The dynamical foundation of fractal stream chemistry: The origin of extremely long retention times

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[1] We present a physical model to explain the behavior of long-term, time series measurements of chloride, a natural passive tracer, in rainfall and runoff in catchments [*Kirchner et al., Nature, 403*(524), 2000]. A spectral analysis of the data shows the chloride concentrations in rainfall to have a white noise spectrum, while in streamflow, the spectrum exhibits a fractal $1/f$ scaling. The empirically derived distribution of tracer travel times $h(t)$ follows a power-law, indicating low-level contaminant delivery to streams for a very long time. Our transport model is based on a continuous time random walk (CTRW) with an event time distribution governed by $\psi(t) \sim A_\beta t^{-1-\beta}$. The CTRW using this power-law $\psi(t)$ (with $0 < \beta < 1$) is interchangeable with the time-fractional advection-dispersion equation (FADE) and has accounted for the universal phenomenon of anomalous transport in a broad range of disordered and complex systems. In the current application, the events can be realized as transit times on portions of the catchment network. The travel time distribution is the first passage time distribution $F(t;l)$ at a distance l from a pulse input (at $t = 0$) at the origin. We show that the empirical $h(t)$ is the catchment areal composite of $F(t;l)$ and that the fractal $1/f$ spectral response found in many catchments is an example of the larger class of transport phenomena cited above. The physical basis of $\psi(t)$, which determines $F(t;l)$, is the origin of the extremely long chemical retention times in catchments. *INDEX TERMS:* 1860 Hydrology: Runoff and streamflow; 1869 Hydrology: Stochastic processes; 1871 Hydrology: Surface water quality; 3210 Mathematical Geophysics: Modeling

1. Introduction

[2] The distribution of travel times required for chemical substances to travel through a catchment is an important hydraulic quantity, determining the retention of pollutants until they are eventually released to a stream or lake. The same distribution controls the transport of chemicals in subsurface hydrological systems. The nature of this distribution determines the expected ecological impact of contaminants.

[3] In a long-term catchment study conducted at Plynlimon, Wales, *Kirchner et al.* [2000] (hereafter denoted KFN) compare the (input) time series of the concentration $c_R(t)$ of chloride tracer in the rainfall to the (output) time series of the concentration $c_s(t)$ into the Hafren stream. They relate the concentrations through the convolution integral

$$c_s(t) = \int_0^\infty h(t')c_R(t-t')dt' \tag{1}$$

where the effective travel time distribution $h(t)$ governs the lag time between injection of the tracer through rainfall and outflow to the stream.

[4] KFN observe that the streamflow (volume of water) responds rapidly to storm rainfall inputs while the $c_s(t)$ response is highly damped (i.e., low-level contaminant delivery to streams for a very long time). The timescales of catchment hydrologic and chemical response are resolved using spectral methods [*Duffy and Gelhar*, 1985] (in which the input/output response can be compared at each (time) wavelength). The spectral power of the water fluxes of rainfall and streamflow coincide while the spectra of $c_s(t)$ show strong attenuation on all wavelengths less than 5–10 years. Further, the $c_R(t)$ spectra scale as white noise in sharp contrast to the fractal $1/f$ scaling of the $c_s(t)$ spectra. Using these results in the Fourier transform of the convolution in (1), with f denoting frequency, and C_s, H and C_R representing the respective Fourier transforms,

$$C_s(f) = H(f)C_R(f) \tag{2}$$

and the relation of the power spectra is

$$|C_s(f)|^2 = |H(f)|^2|C_R(f)|^2 \tag{3}$$

Since $|C_R(f)|^2$ is nearly a white noise spectrum (a constant) one has $|H(f)|^2 \propto |C_s(f)|^2$. From the measured power-law scaling of $|C_s(f)|^2 \propto f^{-0.97}$, KFN conclude that

$$h(t) \sim t^{-m} \tag{4}$$

(from $H(f) \sim f^{-(1-m)}$), where $m \approx 0.5$.

