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 Hafren 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 (~1/frequency, or generally, 1/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

60 distribution, $h(t) = \left(t^{\alpha-1}e^{-t/\beta}\right) / \left(\beta^{\alpha}\Gamma(\alpha)\right)$, with scale parameter $\alpha = 0.5$ (more generally $\alpha < 1$),
61 captures short-term responsiveness and long-tailed behavior and is hence a better model for
62 solute TTDs than the exponential distribution ($\alpha = 1$). Correspondingly, stream concentration
63 power spectra were observed to exhibit 1/frequency behavior (more generally 1/frequency to a
64 power < 2), which they referred to as "fractal stream chemistry". Similar behavior has been
65 documented at other catchments (Godsey et al. 2010), and for a variety of solutes (Kirchner et al.
66 2013), although some catchments do exhibit exponential baseflow TTDs (e.g. McGuire et al.
67 2005).

68 Various mechanisms have been proposed to explain fractal stream chemistry. Kirchner (2001)
69 showed that a model of advection-dispersion along a one-dimensional flowpath with distributed
70 solute inputs and a very large dispersivity (on the order of the hillslope length, equivalently
71 Peclet number (Pe) ~1), produces a solute TTD similar to a gamma distribution with $\alpha = 0.5$.
72 Lindgren et al. (2004) proposed that for moderate heterogeneity and dispersion, first-order
73 mobile-immobile exchange can explain fractal scaling. Both the above models assume uniform
74 mean flow and neglect nonuniform flow commonly associated with hillslope hydrologic systems.
75 Cardenas (2007) demonstrated that advection-dispersion in a nonuniform Tothian hillslope
76 groundwater flow (with significant variation in advective travel times across streamlines)
77 produces power-law solute TTDs. Kollett and Maxwell (2008) employed particle-tracking in
78 simulated flow fields for a real catchment to demonstrate that power-law stream concentration
79 spectra result even with very small dispersivities (Pe ~10^4), due to variations in advective travel
80 time across streamlines. They showed that transient vadose zone processes influence the stream
81 concentration spectra at higher frequencies. Fiori and Russo's (2008) simulations of transient
82 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

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

108 **2. Conceptual Model and Transport Equations**

109 The catchment-scale groundwater flow system is represented as a steady saturated flow in
110 fractured bedrock, receiving spatially uniform recharge. Figure 1 shows a schematic
111 representation (adapted from Haitjema, 1995). Fluid flow is assumed to occur only in fractures
112 with stagnant water in the rock matrix. Solutes undergo rapid advection along streamlines
113 through permeable fractures, while simultaneously diffusing in and out of the rock matrix. The
114 fracture density is assumed to be high so that an equivalent porous medium representation is
115 employed for flow (but not for transport). Thus, the water table and hydraulic head field are
116 assumed to be well defined and smooth. Isochrones I_{T_a} denote contours of equal advective
117 travel time T_a from the water table to the outflow at the stream, and Ω_{T_a} denotes the surface area
118 contained within I_{T_a}. Advective travel times T_a along streamlines (streamsurfaces) from the
119 water table to the stream are assumed to increase monotonically with Ω_{T_a}. The streamtube
120 originating from the surface element $d\Omega_{T_a}$ in Figure 1a is bounded by isochrones I_{T_a} and $I_{T_a+dT_a}$,
121 comprising streamlines along which advective travel times to the stream range from T_a to
122 $T_a + dT_a$. It is important to emphasize the distinction between advective and total solute travel
123 times: the total travel time along a streamline is also influenced by matrix diffusion and thus
124 much longer than the advective travel time. The catchment-scale solute TTD is derived by
125 considering the distribution of total travel times across all streamlines.

