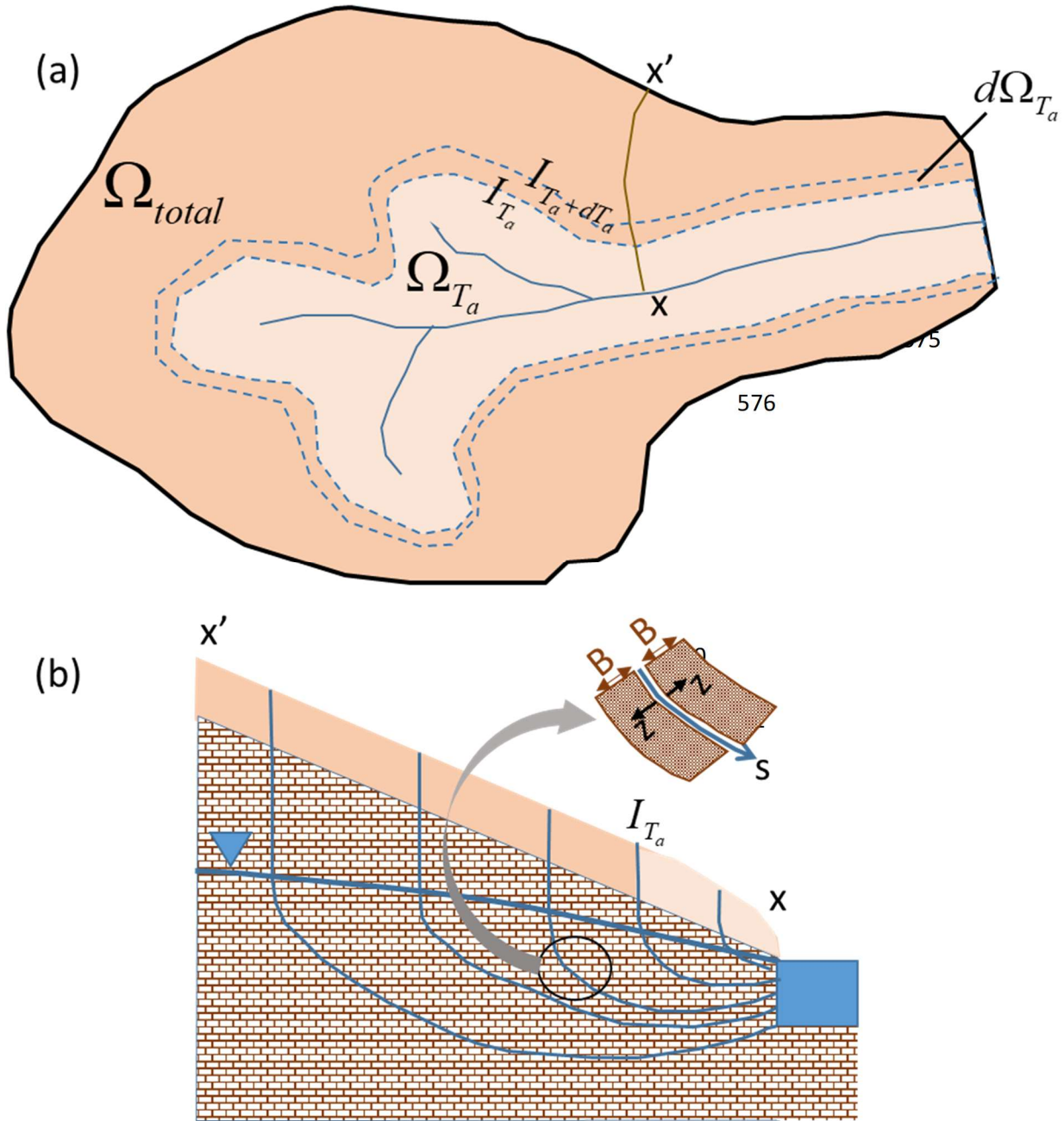


Figure 1. Schematic conceptual model of catchment-scale groundwater flow and transport. (a) Plan view showing total area Ω_{total} and area Ω_{T_a} bounded by isochrone I_{T_a} from which the advective travel time to the stream is T_a . (b) Vertical cross-section along $x-x'$ in (a), showing streamlines from the surface, through the water table to the stream. The streamline coordinate is denoted by s , and z denotes the distance from the fracture-matrix interface. One-dimensional matrix diffusion is assumed, with an accessible matrix width B .