[5] In order to ensure that $h(t)$ is integrable and possesses a finite average travel time, KFN arbitrarily chose the gamma distribution

$$h(t) = \frac{t^{\gamma-1}}{\varrho^\gamma \Gamma(\gamma)} e^{-t/\varrho} \tag{5}$$

with $\gamma = 0.48$ and $\varrho = 1.9$ years, with a characteristic travel time $T_h \equiv \int_0^\infty h(t)tdt = \gamma\varrho$. Due to the relatively large value of ϱ, essentially the entire data correspond to the power-law $h(t) \sim t^{\gamma-1}$ with the power spectrum $|C_s(f)|^2 \propto |H(f)|^2 \sim f^{-2\gamma}$. KFN refer to similar scaling between $f^{-0.7}$ and $f^{-1.2}$ found in Scandinavian and North American field sites, which indicates a certain ubiquity to fractal, scale-free forms (which is the issue we address in this letter).

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2. Transport Models

[6] The first step to understanding transport in the catchment is the clarification of the meaning of (1). The $h(t)$ is the *effective* response to a pulse of rain falling on the entire area of the catchment. Every point of this area is a source of chloride and the stream is a line sink for the chloride. We simplify the area to be a rectangle of width λ about this stream sink (with periodic boundary conditions on the sides perpendicular to the stream [*Scher and Montroll*, 1975]). The sink or absorbing boundary ensures the correct "counting rate" of chloride at the arriving point, i.e., the first passage time distribution $F(t;l)$ is the appropriate travel time distribution from a pulse source at point l. In terms of this *intrinsic* distribution,

$$c_s(t;l_s) = \int_0^\infty \sum_{l\in\Omega} F(t';l-l_s)c_R(t-t';l)dt' \tag{6}$$

where $c_s(t;l_s)$ is the chloride concentration at the stream position l_s at time t, Ω is the size of the catchment and $c_R(t;l)$ the rain-input at a position l in Ω. We can consider the sampling positions $\{l_s\}$ of c_s to be a small region compared to Ω and hence $c_s(t;l_s) \approx c_s(t)$. To do the l-sum we assume that the rainfall is distributed uniformly in Ω, $c_R(t;l) \approx c_R(t)$. Hence, we recover (1) now with

$$h(t) \equiv \sum_{l\in\Omega} F(t;l) \tag{7}$$

The distribution $F(t;l)$ must be integrable in time and thus so $h(t)$ for a finite Ω. The basis of comparison for various transport approaches is the computation in (7).

3. Advection-Dispersion Equation (ADE)

[7] The textbook approach to transport of passive tracers in both surface and subsurface systems usually focuses on the advection-dispersion equation (ADE)

$$\partial W/\partial t + v\partial W/\partial x = D\partial^2 W/\partial x^2 \tag{8}$$

e.g., for 1d with constant v the average fluid velocity and D the dispersion coefficient. This equation governs the temporal evolution of the probability density function (pdf) $W(x,t)$ of finding a tracer particle, which undergoes dispersive motion, at a certain position x at time t after release at $t = 0$. The pdf W is the normalized concentration profile.

[8] The travel time distribution belonging to (8) can be obtained by the Laplace Transform (LT) technique. This yields the $LT\,\tilde{\mathcal{F}}(u;x) \equiv \int_0^\infty \mathcal{F}(t;x)e^{-ut}dt$ of the first passage time from x to the absorbing boundary at $x = 0$, $\tilde{\mathcal{F}}(u;x) = \exp\left(x\left[v - \sqrt{4Du+v^2}\right]/(2D)\right)$. LT inversion delivers the travel time distribution

$$\mathcal{F}(t;x) = \frac{x}{\sqrt{4\pi D t^3}}\exp\left(\frac{-(vt-x)^2}{4Dt}\right) \tag{9}$$

which when inserted for $F(t;x)$ in (7) yields

$$h(t) \propto \int_0^\lambda \mathcal{F}(t;x)dx = \frac{v}{2}\left[\mathrm{erf}(z) + \mathrm{erf}\left(\frac{P_e}{4z} - z\right) + \frac{\exp(-z^2) - \exp\left(-\left(\frac{P_e}{4z} - z\right)^2\right)}{\sqrt{\pi}z}\right] \tag{10}$$