126 Previous studies suggest that when advective travel times across streamlines vary over a
127 large range, the influence of heterogeneity and dispersion is secondary (Gelhar, 1993; Duffy and
128 Gelhar, 1986; Haitjema, 1995; Fiori and Russo, 2008). I therefore neglect streamline tortuosity
129 and dispersion in the analysis presented below. Heterogeneity will lead to additional random
130 variations in advective travel times and may be incorporated using modified advective travel
131 time distributions as in the Lagrangian stochastic frameworks of Cvetkovic et al. (1999), Simic
132 and Destouni (1999) and Cvetkovic et al. (2012). I assume one-dimensional diffusion with an
133 effective matrix width *B* (Figure 1b), which may either be related to the block size or an
134 accessible weathered matrix thickness adjacent to fractures. Although matrix blocks in fractured
135 rock exhibit complex geometries, simplified solutions that assume one-dimensional matrix
136 diffusion (e.g. Tang et al. 1981; Maloszewski and Zuber, 1985) and various effective models
137 (Carrera et al. 1998; Cvetkovic et al. 1999; Haggerty et al. 2000; Berkowitz et al. 2006) are
138 widely used and have provided useful insights. Multi-dimensional diffusion in matrix blocks is
139 similar to one-dimensional diffusion with modified parameters, as discussed by Barker et al.
140 (1985).

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

147 $$\frac{\partial C_f}{\partial t} + u_s \frac{\partial C_f}{\partial s} = \frac{2\phi_m D_e}{b} \frac{\partial C_m}{\partial z}\bigg|_{s,z=0,t} \qquad (1)$$

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

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

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

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

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

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

Correspondingly, the fracture and matrix concentrations may be written as functions of τ_a, i.e. $C_f(\tau_a, t; I_{T_a})$ and $C_m(\tau_a, z, t; I_{T_a})$, and (1) can be rewritten as (Cvetkovic et al. 1999):

$$\frac{\partial C_f}{\partial t} + \frac{\partial C_f}{\partial \tau_a} = \frac{2\phi_m D_e}{b}\left.\frac{\partial C_m}{\partial z}\right|_{\tau_a, z=0, t} \qquad (5)$$

I use (5), together with (2) and (3) to relate the stream concentration to the input concentration. At the inflow end of a streamline (s = 0, τ_a = 0), concentration inputs $C_i(t)$ are assumed to be uniform across the catchment area (i.e. all streamlines), but vary with time:

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

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:

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

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):

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

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):

183 $$\Omega_{T_a} = \Omega_{total}\left(1-\exp\left(-T_a/\overline{T}_a\right)\right) \qquad (9)$$

184 **3. Frequency Domain Analysis: Stream Concentration Power Spectrum**

185 To relate the power spectra of stream and precipitation concentrations, the transport equations
186 are solved in the frequency domain (SI, Sections S.1-2). The Fourier transforms of
187 $C_i(t), C_o(t), C_f(\tau_a, t; I_{T_a})$ 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
188 $\tilde{C}_m(\tau_a, z, \omega; I_{T_a})$ respectively, where ω is the angular frequency. For random concentration
189 variations, the Fourier-Stieltjes spectral representation (Duffy and Gelhar, 1985, 1986; Gelhar,
190 1993), is more rigorous than the Fourier transform (Kirchner, 2000). However, both
191 interpretations involve the same mathematical manipulations and lead to identical concentration
192 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
193 $\tilde{C}_f(\tau_a, \omega; I_{T_a})$ (S7 in SI). Using this relationship in the Fourier transform of (5) produces a
194 differential equation (S8 in SI) for $\tilde{C}_f(\tau_a, \omega; I_{T_a})$:

195 $$\frac{d\tilde{C}_f}{d\tau_a} + k(\omega)\tilde{C}_f = 0 \qquad (10)$$

196 where (S10-11 in SI):

197 $$k(\omega) = i\omega + \frac{2\phi_m\sqrt{RD_e\omega}}{b}\sqrt{i} - \frac{\frac{4\phi_m\sqrt{RD_e\omega}}{b}\sqrt{i}}{\left(1+\exp\left(2\sqrt{\frac{R\omega}{D_e}}B\sqrt{i}\right)\right)} \qquad (11)$$