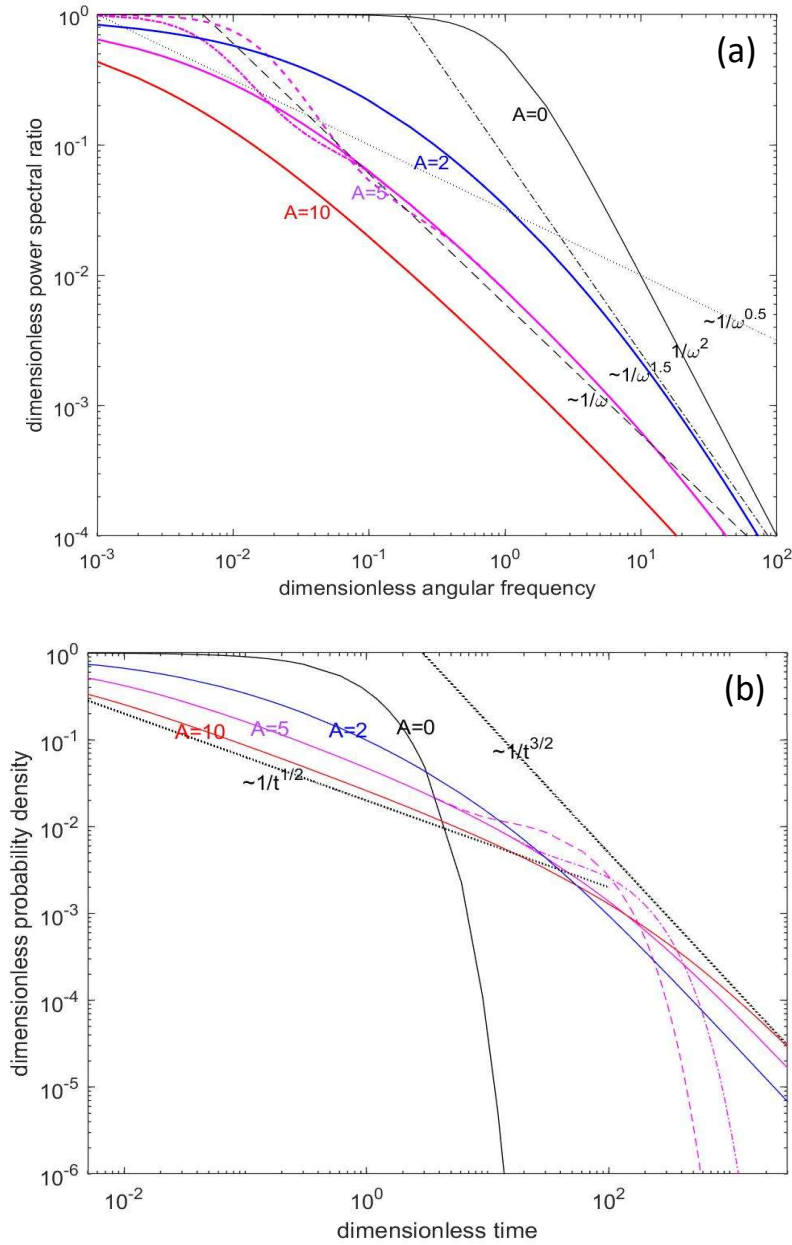
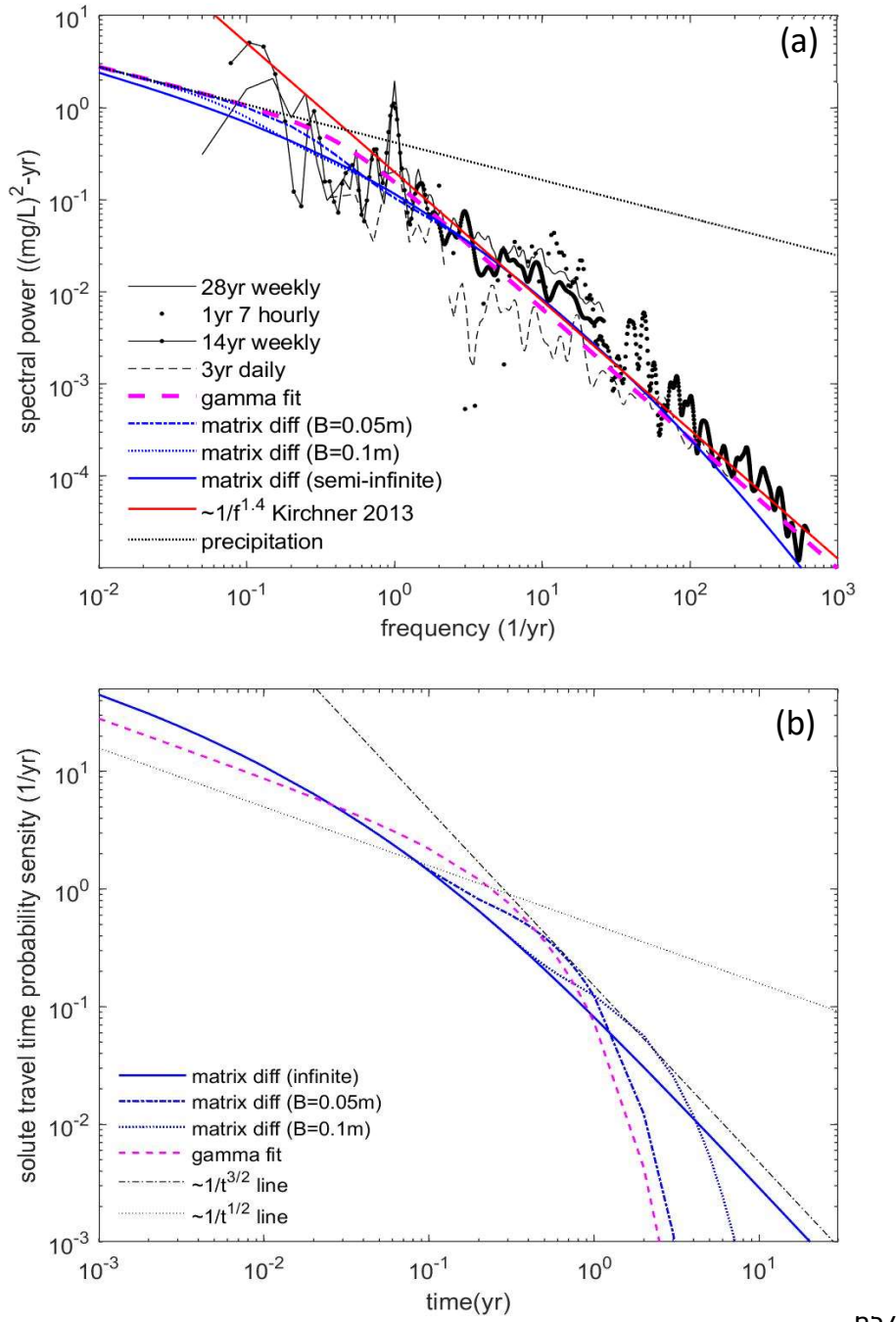


Figure 2. Influence of the matrix diffusion parameter A . (a) Dimensionless power spectral ratio $(S_{C_o C_o} / S_{C_i C_i})(15)$ plotted against dimensionless angular frequency $(\omega \bar{T}_a)$. Black lines indicate various power-law slopes. For $A=0$ (solid black), $S_{C_o C_o} / S_{C_i C_i}(\omega) = (1 + \omega^2 \bar{T}_a^2)$. (b) Dimensionless solute TTD $h(t / \bar{T}_a) \bar{T}_a$ from (18) with an exponential $P(T_a)$, plotted against dimensionless time (t / \bar{T}_a) . Solid lines correspond to different values of A and an infinite matrix. The dashed and dash-dotted magenta lines correspond to $B / \sqrt{D_e \bar{T}_a} = 5$ and 10 respectively, for $A=5$. Black dotted lines show intermediate ($\sim 1 / t^{1/2}$) and late-time ($\sim 1 / t^{3/2}$) power-law regimes.



057

658 **Figure 3.** (a) Chloride power spectrum and (b) solute travel time distribution (TTD) for Lower
 659 Hafren, based on the matrix diffusion model ($\phi_m = 0.15, D_e = 1.5 \times 10^{-10} \text{ m}^2/\text{s}, b = 5 \times 10^{-4} \text{ m},$
 660 $\bar{T}_a = 0.01 \text{ yr}$) and matrix widths $B = 0.05 \text{ m}, 0.1 \text{ m}$ and ∞ ; and a gamma model ($\alpha = 0.5, \beta = 0.4 \text{ yr}$)
 661 fit to the power spectral estimates from Kirchner et al. (2013). A line with the fitted power law
 662 slope of -1.4 (Kirchner et al. 2013) is also shown in (a). Dotted and dash-dotted lines in (b)
 663 respectively show the intermediate ($\sim 1/t^{1/2}$) and late-time ($\sim 1/t^{3/2}$) power-law regimes.

Matrix Diffusion as a Mechanism Contributing to Fractal Stream Chemistry

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Contents of this file

- S.1 Mathematical details – derivation of Equations (11-12) in the manuscript
- S.2 Mathematical details – derivation of Equation (15) in the manuscript and extension to a gamma advective travel time distribution
- S.3 Review of Laplace Transforms of $g(T_a; t - T_a)$ relevant to Equation (18)
- S.4 Non-dimensionalization and approximate analytical forms of Equation (18) for exponential and gamma advective travel time distributions (includes Figures S1, S2)
- S.5 Alternative parameter sets for Lower Hafren (includes Figures S3, S4; Table S1)

Introduction

Sections S.1 and S.2 provide detailed mathematical steps involved in the derivation of the key results pertaining to the stream concentration power spectrum (Equations (11-12) and (15)). Section S.2 includes a generalization of Equation (15) for the case of a gamma advective travel time distribution. Section S.3 provides a review of Laplace transforms (from previous literature), which are involved in the representation of the Green's function $g(T_a; t - T_a)$ needed for the evaluation of the solute TTD (Equation (18)) for finite matrix widths. Although the integral (Equation (18)) for the solute TTD can be evaluated exactly only by numerical integration, analytical approximations can be derived for infinite matrix width in three different dimensionless time regimes – these analytical approximations are presented in Section S.4, and provide additional insights into the power-law behavior of solute TTDs. Calculations of the stream concentration power spectrum for Lower Hafren, based on alternative parameter sets and an alternative precipitation concentration spectrum are presented in Section S.5.