where the Peclet number $P_e \equiv \lambda v/D$, $z \equiv \frac{1}{2}\sqrt{v^2 t/D}$ and erf(z) is the error function (the same result (10) was also derived in *Kirchner et al.*, 2001). For $t < 0.1D/v^2$, $h(t) \sim t^{-1/2}$ which is similar to (4) for $m \approx 0.5$. [This upper limit on the time range holds for $P_e \geq 1$; for $P_e < 1$ the limit is smaller.] The range is estimated by assuming D to be the macrodispersion, $D = v\alpha$, where α is the dispersivity. Assuming $v \approx 10^2$ m/yr and on the km scale $\alpha \sim (1-10^2)$ m, $t < 0.1\alpha/v \sim (10^{-3}-10^{-1})$ yr. One needs $v \approx 10$ m/yr and $\alpha \sim 10^2$ m in (10), for $h(t) \sim t^{-1/2}$ to partially overlap the time range of observation of this dependence [*Kirchner et al.*, 2000]. Moreover, this behavior is only the same as (4) in the special case where m (or γ) = 1/2. The catchment data (spectral power $\sim f^{-2\gamma}$) quoted above cover a range of $0.7 \leq 2\gamma \leq 1.2$.

[9] For large t, $h(t)$ in (10) exhibits an exponential decrease $\sim t^{-3/2}\exp(-v^2(4D)^{-1}t)$ which is faster than (5). The decrease in $h(t)$ at large t ($t \gg \lambda/v$) is due to the finite size of the catchment and not an arbitrary limiting time. The relation between the operative time range of (4) and λ will be determined in the following.

4. Continuous-Time Random Walk and Time-Fractional-ADE

[10] As shown above the standard treatment of the transport using the ADE yields a marginal accounting of the data. A transport model must determine a $F(t;l)$ that when inserted in (7) gives rise to (4) for over three decades of time [*Kirchner et al.*, 2000]. As we will show this is best expedited with a non-Gaussian form of $F(t;l)$. A particularly dispersive form of $F(t;l)$ is associated with anomalous transport which has been observed in a wide range of disordered and complex systems: electron hopping/multiple-trapping in amorphous semiconductors [*Scher and Montroll*, 1975], particle migration in fracture networks [*Kosakowski et al.*, 2001], contaminant transport in heterogeneous porous media [*Berkowitz and Scher*, 1998], anomalous diffusion [*Metzler and Klafter*, 2000], and Hamiltonian chaos [*Klafter et al.*, 1996]. There are key common features in these anomalous transport phenomena, e.g., non-Gaussian propagation of an initial pulse of particles with a mean position $\ell(t)$ and standard deviation $\sigma(t)$ exhibiting the same sublinear dependence on t (in the presence of a bias or head). A continuous time random walk (CTRW) transport process has successfully accounted for these unusual basic features. The anomalous behavior is an outcome of a CTRW governed by a long-tail distribution of the individual transition times or event times (which have to be defined in each physical context, e.g., trap release),

$$\psi(t) \sim A_\beta t^{-1-\beta} \tag{11}$$

where A_β is a constant. Over the observation time range in which (11) obtains we have for the propagating plume $P(l,t)$

$$\ell(t) \sim t^\beta, \qquad \sigma(t) \sim t^\beta \qquad 0 < \beta < 1 \tag{12}$$

The highly dispersive nature of this $P(l,t)$ can be discerned by the ratio $\sigma(t)/\ell(t) \sim$ constant, instead of the familiar $1/\sqrt{t}$ for a Gaussian plume. The latter is produced for $\beta > 2$ (while for $1 < \beta < 2$ one has an intermediate t-dependence).

[11] The CTRW accounts naturally for the cumulative effects of a sequence of transitions which constitutes the particle transport. The formalism of the CTRW has been well documented in the literature [*Berkowitz and Scher*, 1998; *Metzler and Klafter*, 2000]. For brevity we show the key equation for our purpose here in Laplace space (for three dimensions)

$$\tilde{\mathcal{F}}(\mathbf{s},u) = \tilde{P}(\mathbf{s},u)/\tilde{P}(0,u) \qquad \mathbf{s} \neq 0 \tag{13}$$

where the particle starts at the origin at $t = 0^+$, $\tilde{\mathcal{P}}(\mathbf{s}, u)$ is the LT of $P(s, t)$, the probability density to find the particle on $\mathbf{s}$ at time t (plume), and $\tilde{\mathcal{F}}(\mathbf{s}, u)$ is the LT of $F(\mathbf{s}, t)$, the probability per time for the particle to first arrive at $\mathbf{s}$ at time t.