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

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

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

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

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

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

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

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

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

$$S_{C_o C_o}(\omega) = S_{C_i C_i}(\omega) \frac{1}{1 + 2\sqrt{2} AM \sqrt{\omega \overline{T_a}} + 2A^2 (M^2 + N^2) \omega \overline{T_a} + 2\sqrt{2} AN \left(\omega \overline{T_a}\right)^{3/2} + \omega^2 \overline{T_a}^2} \qquad (15)$$

where

$$A=\frac{\phi_m\sqrt{RD_e\overline{T_a}}}{b},\ m=1+\exp\left(\sqrt{2\omega\overline{T_a}}\,\frac{B\sqrt{R}}{\sqrt{D_e\overline{T_a}}}\right)\cos\left(\sqrt{2R\omega\overline{T_a}}\,\frac{B\sqrt{R}}{\sqrt{D_e\overline{T_a}}}\right)$$

$$n=\exp\left(\sqrt{2\omega\overline{T_a}}\,\frac{B\sqrt{R}}{\sqrt{D_e\overline{T_a}}}\right)\sin\left(\sqrt{2\omega\overline{T_a}}\,\frac{B\sqrt{R}}{\sqrt{D_e\overline{T_a}}}\right),\ M=1-\frac{2(m+n)}{m^2+n^2},\ N=1-\frac{2(m-n)}{m^2+n^2} \quad (16)$$

Equation (15) is written in terms of a dimensionless frequency ($\omega\overline{T_a}$) 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 $B/\sqrt{D_e\overline{T}_a/R}$ represents the influence of matrix thickness. If B >> the characteristic matrix diffusion length ($\sqrt{D_e\overline{T}_a/R}$), 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 $S_{C_oC_o}/S_{C_iC_i}$ 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 $S_{C_oC_o}(\omega)=S_{C_iC_i}(\omega)/(1+\omega^2\overline{T_a}^2)$, 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).

232 Figure 2a shows the behavior of the spectral ratio $S_{C_oC_o} / S_{C_iC_i}$ for different values of A (0,

233 2, 5 and 10) and $B/\sqrt{De\overline{T}_a}$ (5, 10 and ∞) for $A = 5$, assuming no sorption $(R = 1)$. For context,

234 $A = 5$ would be obtained with $\phi_m = 0.05, D_e = 10^{-10}$ m^2/s, $b = 10^{-4}$ m, $\overline{T}_a = 12$ days, which are

235 realistic values. The mean total travel time is $\overline{T}_a\left(1 + 2B\phi_m / b\right) \approx$ 612 and 1212 days for

236 $B/\sqrt{De\overline{T}_a} = 5$ and 10, respectively. For an infinite matrix, the mean total travel time is

237 theoretically unbounded. For $A = 5$ and 10, the slope of the spectral ratio is close to -1 over

238 several orders of magnitude in frequency. For $A = 2$, the spectral ratio exhibits an apparent slope

239 close to -1 at intermediate dimensionless frequencies, approaching -1.5 at higher dimensionless

240 frequencies. In general, the spectral ratio in Figure 2a exhibits curvature and deviates from true

241 linear behavior in a log-log plot. However, the curvature is relatively mild at dimensionless

242 frequencies > 0.1. The scatter inherent in spectral estimates from noisy real-world data may

243 obscure such curvature and accommodate acceptable straight-line fits. A finite matrix width

244 does not influence the spectral ratio at high frequencies corresponding to time scales smaller than

245 the diffusion time scale across the width. At lower frequencies, spectral ratios for a finite matrix

246 width deviate from that for an infinite matrix and become steeper. This steepening could in fact

247 produce a closer tendency to straight-line behavior when estimating spectra from noisy data (see

248 *1/f* line plotted in Figure 2a).