31 **S.1 Detailed Derivation of the Fourier Transform Solution for \tilde{C}_f (Equations 11-12 in the**
 32 **manuscript)**

33 The transport equation in the fracture is given by:

$$34 \quad \frac{\partial C_f}{\partial t} + \frac{\partial C_f}{\partial \tau_a} = \frac{2\phi_m D_e}{b} \frac{\partial C_m}{\partial z} \bigg|_{\tau_a, z=0, t} \quad (\text{S1}) \text{ (Equation 5 in the manuscript)}$$

35 The inflow boundary condition at the entrance to the streamline ($\tau_a = 0$) is:

$$36 \quad C_f(\tau_a = 0, t; I_{T_a}) = C_i(t) \quad (\text{S2}) \text{ (Equation 6 in the manuscript)}$$

37 The right-hand side of (S1) may be evaluated by considering the diffusion equation in the rock
 38 matrix:

$$39 \quad (\phi_m + \rho_b K_d) \frac{\partial C_m}{\partial t} - \phi_m D_e \frac{\partial^2 C_m}{\partial z^2} = 0 \quad (\text{S3}) \text{ (Equation 2 in the manuscript)}$$

40 Boundary conditions for (S3) are:

$$41 \quad C_m(\tau_a, z = 0, t; I_{T_a}) = C_f(\tau_a, t; I_{T_a}), \quad \frac{\partial C_m}{\partial z}(\tau_a, z = B, t; I_{T_a}) = 0 \quad (\text{S4}) \text{ (Equation 3 in the manuscript,}$$

42 with τ_a in place of s)

43 The notation $\tilde{C}_i(\omega)$, $\tilde{C}_o(\omega)$, $\tilde{C}_f(\tau_a, \omega; I_{T_a})$ and $\tilde{C}_m(\tau_a, z, \omega; I_{T_a})$ is used for the Fourier transforms
 44 of $C_i(t)$, $C_o(t)$, $C_f(\tau_a, t; I_{T_a})$ and $C_m(\tau_a, z, t; I_{T_a})$ respectively, with ω denoting the angular
 45 frequency.

46 The first step is to take the Fourier Transform of the matrix diffusion equation (S3) and boundary
 47 conditions (S4), which yields (S5) and (S6):

$$48 \quad i\omega \tilde{C}_m - \frac{D_e}{R} \frac{d^2 \tilde{C}_m}{dz^2} = 0 \quad (\text{S5})$$

49 where $R = (1 + \rho_b K_d / \phi_m)$ is the retardation factor in the matrix and $i = \sqrt{-1}$.

$$50 \quad \tilde{C}_m(\tau_a, z=0, \omega; I_{T_a}) = \tilde{C}_f(\tau_a, \omega; I_{T_a}), \quad \frac{d\tilde{C}_m}{dz}(\tau_a, z=B, \omega; I_{T_a}) = 0 \quad (\text{S6})$$

51 Equations (S5-S6) are then readily solved to obtain \tilde{C}_m in terms of \tilde{C}_f :

$$52 \quad \tilde{C}_m = \tilde{C}_f \left(\frac{e^{-\sqrt{i}uz} + e^{\sqrt{i}u(z-2B)}}{1 + e^{-2\sqrt{i}uB}} \right), \text{ where } u = \sqrt{\frac{\omega R}{D_e}} \quad (\text{S7})$$

53 The Fourier transform of (S1) is:

$$54 \quad i\omega\tilde{C}_f + \frac{d\tilde{C}_f}{d\tau_a} = \frac{2\phi_m D_e}{b} \frac{\partial \tilde{C}_m}{\partial z} \bigg|_{\tau_a, z=0, \omega} \quad (\text{S8})$$

55 The right hand side of (S8) involves the derivative of \tilde{C}_m at the fracture-matrix interface ($z=0$),

56 which can be obtained from (S7):

$$57 \quad \frac{\partial \tilde{C}_m}{\partial z} \bigg|_{\tau_a, z=0, \omega} = \tilde{C}_f(\tau_a, \omega) \left(-\sqrt{i}u + \frac{2\sqrt{i}u}{1 + e^{2\sqrt{i}uB}} \right) \quad (\text{S9})$$

58 Using (S9) in (S8) yields the following first-order ordinary differential equation for \tilde{C}_f :

$$59 \quad i\omega\tilde{C}_f + \frac{d\tilde{C}_f}{d\tau_a} = \frac{2\phi_m D_e}{b} \tilde{C}_f \left(-\sqrt{i}u + \frac{2\sqrt{i}u}{1 + e^{2\sqrt{i}uB}} \right) \quad (\text{S10})$$

60 Equation (S10) can be rewritten as:

$$61 \quad \frac{d\tilde{C}_f}{d\tau_a} + \left(i\omega + \frac{2\phi_m \sqrt{RD_e \omega}}{b} \sqrt{i} - \frac{\frac{4\phi_m \sqrt{RD_e \omega}}{b} \sqrt{i}}{\left(1 + \exp \left(2\sqrt{\frac{R\omega}{D_e}} B \sqrt{i} \right) \right)} \right) \tilde{C}_f = 0 \quad (\text{S11})$$

$$62 \quad \text{With } k(\omega) = i\omega + \frac{2\phi_m \sqrt{RD_e \omega}}{b} \sqrt{i} - \frac{\frac{4\phi_m \sqrt{RD_e \omega}}{b} \sqrt{i}}{\left(1 + \exp \left(2\sqrt{\frac{R\omega}{D_e}} B \sqrt{i} \right) \right)}, \text{ (Equation 11 in the manuscript)}$$

the solution for \tilde{C}_f is obtained in compact form as:

$$\tilde{C}_f(T_a, \omega; I_{T_a}) = \tilde{C}_i(\omega) \exp\{-k(\omega)T_a\} \quad (\text{S12}) \quad (\text{Equation 12 in manuscript})$$

S.2 Detailed Derivation of the Power Spectrum of Stream Concentration Variations $S_{C_o C_o}$ or catchment spectral filter $S_{C_o C_o} / S_{C_i C_i}$ (Equation 15 in the manuscript)

The Fourier transform of the stream (outflow) concentration, $\tilde{C}_o(\omega)$, can be obtained starting from Equations (13) and (8) in the manuscript:

$$\tilde{C}_o(\omega) = \tilde{C}_i(\omega) \int_0^\infty \exp\{-k(\omega)T_a\} P(T_a) dT_a \quad (\text{S13}) \quad (\text{Equation 13 in manuscript})$$

$$P(T_a) = \frac{1}{\bar{T}_a} \exp\left(-\frac{T_a}{\bar{T}_a}\right) \quad (\text{S14}) \quad (\text{Equation 8 in the manuscript})$$

(S14) is the exponential advective travel time distribution with mean advective travel time \bar{T}_a .