[12] Explicit evaluations for $\tilde{\mathcal{F}}(\mathbf{s}, u)$ have been determined for symmetric situations (e.g., plane (line) source to plane (line) sink) and with the use of (11) [*Scher and Montroll*, 1975]. The symmetric cases allow a reduction of the problem to a one-dimensional form of F which we write as $F(t; x)$ and

$$\tilde{\mathcal{F}}(u; x) = \exp\left(-xu^{\beta}/\bar{l}\right) \qquad (0 < \beta < 1) \tag{14}$$

(u dimensionless). The inverse LT of $\tilde{\mathcal{F}}(u; x)$ has been expressed in terms of a class of Fox H-functions [*Metzler and Klafter*, 2000], but it is more expedient to work directly with (14) in the evaluation of $h(t)$, which will be considered in the next section.

[13] Mathematically, the CTRW (in the special case using (11) and $0 < \beta < 1$) is interchangeable with the time-fractional advection-dispersion equation (FADE) [*Metzler and Klafter*, 2000]

$$\frac{\partial W}{\partial t} = {}_0D_t^{1-\beta}\left(-v_\beta \frac{\partial}{\partial x} + d_\beta \frac{\partial^2}{\partial x^2}\right) W(x, t) \tag{15}$$

where the Riemann-Liouville operator is defined in terms of the convolution [*Metzler and Klafter*, 2000],

$${}_0D_t^{1-\beta} W(x, t) = \frac{1}{\Gamma(\beta)} \frac{d}{dt} \int_0^t dt' \frac{W(x, t')}{(t - t')^{1-\beta}}, \qquad 0 < \beta < 1. \tag{16}$$

The form of FADE (15) is the natural generalization of the ADE (8) for power-law forms of ψ. The solutions of FADE reproduce those of the CTRW in this special case, and in the spatial continuum limit they form a natural bridge between the CTRW and the ADE [*Berkowitz and Scher*, 2001].

5. Long Retention Times

[14] We proceed to insert (14) into the LT of (7) to obtain

$$\tilde{h}(u) \propto \int_0^{\lambda} \exp\left(-lu^{\beta}/\bar{l}\right) dl = \bar{l}u^{-\beta}\left(1 - \exp\left(-\lambda u^{\beta}/\bar{l}\right)\right) \tag{17}$$

where $\bar{l}$ is the mean step distance. The expression for $\tilde{h}(u)$ in (17) has been thoroughly studied in another context [*Scher and Montroll*, 1975]; the main features are

$$h(\tau) \sim \begin{cases} \tau^{\beta-1}, & \tau < \tau^* \\ \tau^{-\beta-1}, & \tau > \tau^* \end{cases} \tag{18}$$

(τ dimensionless time). The exponent for $\tau > \tau^*$ ensures that $h(\tau)$ is integrable. On a log-log plot $h(\tau)$ is two constant slopes, $\beta - 1$, $-1 - \beta$, with a turnover range between them. The center time of this range, τ^*, can be estimated as the time for the argument of the exponent in (17) to be $\sim O(1)$ (using $u \sim 1/\tau$)

$$\tau^* \sim \left(\frac{1 - \beta}{\beta}\right)^{\frac{1-\beta}{\beta}} \left(\beta\lambda/\bar{l}\right)^{\frac{1}{\beta}} \tag{19}$$

(The β-factors derive from a more detailed analysis [*Scher and Montroll*, 1975, Appendix C].) For $\beta = 1/2$, in (17) one can do the inverse LT and obtain $h(\tau) \sim (\pi\tau)^{-1/2}(1 - \exp(-\lambda^2/4\bar{l}^2\tau))$, clearly showing (18)–(19).