249 A generalization of (15) for a gamma advective travel time distribution (e.g. representing

250 non-Dupuit flow) is presented in SI (S25, Section S.2). With a scale parameter α, the $1/\omega^{2\alpha}$

251 scaling in the spectral ratio of the advective travel time distribution is modified to $1/\omega^{\alpha}$ by

252 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):

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

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:

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

At any time *t* after input, the solute TTD (18) only includes contributions from streamlines for which the advective travel time to the stream $T_a \le t$. 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 $h\left(t/\overline{T}_a\right)\overline{T}_a$ 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 $(t, T_a \to 0)$, $g\left(T_a; t-T_a\right) \to \delta\left(t-T_a\right)$ and $h(t) \to P(t)$, 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 $\overline{T}_a\left(1+2B\phi_m/b\right)$. 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

293 Neal et al. (1997) describe the hydrology and geology of the Hafren catchment. Storm
294 runoff is dominated by groundwater and interflow, and groundwater levels are highly responsive
295 to rainfall. The shallow groundwater system is hosted in highly fractured shale, mudstone, and
296 greywacke rocks, overlain by relatively thin soils (~0.7m). Typical water table depths are around
297 5m. Although groundwater is estimated to occur down to 30m below the stream, rapid
298 circulation and significant groundwater storage only occurs down to 9m depth, suggesting a
299 saturated thickness (H) of ~4m for the active portion of the groundwater system. The net
300 recharge rate (r) is about 2 m/year.

301 Kirchner (2000) and Kirchner et al. (2013) presented stream and precipitation power
302 spectra for chloride at Lower Hafren. The spectra presented by Kirchner et al. (2013) differ from
303 those of Kirchner (2000), due to refined spectral analysis methods and additional and longer
304 datasets. Both analyses suggest that the power spectral ratio $S_{C_oC_o}(\omega)/S_{C_iC_i}(\omega)$ exhibits close to
305 $1/\omega$ behavior. To represent this behavior, Kirchner et al. (2000) proposed a gamma distribution
306 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
307 frequency. Kirchner et al. (2000) fitted values of $\alpha = 0.48,\ \beta = 1.9\,\mathrm{yr}$ to the observed power
308 spectra; which corresponds to a mean total travel time of $\alpha\beta = 0.91\,\mathrm{yr}$. The power spectra of
309 Kirchner et al. (2013) are better fit with $\alpha = 0.5,\ \beta = 0.4\,\mathrm{yr}$ (Figure 3a), which corresponds to a
310 shorter mean travel time of 0.2 years. Kirchner et al. (2013) reported that the precipitation
311 chloride spectrum exhibits $1/f^{0.41}$ behavior. From a precipitation spectrum based on a subset of
312 the full dataset (Harman, 2015), I obtained a best fit of $0.38/f^{0.34}$ (mg/L)^2-yr, and with the
313 exponent fixed at 0.41, I obtained a best fit $0.42/f^{0.41}$ (mg/L)^2-yr, which I used in the
314 calculations below. These two alternative forms for the precipitation chloride spectra do not

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

317 The power spectral ratio (15, 16) depends on two key variables: the mean advective
318 travel time $\overline{T}_a$ and the matrix diffusion parameter A. Because A contains products and ratios of
319 other physical parameters, these parameters cannot be fit uniquely. My intention here is not to
320 produce a "best-fit" parameter set, but rather to present reasonable parameter values that are
321 consistent with the site description and match the spectral estimates of Kirchner et al. (2013). I
322 assume an exponential advective travel time distribution (8). Estimation of $\overline{T}_a$ requires an
323 estimate of the effective fracture porosity ϕ_a associated with the hydrologically responsive flow
324 system at the scale of the watershed, which is a highly uncertain parameter. Assuming a value of
325 $\phi_a = 0.005$, the mean advective travel time is estimated as $\overline{T}_a = \phi_a H / r = 0.01$ years (3.65 days).
326 To put this estimate in context, a regular arrangement of cubic matrix blocks with 0.3m sides,
327 interspersed with $b = 0.5mm$ wide connected fractures, would produce $\phi_a = 0.005$. The one-
328 dimensional accessible matrix width B in (15,16) could be smaller than the block size for two
329 reasons – first, Barker's (1985) analysis suggests an effective one-dimensional width equal to 1/6
330 of the block size for cubical blocks, and secondly, significant matrix diffusion is often restricted
331 to the weathered periphery of matrix blocks. Values for the matrix porosity ($\phi_m = 0.15$), and
332 effective diffusivity for chloride ($D_e = 1.5 \times 10^{-10}$ m^2/s), were assigned to fall within the ranges
333 reported for shale and mudstone (Manger, 1963; Barone et al. 1992). These parameter values
334 result in $A = 2.06$.