Using (S14), the integral in (S13) evaluates to:

$$\int_0^\infty \exp\{-k(\omega)T_a\} P(T_a) dT_a = \frac{1}{1 + k(\omega)\bar{T}_a} \quad (\text{S15})$$

To proceed further, I start from the denominator:

$$1 + k(\omega)\bar{T}_a = 1 + \left(i\omega + \frac{2\phi_m \sqrt{RD_e \omega}}{b} \sqrt{i} - \frac{\frac{4\phi_m \sqrt{RD_e \omega}}{b} \sqrt{i}}{\left(1 + \exp\left(2\sqrt{\frac{R\omega}{D_e}} B \sqrt{i}\right)\right)} \right) \bar{T}_a \quad (\text{S16})$$

To evaluate (S16), first note that

$$1 + \exp\left(2\sqrt{\frac{R\omega}{D_e}} B \sqrt{i}\right) = 1 + \exp\left(2\sqrt{\frac{R\omega}{D_e}} B \frac{1+i}{\sqrt{2}}\right) = 1 + \exp\left(\sqrt{\frac{2R\omega}{D_e}} B\right) \left(\cos\left(\sqrt{\frac{2R\omega}{D_e}} B\right) + i \sin\left(\sqrt{\frac{2R\omega}{D_e}} B\right) \right)$$

Now, let

$$m = 1 + \exp\left(\sqrt{\frac{2R\omega}{D_e}}B\right) \cos\left(\sqrt{\frac{2R\omega}{D_e}}B\right), n = \exp\left(\sqrt{\frac{2R\omega}{D_e}}B\right) \sin\left(\sqrt{\frac{2R\omega}{D_e}}B\right)$$

$$\text{Thus, } 1 + k(\omega)\bar{T}_a = 1 + \left(i\omega + \frac{2\phi_m\sqrt{RD_e\omega}}{b} \frac{1+i}{\sqrt{2}} - \frac{4\phi_m\sqrt{RD_e\omega}}{b} \frac{1+i}{\sqrt{2}} \frac{m-in}{m^2+n^2} \right) \bar{T}_a \quad (\text{S17})$$

The right side of (S17) can be rewritten after separating the real and imaginary parts, as:

$$\left(1 + \frac{\sqrt{2RD_e\omega}}{b} \phi_m \bar{T}_a \left(1 - \frac{2(m+n)}{m^2+n^2} \right) \right) + i \left(\omega \bar{T}_a + \frac{\sqrt{2RD_e\omega}}{b} \phi_m \bar{T}_a \left(1 - \frac{2(m-n)}{m^2+n^2} \right) \right)$$

$$\text{Now, let } M = 1 - \frac{2(m+n)}{m^2+n^2}, N = 1 - \frac{2(m-n)}{m^2+n^2}, A = \frac{\phi_m\sqrt{RD_e\bar{T}_a}}{b}.$$

We can thus write:

$$\frac{1}{1 + k(\omega)\bar{T}_a} = \frac{1}{\left(1 + \sqrt{2}AM\sqrt{\omega\bar{T}_a} \right) + i \left(\omega\bar{T}_a + \sqrt{2}AN\sqrt{\omega\bar{T}_a} \right)} \quad (\text{S18})$$

Finally, $S_{C_oC_o} / S_{C_iC_i}$ is obtained by evaluating the integral in Equation (14) of the manuscript,

$$\begin{aligned} \left| \int_0^\infty \exp\{-k(\omega)T_a\} P(T_a) dT_a \right|^2 &= \left| \frac{1}{1 + k(\omega)\bar{T}_a} \right|^2 \\ &= \frac{1}{1 + 2\sqrt{2}AM\sqrt{\omega\bar{T}_a} + 2A^2(M^2 + N^2)\omega\bar{T}_a + 2\sqrt{2}AN(\omega\bar{T}_a)^{3/2} + \omega^2\bar{T}_a^2} \end{aligned} \quad (\text{S19})$$

89

Equation (S19) leads to the power spectrum of stream concentration variations as Equation (15)

in the manuscript.

A simpler form of (S19) can be derived for the simpler special case of $B \rightarrow \infty$. For this case, the

boundary condition at $z = B$ in (S4) is replaced with the requirement that \tilde{C}_m remains bounded.

This leads to a simpler expression for \tilde{C}_m :

$$\tilde{C}_m = \tilde{C}_f e^{-\sqrt{iuz}} \quad (\text{S20})$$

The simpler form of (S11) for this case is:

$$\frac{d\tilde{C}_f}{d\tau_a} + \left(i\omega + \frac{2\phi_m \sqrt{RD_e \omega}}{b} \sqrt{i} \right) \tilde{C}_f = 0 \quad (\text{S21})$$

The corresponding simpler form of (S17) is:

$$1 + k(\omega) \bar{T}_a = \left(1 + \frac{\sqrt{2RD_e \omega}}{b} \phi_m \bar{T}_a \right) + i \left(\omega \bar{T}_a + \frac{\sqrt{2RD_e \omega}}{b} \phi_m \bar{T}_a \right) \quad (\text{S22})$$

The spectral filter $S_{C_o C_o} / S_{C_i C_i}$ is then obtained as:

$$\left| \frac{1}{1 + k(\omega) \bar{T}_a} \right|^2 = \frac{1}{1 + 2\sqrt{2}A\sqrt{\omega \bar{T}_a} + 4A^2 \omega \bar{T}_a + 2\sqrt{2}A(\omega \bar{T}_a)^{3/2} + \omega^2 \bar{T}_a^2} \quad (\text{S23})$$

It is readily verified that (S19) reduces to (S23) when $B \rightarrow \infty$, in which case $M, N \rightarrow 1$.

In Dupuit flow systems with significant water table relief (i.e. significant increase in saturated thickness H from stream to divide), or in the case of deep-circulating groundwater flow, the exponential distribution is not a suitable model for the advective travel time distribution. A gamma distribution (especially with $\alpha < 1$), which has two parameters, provides a more flexible model of the advective travel time distribution in such cases. Equation (14) in the manuscript can be employed with any advective travel time distribution. Below, I present the spectral ratio $S_{C_o C_o} / S_{C_i C_i}$ for a gamma advective travel time distribution (rewritten in terms of the mean advective travel time \bar{T}_a):

$$P(T_a) = \frac{\alpha^\alpha}{\Gamma(\alpha) \bar{T}_a} \left(\frac{T_a}{\bar{T}_a} \right)^{\alpha-1} \exp\left(-\alpha \frac{T_a}{\bar{T}_a}\right) \quad (\text{S24})$$

112 Using (S24) in Equation (14) of the manuscript, the spectral ratio $S_{C_o C_o} / S_{C_i C_i}$ for a gamma
 113 advective travel time distribution is obtained as:

$$114 \left| \int_0^\infty \exp\{-k(\omega)T_a\}P(T_a)dT_a \right|^2 = \left| \frac{\alpha^\alpha}{(\alpha + k(\omega)\bar{T}_a)^\alpha} \right|^2 = \frac{\alpha^{2\alpha}}{\left(\alpha^2 + 2\sqrt{2}AM\alpha\sqrt{\omega\bar{T}_a} + 2A^2(M^2 + N^2)\omega\bar{T}_a + 2\sqrt{2}AN(\omega\bar{T}_a)^{3/2} + \omega^2\bar{T}_a^2 \right)^\alpha} \quad (S25)$$

115 Equation (S25) shows that matrix diffusion combined with a gamma distributed advective travel
 116 times across streamlines leads to a richer variety of power-law exponents in stream concentration
 117 spectra. For $\alpha = 1$, (S25) reduces to (S19). For strong matrix diffusion ($A \gg 1$), the third term in
 118 the denominator dominates and the spectral ratio behaves as $1/\omega^\alpha$ for a large frequency range,
 119 rather than $1/\omega$ as in (S19 or Equation 15 in the manuscript). For pure advection ($A \rightarrow 0$), the
 120 spectral filter reduces to $1/(1 + \omega^2\beta^2)^\alpha$, where $\beta = \bar{T}_a/\alpha$; which is consistent with that of the
 121 gamma distribution and behaves as $1/\omega^{2\alpha}$ at high frequencies. In general, when matrix diffusion
 122 is strong, the spectral ratio behaves as $1/\omega^\alpha$, rather than the $1/\omega^{2\alpha}$ behavior of the
 123 corresponding advective travel time distribution, i.e. the power-law exponent of the advective
 124 travel time power spectrum is halved as a result of matrix diffusion.