[15] The change from τ to t is model dependent (to be discussed below). We use $\tau = v_o t/\bar{l}\varepsilon$, where v_o is a characteristic velocity (of the velocity distribution) and ε is a constant. For $\beta = 1/2$, $v_o \sim 100$ m/yr, $\lambda \sim 1/2$ km, $\bar{l} \sim 30$ m and $\varepsilon \sim 1/2$, one has (from (19) with $\tau^* = v_o t^*/\bar{l}\varepsilon$), $t^* \sim 10$ yr, which is a reasonable time scale for the change from $h(t) \sim t^{\beta-1}$. Hence, our scaling result (18) agrees with the KFN data (4) over the measurement time range (>3 decades for $t \leq 10$ yrs) with $\beta = \gamma$ ($\equiv 1 - m$). The t-"cutoff" for $h(t)$ in (18) is algebraic, $t^{-\beta-1}$, not exponential as in (5)! This behavior of $h(t)$ is indicative of extremely long chemical retention times in catchments. The turnover to the $t^{-\beta-1}$ dependence (in (18)) is a prediction of the CTRW theory and has not yet been observed. A finite value of T_h depends on a change in the behavior of (11). For $t \gg t^*$, the tail of $\psi(t)$ becomes steeper and for $\beta > 2$, the *intrinsic* arrival time distribution evolves to $\tilde{\mathcal{F}}(t; x)$.

[16] Independent tests of our transport model can be obtained with experiments using a different tracer (d) and boundary conditions. For injection of the tracer d at various catchment points $\{\mathbf{x}\}$, the concentration in the stream $c_d(t; \mathbf{l_s})$ is proportional to $F(\mathbf{x} - \mathbf{l_s}, t)$, determined for these boundary conditions. [This result answers the question raised by *Stark and Stieglitz* [2000] about a site-specific spill.] This is also a method for obtaining a value of β, which determines the shape of $F(\mathbf{x}, t)$.

[17] There are many different physical mechanisms (cf. Refs. above) that can give rise to the $\psi(t)$ in (11) that has generated our results for $h(t)$. The common features are the representation of the transport process as a series of transitions [*Berkowitz and Scher*, 1998, 2001] and the encounter within this series of a sufficient number of transition-times that are much larger than the median one. These relatively few long-time events, which can be due to release from traps/stagnant-regions and/or passage through low velocity segments, can have a dominant influence on the overall transport. The relative weighting of these events is expressed by the exponent of the power-law in (11).

[18] The hydrologic environments beneath the catchment subregions can contain a sufficient number of these low velocity sections and stagnant dead-ends. The local slope (and interconnection [*Rodriguez-Iturbe and Rinaldo*, 1997]) of the catchment side-channels also affects the velocity distribution. The subsurface of the catchment basin can be modeled as a heterogeneous porous medium and/or a random fracture network [*Berkowitz and Scher*, 1998]. In the latter the fragment-length distribution, $f(s)$, and the fragment-velocity histogram, $\Phi(\boldsymbol{\xi})$, are mapped onto the probability rate for a transit time t (through a fragment) with a displacement $\mathbf{s}$,

$$[\psi(\mathbf{s}, t) \propto \Phi(\boldsymbol{\xi}) f(s)] \tag{20}$$

where $\xi = 1/v$, $\hat{\boldsymbol{\xi}} = \hat{\mathbf{v}}$, $t = s\xi$ and $\psi(t) \equiv \sum_s \psi(\mathbf{s}, t)$. The anomalous transport observed in the fracture network particle tracking simulations is due to the power-law tail of $\Phi(\boldsymbol{\xi}) \rightarrow \xi^{-1-\beta}$ at large ξ. This is the expected behavior to be found in the catchment subsurface $\Phi_c(\boldsymbol{\xi})$ distribution because this hydrologic environment is the same as ones modeled successfully by the CTRW theory [*Berkowitz and Scher*, 1998, 2001]. The experiments outlined above can test these properties.

6. Conclusion

[19] In this letter we introduce the phenomenon of anomalous transport into an analysis of the comparison of the power spectra of the time series of chloride in rainfall and in (stream) runoff. An *effective* distribution of travel times $h(t)$ is derived (by KFN from the data) which we show is composed of the summation from all sites of the source distribution $F(\mathbf{s}, t)$ in the catchment. The latter, in turn, is composed of a sequence of transitions governed by a power-law (tail) distribution (11). The results agree naturally with the data reported from a number of catchment studies, in the sense of a power-law scaling of $h(t)$ over decades of t in the observational time range (using reasonable parameters). A consequence of our transport model is a power-law "cutoff" of $h(t)$ predicting

extremely long chemical retention times with subsequent impact on the long-term effects of contaminants on these ecosystems.

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