Figure 3a compares $S_{C_oC_o}(f)$ calculated using $S_{C_iC_i}(f) = 0.42 / f^{0.41}$ and the above parameter values in (15), the gamma model with $\alpha = 0.5$, $\beta = 0.4\,\mathrm{yr}$, 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 = 0.05m ($B / \sqrt{De\bar{T}_a} = 7.27$) 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 yr^{-1}. At the high frequency end (> 20 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 0.1m), 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=0.05m) and 0.61 years (B=0.1m). Greater differences between the matrix diffusion models and the fitted

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

358 **6. Discussion**

359 Although the role of matrix diffusion in influencing environmental solute ages has been
360 recognized previously, it is seldom explicitly considered in investigations and interpretations of
361 catchment solute TTDs. This paper quantitatively demonstrates that matrix diffusion in fractured
362 bedrock can generate fractal stream chemistry, and power-law behavior and long-term memory
363 in solute TTDs. The general relationships (14) and (18) provide a framework for quantifying
364 catchment-scale stream concentration power spectra and solute TTDs, by superposing the
365 influence of matrix diffusion on any general advective travel time distribution derived from
366 analytical or numerical subsurface flow models (e.g. Ameli et al. 2016; Kollett and Maxwell,
367 2008; Carroll et al. 2020). Availability of concentration data for multiple solutes will facilitate
368 inverse estimation of catchment-scale matrix diffusion parameters. The matrix diffusion
369 mechanism is physically consistent with the large residual or passive storage component inferred
370 while calibrating compartmental models of catchment hydrochemical response (e.g. Birkel et al.
371 2011, Benettin et al. 2014). The analysis presented here can be extended to incorporate
372 alternative representations of matrix diffusion and retention (e.g., multi-rate models or memory
373 functions) and heterogeneity within the fracture flow system (Cvetkovic and Haggerty, 2002;
374 Shapiro, 2001; Zhou et al. 2007), and layered hydrostratigraphy. One limitation of the analysis
375 is the neglect of transient flow effects and vadose zone processes, although some previous
376 studies (e.g. Fiori and Russo, 2008; Cvetkovic et al. 2012, Carroll et al. 2020) suggest that steady
377 state approximations are adequate for the dominant subsurface flow paths. Numerical models of
378 unsaturated-saturated flow and transport (e.g. Kollett and Maxwell, 2008; Carroll et al. 2020) can