125 **S.3 Review of the Laplace Transform Solutions to (S1) - (S4), relevant to the catchment** 126 **solute TTD $h(t)$ (Equation 18 in the manuscript)**

127 Laplace transform solutions for transport with matrix diffusion in fractured rock date back to
 128 Grisak and Pickens (1980), Tang et al. (1981) and Maloszewski and Zuber (1985). For
 129 completeness, I present the specific forms of the Laplace transforms used in the manuscript here.

130 I use the following notation to denote a Laplace transform $\hat{f}(s)$ of a function $f(t)$ and the
 131 corresponding inverse transform, where t denotes time and s is the Laplace transform variable:

$$132 \quad \mathcal{L}\{f(t)\}(s) = \hat{f}(s) = \int_0^{\infty} e^{-st} f(t) dt, \quad \mathcal{L}^{-1}\{\hat{f}(s)\}(t) = f(t)$$

133 The Laplace transform of the fracture concentration at the end of a streamline is defined as:

$$134 \quad \mathcal{L}\{C_f(T_a, t; I_{T_a})\}(s) = \hat{C}_f(T_a, s; I_{T_a}) \quad (\text{S24})$$

135 The corresponding inverse Laplace transform is defined by:

$$136 \quad \mathcal{L}^{-1}\{\hat{C}_f(T_a, s; I_{T_a})\}(t) = C_f(T_a, t; I_{T_a}) \quad (\text{S25})$$

137 For a Dirac Delta input function, i.e. $C_i(t) = \delta(t)$, solving (S1) - (S4) using Laplace transforms
 138 yields:

$$139 \quad \hat{C}_f(T_a, s; I_{T_a}) = \exp\left(-\left(s + 2a\sqrt{s} \tanh\left(\sqrt{\frac{Rs}{D_e}} B\right)\right) T_a\right) \quad (\text{S26})$$

140 where $a = \phi_m \sqrt{RD_e} / b$.

141 The corresponding inverse Laplace transform is:

$$142 \quad C_f(T_a, t; I_{T_a}) = H(t - T_a) \mathcal{L}^{-1}\left\{\exp\left(-2a\sqrt{s} \tanh\left(\sqrt{\frac{Rs}{D_e}} B\right) T_a\right)\right\}(t - T_a) \quad (\text{S27})$$

143 where $H(t - T_a)$ is the Heaviside function (0 for $t \leq T_a$ and 1 for $t > T_a$). Thus, if the Green's

144 function (solution for a Dirac delta input) for the coupled equations (S1-S4) is denoted as

145 $H(t - T_a)g(T_a; t - T_a)$, the function $g(T_a; t - T_a)$ is defined as:

$$146 \quad g(T_a; t - T_a) = \mathcal{L}^{-1}\left\{\exp\left(-2a\sqrt{s} \tanh\left(\sqrt{\frac{Rs}{D_e}} B\right) T_a\right)\right\}(t - T_a) \quad (\text{S28})$$

147 For $B \rightarrow \infty$, the tanh term in (S28) becomes 1 and the inverse Laplace transform

148 $\mathcal{L}^{-1}\left\{\exp\left(-2a\sqrt{s}T_a\right)\right\}(t-T_a)$ is obtained analytically (Maloszewski and Zuber, 1985) to yield:

149
$$g(T_a; t-T_a) = \frac{aT_a}{\sqrt{\pi}(t-T_a)^{3/2}} \exp\left(-\frac{a^2T_a^2}{(t-T_a)}\right) \quad (\text{S29}) \quad (\text{Equation 17 in the manuscript})$$

150 For finite B , the inverse Laplace transform can be written in an integral form (Maloszewski and

151 Zuber, 1985), but is easier to evaluate by numerical inversion of (S28). I used a numerical

152 inversion to evaluate $g(T_a; t-T_a)$ in (18) for cases with finite matrix width. The MATLAB

153 function “talbot_inversion” (McClure, 2020) was used for numerical Laplace transform

154 inversion. The implementation of the inversion algorithm was verified by computing

155 $\mathcal{L}^{-1}\left\{\exp\left(-2a\sqrt{s}T_a\right)\right\}(t-T_a)$ numerically and verifying that it matches the analytical form (S29).

156 **S.4. Non-dimensionalization and Approximate Analytical Forms for the solute TTD $h(t)$**

157 **with Exponential and Gamma Advective Travel Time Distributions $P(T_a)$ for infinite**

158 **matrix widths ($B/\sqrt{De\bar{T}_a} \gg 1$)**

159 For infinite matrix widths, the general expression (18) for $h(t)$ can be non-dimensionalized and

160 written in terms of dimensionless total $(t^* = t/\bar{T}_a)$ and advective $(T_a^* = T_a/\bar{T}_a)$ travel times as:

161
$$h(t^*)\bar{T}_a = \int_0^{t^*} \frac{AT_a^*}{\sqrt{\pi}(t^* - T_a^*)^{3/2}} \exp\left(-\frac{A^2T_a^{*2}}{(t^* - T_a^*)}\right) \left(P(T_a^*)\bar{T}_a\right) dT_a^* \quad (\text{S30})$$

162 Note that $h(t^*)\bar{T}_a$ is the dimensionless solute TTD and $P(T_a^*)\bar{T}_a$ is the dimensionless advective

163 travel time distribution. Also note that $A = \phi_m \sqrt{RD_e\bar{T}_a}/b = a\sqrt{\bar{T}_a}$, as defined in Equation (16) in

164 the main manuscript. For exponential and gamma advective travel time distributions, the

165 advective travel time distributions are rewritten in dimensionless form below:

166 Exponential: $P(T_a^*)\overline{T_a} = \exp(-T_a^*)$ (S31)

167 Gamma: $P(T_a^*)\overline{T_a} = \frac{\alpha^\alpha}{\Gamma(\alpha)}(T_a^*)^{\alpha-1} \exp(-\alpha T_a^*)$ (S32)

168 Numerical integration of (S30) was performed using the MATLAB function “integral” to obtain
 169 the exact dimensionless solute TTD.

170 There are three dimensionless time regimes in which simpler approximations to (S30) can be
 171 developed.

172 VERY EARLY TIME: As noted in the main manuscript, for very early times ($t^* \ll 1$),

173 $h(t^*)\overline{T_a} \rightarrow P(t^*)\overline{T_a}$ for any form of the advective travel time distribution, because

174 $g(T_a; t - T_a) \rightarrow \delta(t - T_a)$ at short times ($t, T_a \rightarrow 0$). In other words, the solute TTD approaches
 175 the advective travel time distribution at very early times. The behavior is confirmed in Figure S1.

176 ANALYTICAL APPROXIMATION FOR $t^* > 1/A$: Approximate analytical forms of (S30) can

177 be obtained after change of variables and asymptotic approximation of the resulting integral for

178 $t^* > 1/A$ (Hyman et al. 2019):

179 Exponential: $h(t^*)\overline{T_a} \approx \frac{1}{4A^2} \left(\frac{2A}{\sqrt{\pi t^*}} - \exp\left(\frac{t^*}{4A^2}\right) \operatorname{erfc}\left(\frac{\sqrt{t^*}}{2A}\right) \right)$ (S33)

180 Gamma: $h(t^*)\overline{T_a} \approx \left(\frac{\alpha}{2}\right)^{\alpha+1} \frac{(t^*)^{-1+\frac{\alpha}{2}} U\left(\frac{1+\alpha}{2}, \frac{1}{2}, \frac{\alpha^2 t^*}{4A^2}\right)}{A^\alpha \sqrt{\pi}}$ (S34)

181 where $U(.,.,.)$ is the confluent hypergeometric function of the second kind (Weisstein, 2021),

182 also known as the confluent hypergeometric Kummer U function. It should also be noted that

183 (S33) is essentially a special case of (S34) for $\alpha = 1$, in as much as the exponential distribution is

184 a special case of the gamma distribution for $\alpha = 1$.

Figure S1 shows comparisons between the exact $h(t^*)\overline{T}_a$ obtained by numerical integration of (S30) and analytical approximations (S33) and (S44). Figure S1 confirms that (S33) and (S34) are excellent approximations to the numerical integral of (S30) for $t^* > 1/A$. The expressions (S33) and (S34) can be further approximated in intermediate and late time regimes.

INTERMEDIATE-TIME ($1/A < t^* < 4A^2/\alpha^2$) POWER LAW REGIME: An intermediate power-law regime prevails in the dimensionless time range $1/A < t^* < 4A^2/\alpha^2$ (note that this dimensionless time range may not exist for small values of A and larger values of α). This power-law regime is most clearly evident for $A = 10$ in Figure S1, but also for $A = 5$ and $\alpha = 1$, 0.7. From a MacLaurin series expansion of (S34), this power-law regime can be identified as

$$h(t^*)\overline{T}_a \approx \frac{(\alpha/2)^{\alpha+1}}{A^\alpha \Gamma\left(1 + \frac{\alpha}{2}\right)} (t^*)^{-1+\frac{\alpha}{2}} \quad (\text{S35})$$

Equation (S35) is not plotted in Figure S1 to keep it from getting too crowded. Figure S2 shows a comparison between (S35) and (S30) for different values of α and A , and confirms its validity, especially for larger values of A and smaller values of α .

LATE-TIME ($t^* \gg A^2$) BEHAVIOR AND POWER LAW REGIME: It is also evident from

Figure S1 that at dimensionless times $t^* \sim A$, $h(t^*)\overline{T}_a$ becomes largely insensitive to the advective travel time distribution (i.e. α), and approaches a limiting distribution (controlled by matrix diffusion, with little dependence on the advective travel time distribution) for a given A . A late time power law regime is identified for $t^* \gg A^2$, where further asymptotic expansion of

204 (S33) and (S44) produces the leading behavior shown in (S36) for any advective travel time
 205 distribution, which is also verified in Figures S1 and S2.

$$206 \quad h(t^*)\overline{T}_a \sim \frac{A}{\sqrt{\pi t^{*3/2}}} \quad (\text{S36})$$

207 However, this limit appears to be of limited practical value because it is only valid at very late
 208 times when the influence of a finite matrix width may already be manifest.

209 IN SUMMARY: The general analytical approximations (S33) and (S34) are valid for $t^* > 1/A$,
 210 and the approximate power law (S35) is valid for $1/A < t^* < 4A^2/\alpha^2$, when the values of A and
 211 α are such that this time regime exists. For finite matrix widths, the influence of a finite matrix
 212 is not experienced for $t^* < B^2/(D_e\overline{T}_a)$. Thus, the power law regime (S35) is valid even for

213 finite matrix widths, in the dimensionless time range $1/A < t^* < \min(B^2/(D_e\overline{T}_a), 4A^2/\alpha^2)$.

214 This behavior is evident in Figures 2b and 3b in the main manuscript, where the infinite and
 215 finite matrix width cases follow the same solute TTD for a significant time range. At $t^* \sim A$,

216 $h(t^*)\overline{T}_a$ becomes largely insensitive to the advective travel time distribution (i.e. α), and

217 approaches a limiting distribution that only depends on A .

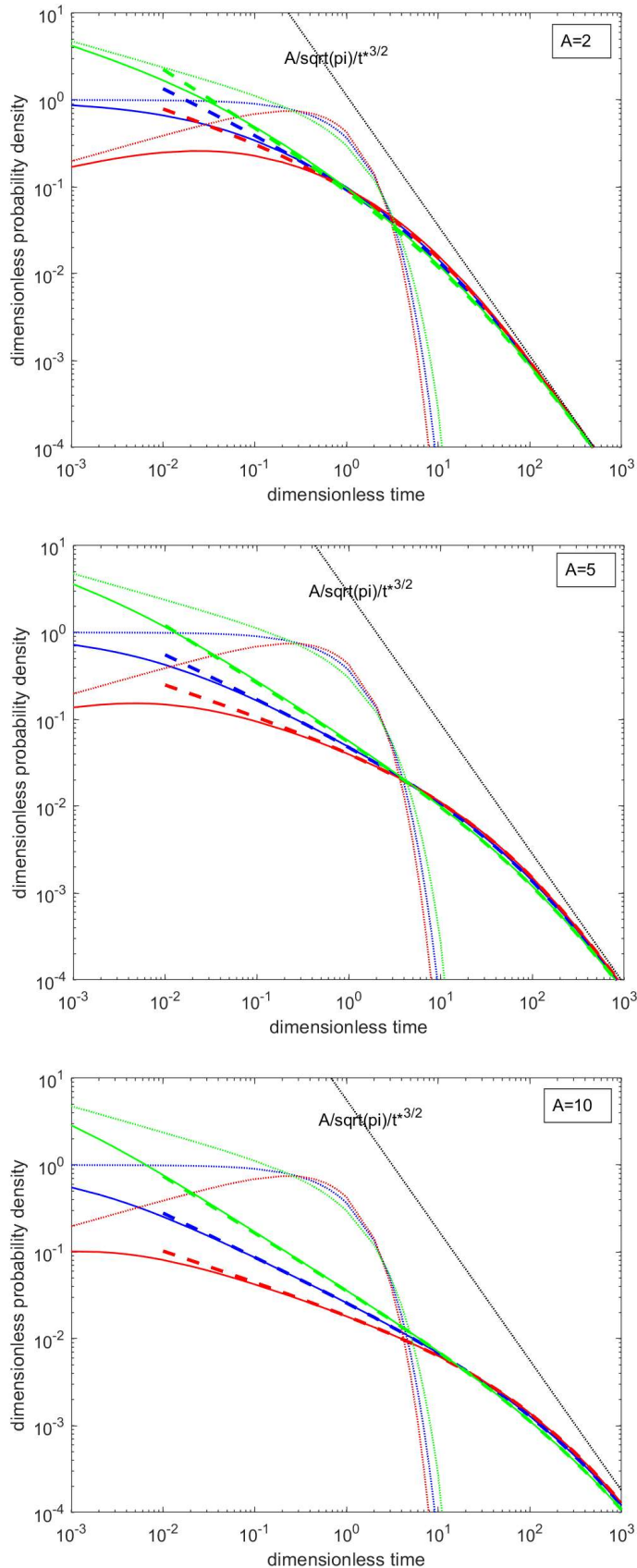


Figure S1. Dimensionless solute TTD $h(t^*)\overline{T}_a$ versus dimensionless time (t^*) for infinite matrix widths and different values of A , for gamma distributions with $\alpha = 0.7$ (green), 1 (blue) and 1.3 (red). Note that $\alpha = 1$ corresponds to the exponential distribution. Dotted lines: Dimensionless advective travel time distributions $P(T_a^*)\overline{T}_a$, Solid lines - Exact $h(t^*)\overline{T}_a$ from numerical integration of (S30), Dashed lines - Approximations (S33) and (S34). The straight line representing the late-time asymptote $h(t^*)\overline{T}_a \rightarrow A / (\sqrt{\pi} t^{*3/2})$ (S36) is also shown.