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

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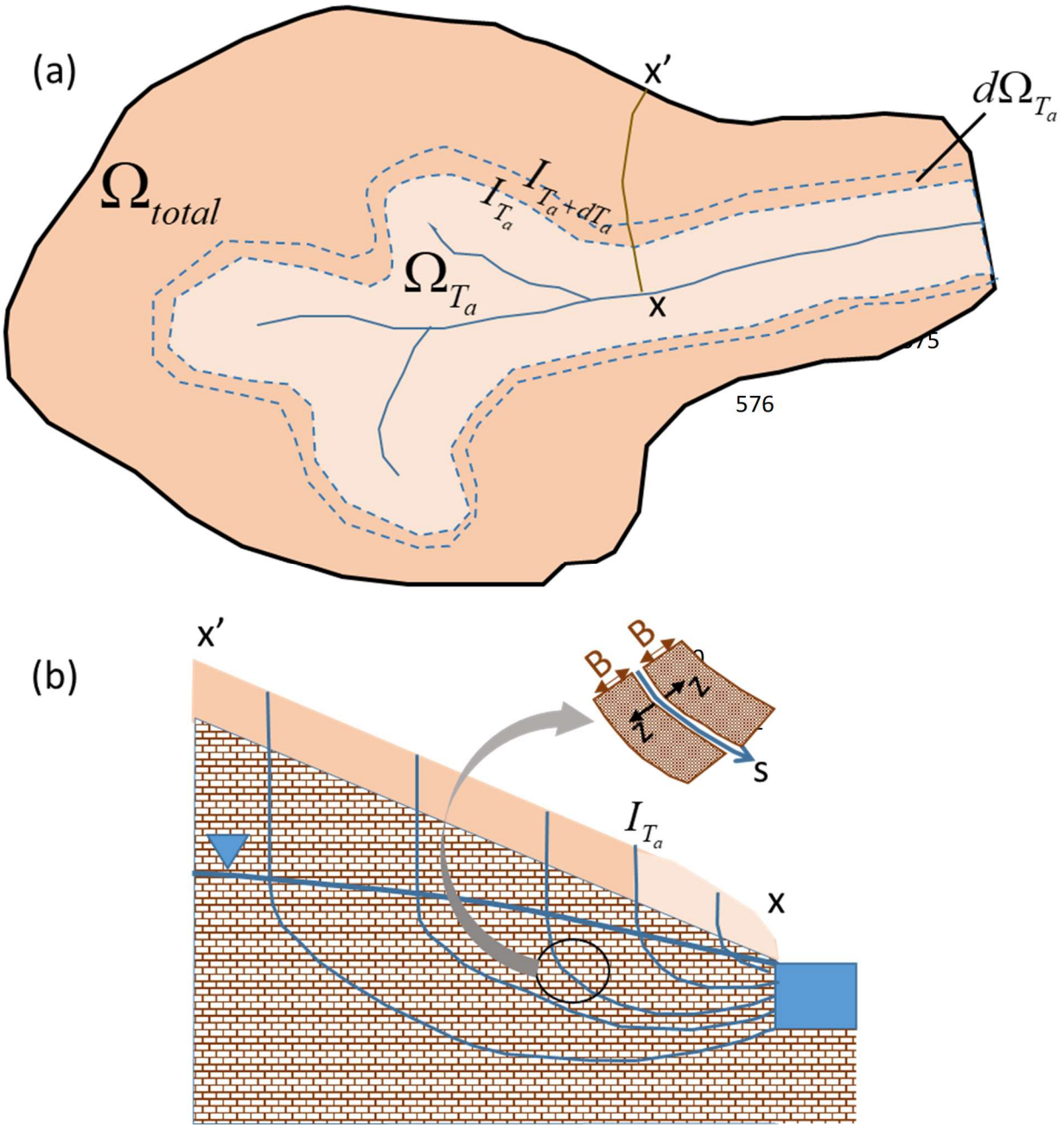
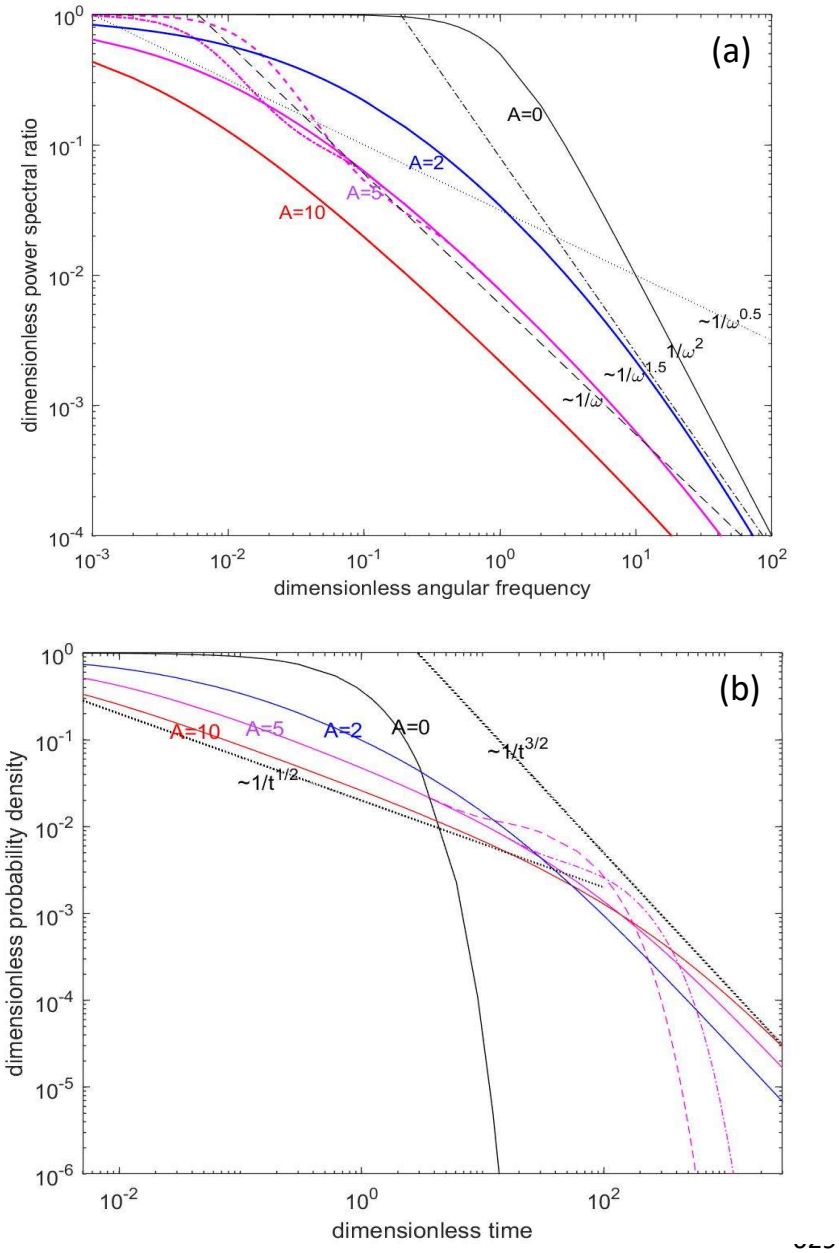
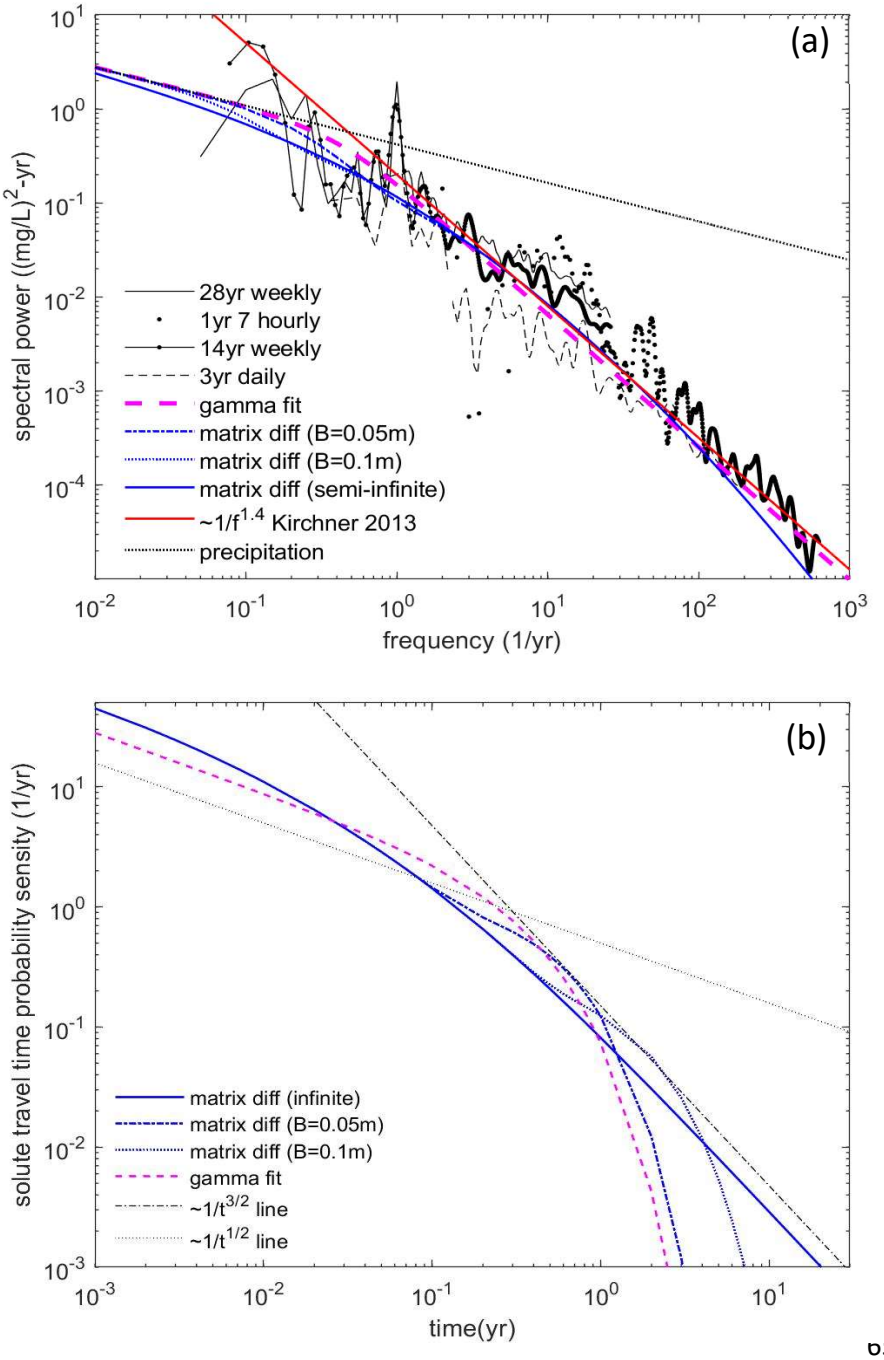