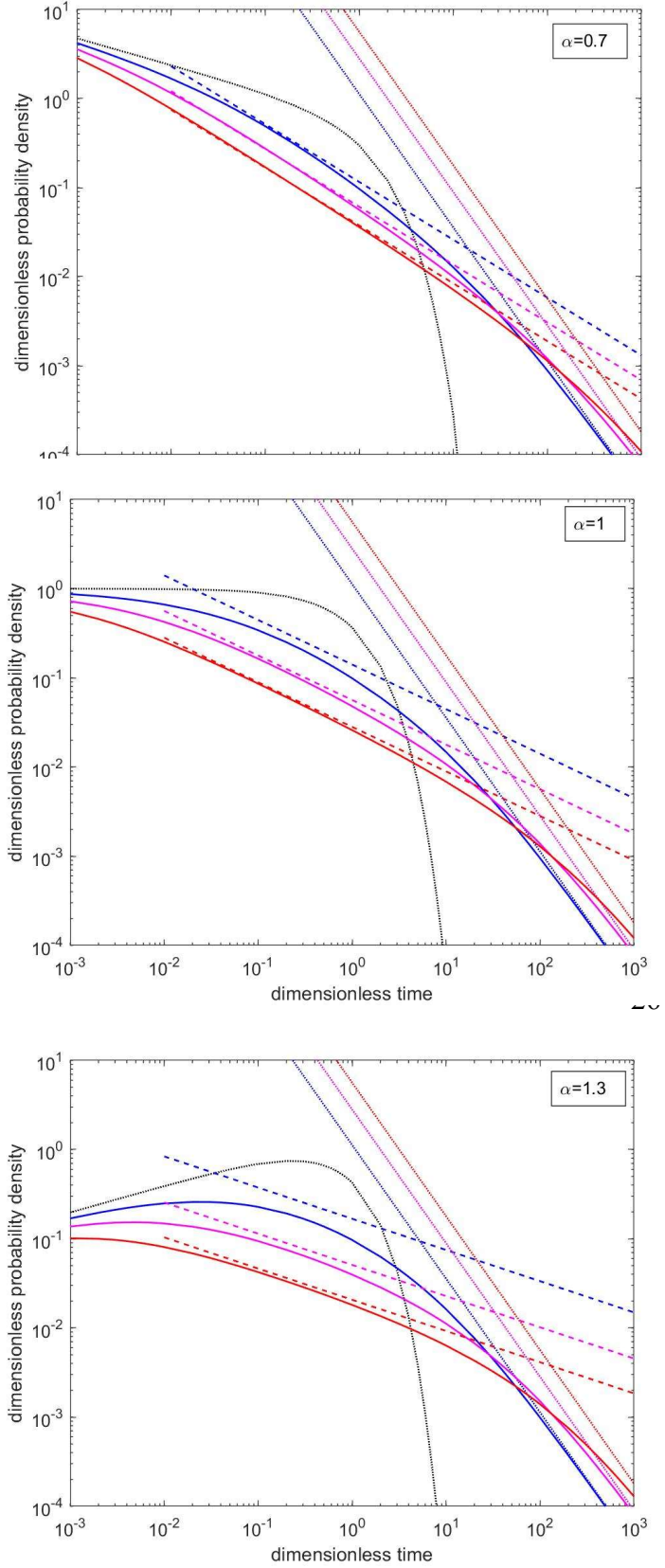


Figure S2. Dimensionless solute TTD $h(t^*)\overline{T}_a$ versus dimensionless time (t^*) for infinite matrix widths and gamma distributions with different values of α . For each value of α , the behavior is shown for different values of A , $A=2$ (blue), 5 (magenta) and 10 (red). The dotted black line in each plot shows the advective travel time distributions $P(T_a^*)\overline{T}_a$ for the corresponding α .
Solid lines - Exact $h(t^*)\overline{T}_a$ from numerical integration of (S30),
Dashed lines - intermediate-time power-law approximation from (S35)
Dotted lines - very late time asymptote $h(t^*)\overline{T}_a \rightarrow A / (\sqrt{\pi} t^{*3/2})$ (S36)

S.5 Stream Concentration Power Spectra Obtained with Alternative Parameter Sets for Lower Hafren

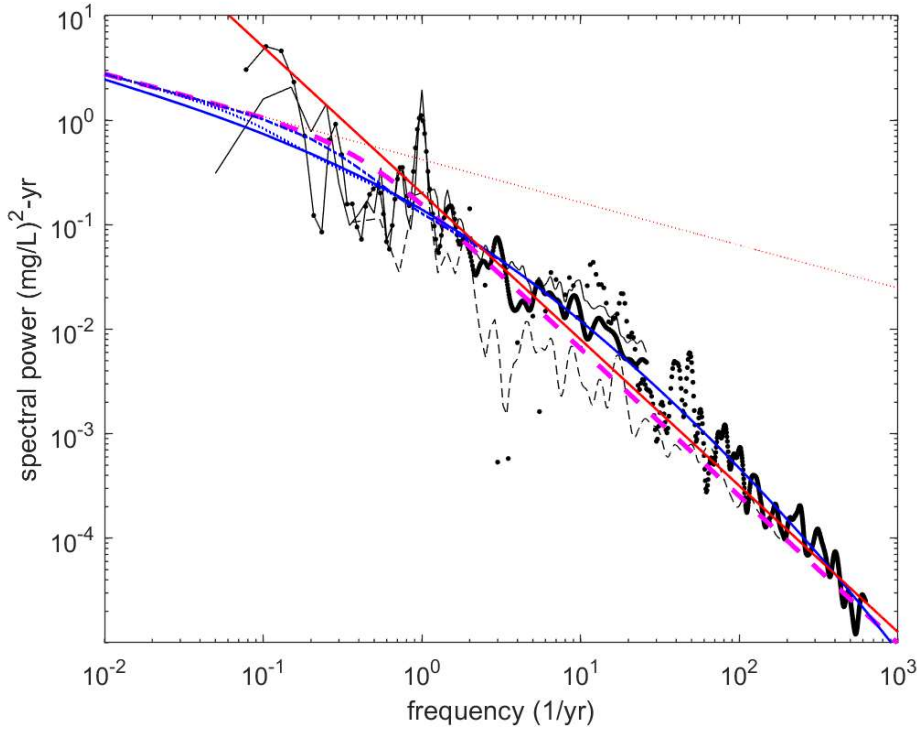
As noted in the main body of the paper, the power spectral ratio $S_{C_oC_o} / S_{C_iC_i}$ depends on two parameters, the mean advective travel time \bar{T}_a and the matrix diffusion parameter A . The dimensionless parameter A involves products and ratios of other physical parameters. I present calculations of $S_{C_oC_o} / S_{C_iC_i}$ for two additional sets of parameters below. The rationale for these additional sets was simply that I used values of $\bar{T}_a = 0.5$ and 2 times the value in the base case included in the main manuscript, and refitted other parameters to match the estimated stream concentration power spectrum in Figure (3a). The parameter values are shown in Table S.1.

	\bar{T}_a (years)	ϕ_m	D_e (m ² /s)	b (m)	A
Base Case	0.01	0.15	1.5e-10	5e-4	2.06
Half \bar{T}_a	0.005	0.1	1.5e-10	2e-4	2.43
Double \bar{T}_a	0.02	0.05	1.5e-10	5e-4	0.97

Table S1. Alternative Parameter Combinations

Figure S3 shows the power spectra obtained with parameters in the second and third rows of Table S1. The “Half \bar{T}_a ” parameter set produces an acceptable fit and improves the match to sample spectra at higher frequencies. The “Double \bar{T}_a ” parameter set produces an acceptable fit with a larger mismatch compared to the base case at frequencies $> 10^2 \text{ year}^{-1}$. The non-uniqueness involved in the estimating catchment-scale matrix diffusion parameters is acknowledged. However, the fitted parameter values are within acceptable ranges for these parameters. Figure S4 shows the power spectra obtained with the base case parameters and the alternative precipitation concentration power spectrum $0.38 / f^{0.34} \text{ (mg/L)}^2\text{-yr}$.

(a)



(b)

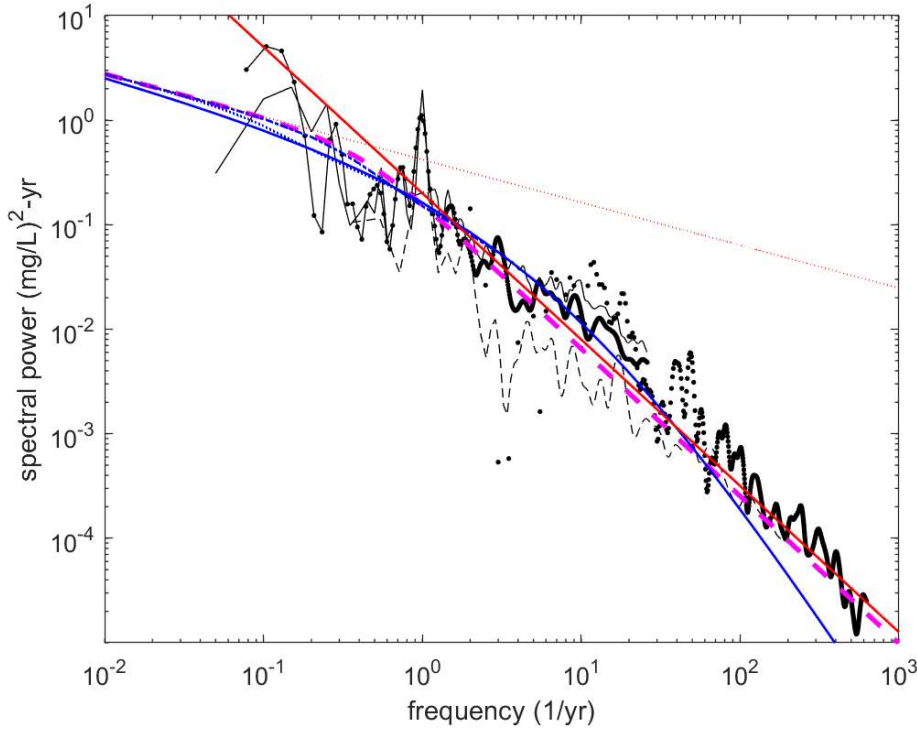


Figure S3. Stream (concentration power spectra calculated using alternative parameter sets shown in Table S1. (a) Half \bar{T}_a and (b) Double \bar{T}_a , compared to \bar{T}_a in the base case (Figure 3a in the main body of the paper). Color schemes are same as in Figure 3a. Black symbols and lines represent spectral estimates from Kirchner et al. (2013), magenta dashed line is the power spectrum corresponding to a gamma distribution ($\alpha = 0.5$, $\beta = 0.4 \text{ yr}$), blue lines are power spectra obtained from the matrix diffusion model (solid – infinite matrix, dashed – $B = 0.1 \text{ m}$,

dash-dotted – $B = 0.05\text{m}$), the red solid line indicates a spectral slope of -1.4, and the red dotted line shows the precipitation concentration spectrum.

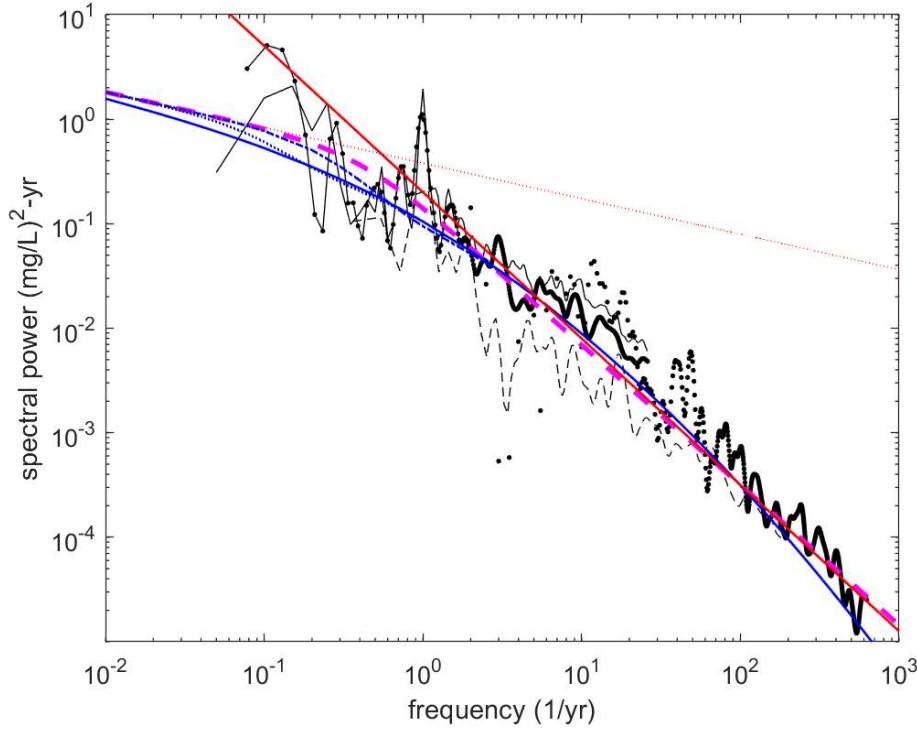


Figure S4. Stream concentration power spectra calculated using alternative precipitation chloride power spectrum $S_{C_i}(f) = 0.38 / f^{0.34}$. Compared to Figure 3a, the differences are minor. Color schemes are same as in Figure 3a. Black symbols and lines represent spectral estimates from Kirchner et al. (2013), magenta dashed line is the power spectrum corresponding to a gamma distribution ($\alpha = 0.5$, $\beta = 0.4\text{yr}$), blue lines are power spectra obtained from the matrix diffusion model (solid – infinite matrix, dashed – $B = 0.1\text{m}$, dash-dotted – $B = 0.05\text{m}$), the red solid line indicates a spectral slope of -1.4, and the red dotted line indicates the precipitation concentration spectrum.