Figure 1. Schematic conceptual model of catchment-scale groundwater flow and transport. (a) Plan view showing total area Ω_{total} and area Ω_{T_a} bounded by isochrone I_{T_a} from which the advective travel time to the stream is T_a. (b) Vertical cross-section along x-x' in (a), showing streamlines 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*.



630

631 **Figure 2**. Influence of the matrix diffusion parameter A. (a) Dimensionless power spectral ratio
632 $\left(S_{C_oC_o} / S_{C_iC_i}\right)(15)$ plotted against dimensionless angular frequency ($\omega\overline{T_a}$). Black lines indicate
633 various power-law slopes. For $A=0$ (solid black), $S_{C_oC_o} / S_{C_iC_i}(\omega) = (1+\omega^2\overline{T_a}^2)$. (b)
634 Dimensionless solute TTD $h(t/\overline{T}_a)\overline{T}_a$ from (18) with an exponential $P(T_a)$, plotted against
635 dimensionless time ($t/\overline{T}_a$). Solid lines correspond to different values of A and an infinite matrix.
636 The dashed and dash-dotted magenta lines correspond to $B/\sqrt{D_e\overline{T}_a}$ = 5 and 10 respectively, for
637 A=5. Black dotted lines show intermediate ($\sim 1/t^{1/2}$) and late-time ($\sim 1/t^{3/2}$) power-law regimes.



657

658 **Figure 3**. (a) Chloride power spectrum and (b) solute travel time distribution (TTD) for Lower
659 Hafren, based on the matrix diffusion model ($\phi_m = 0.15, D_e = 1.5\times10^{-10}\,\mathrm{m}^2/\mathrm{s}$, $b = 5\times10^{-4}\,\mathrm{m}$,
660 $\overline{T}_a = 0.01\mathrm{yr}$) and matrix widths $B = 0.05m, 0.1m$ and ∞; and a gamma model ($\alpha = 0.5, \beta = 0.4\mathrm{yr}$)
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.