Scaling and predicting solute transport processes in streams

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[1] We investigated scaling of conservative solute transport using temporal moment analysis of 98 tracer experiments (384 breakthrough curves) conducted in 44 streams located on five continents. The experiments span 7 orders of magnitude in discharge ($10^{-3}$ to $10^3$ m$^3$/s), span 5 orders of magnitude in longitudinal scale ($10^1$ to $10^5$ m), and sample different lotic environments—forested headwater streams, hyporheic zones, desert streams, major rivers, and an urban manmade channel. Our meta-analysis of these data reveals that the coefficient of skewness is constant over time (CSK = 1.18±0.08, $R^2 > 0.98$). In contrast, the CSK of all commonly used solute transport models decreases over time. This shows that current theory is inconsistent with experimental data and suggests that a revised theory of solute transport is needed. Our meta-analysis also shows that the variance (second normalized central moment) is correlated with the mean travel time ($R^2 > 0.86$), and the third normalized central moment and the product of the first two are very strongly correlated ($R^2 > 0.96$). These correlations were applied in four different streams to predict transport based on the transient storage and the aggregated dead zone models, and two probability distributions (Gumbel and log normal).


1. Introduction

[2] Two of the most challenging problems in surface hydrology are scaling and predicting solute transport in streams [Young and Wallis, 1993; Jobson, 1997; Wörman, 2000; O’Connor et al., 2010]. We must resolve these challenges to wisely manage water resources because there is a need to understand controls on stream ecosystems at local, regional, and continental scales, and because we need to predict transport in environments and conditions that do not have supporting tracer test data.

[3] Quantitative representations of hydrobiogeochemical processes are based on mathematical and numerical simplifications. Each simplification, the need to parameterize and integrate spatial and temporal processes, and the limitation of available observations to constrain models introduce structural errors and uncertainty in the predictions derived from such models [Beven, 1993; Wagener et al., 2004]. On the other hand, the transferability of empirical relationships from intensely instrumented catchments (mainly located in developed countries) to ungauged catchments relies on the similarity of hydrobiogeochemical characteristics [Sivapalan, 2003], thus limiting their practical application in regions where they are more needed.

[4] Solute transport and nutrient processing have been analyzed from different modeling perspectives, i.e., physically based, stochastic [Botter et al., 2010; Cvetkovic et al., 2012] and data-based mechanistic approaches [Young and Wallis, 1993; Young 1998; Ratto et al., 2007]. Although these approaches have increased our awareness about key compartments and hydrologic conditions that exert important influence on biogeochemical processes, i.e., identification of hot spots and hot moments [McClain et al., 2003], there is not yet a unified approach that has proven successful to scale and predict solute transport and nutrient processing.

[5] In the last three decades, research on solute transport and nutrient processing has revealed complex interactions between landscape and stream ecosystems, and attempts to scale and predict these processes have been limited by the difficulty of measuring and extrapolating hydrodynamic and geomorphic characteristics [Scordo and Moore, 2009; O’Connor and Harvey, 2008; O’Connor et al., 2010], and by the qualitatively confusing analyses derived from poorly constrained parametric interpretations of model-based approaches. A literature review presented hereafter (chronologically organized) shows contradictory evidence about the relationship between transient storage (TS) [Bencala and Walters, 1983; Beer and Young, 1983], the theory most frequently used to explain solute transport and in-stream processing. Valett et al. [1996] found a strong correlation ($R^2 = 0.77$) between TS and NO$_3$ retention in three first-order streams in New Mexico. Mulholland et al. [1997] found larger PO$_4$ uptake rates in a stream with higher TS, when they compared two forested streams. Martí et al. [1997] found no correlation between NH$_3$
uptake length and \( A_x / A \) (TS to main channel sizing ratio) in a desert stream. Hall et al. [2002] found a very weak correlation \( (R^2 = 0.14 – 0.35) \) between TS parameters and NH\(_4\) demand in Hubbard Brook streams. In the 11 stream LINX-I data set, Webster et al. [2003] found no statistically significant relationship between NH\(_4\) uptake and TS. Thomas et al. [2003] showed that TS accounted for 44%–49% of NO\(_3\) retention measured by \(^{15}\)N in a small headwater stream in North Carolina. Niyogi et al. [2004] did not find significant correlations among soluble reactive phosphorous (P-SRP) and NO\(_3\) uptake velocities, and TS parameters. Ensign and Doyle [2005] found an increase of \( A_x / A \) and uptake velocities for NH\(_4\) and PO\(_4\), after the addition of flow baffles to the streams studied. Ryan et al. [2007] found strong relationships in two urban streams between P-SRP retention and TS when the variables were measured at different regimes in the same stream. Lautz and Siegel [2007] found a modest correlation \( (R^2 = 0.44) \) between NO\(_3\) retention efficiency and TS in the Red Canyon Creek watershed (WY). Bukaveckas [2007] reported an indefinite relationship between TS and NO\(_3\) and P-SRP retention efficiencies. Lastly, the LINX-II data set from \(^{15}\)N-NO\(_3\) injections in 72 streams showed no relationship between NO\(_3\) uptake and TS [Hall et al., 2009].

One factor that might contribute to the absence of strong relationships between TS and nutrient processing is the use of metrics that obscure the importance of TS across study sites (see discussions by Runkel [2002, 2007]). Also, it has become apparent that there are important limitations to identifying TS parameters with current techniques [Wagener et al., 2002; Schmid, 2003; Camacho and González-Pinzón, 2008], i.e., multiple sets of parameters might represent field observations “equally well” [Beven and Binley, 1992], and choosing a unique set of parameters to describe the behavior of a system might lead to misinterpretations of their physical meaning (if any), especially when those parameter sets are used to compare streams from different ecosystems and/or hydrologic conditions.

In spite of the observed complexity of solute transport processes in streams, it is surprising that systems governed by physical processes that are considered “well understood” and by reasonably predictable biochemical interactions behave so unpredictably when combined. More robust methods are required to deconvolve signal imprints of solute transport and nutrient processing, thus allowing the development and implementation of improved decision-making approaches for stream management.

In this paper, we investigated the existence of temporal patterns that can be used to scale and predict solute transport processes using an extensive database of tracer experiments that span 7 orders of magnitude in discharge, 5 orders of magnitude in longitudinal scale, and sample different lotic environments on five continents—forested headwater streams, hyporheic zones, desert streams, major rivers, and an urban manmade channel. From this meta-analysis, which is only implicitly dependent on hydrogeomorphic characteristics, we have proposed an approach to perform uncertainty analysis on solute transport processes and discussed some inconsistencies of the classic solute transport theory.

2. Methodology

2.1. Temporal Moments From Time Series

We investigated conservative solute transport using temporal moments of the histories of multiple conservative tracer tests. Our analysis is based on an Eulerian approach, where the time series have been collected at different fixed spatial locations in each stream. Temporal moments have been widely used in the study of solute transport and biochemical transformations. Das et al. [2002] and Govindaraju and Das [2007] presented an extensive review of the theory and applications of temporal moment analysis to study the fate of conservative and reactive solutes. Recently, Leube et al. [2012] discussed the efficiency and accuracy of using temporal moments for the physically based model reduction of hydrogeological problems.

Moments of distributions are commonly expressed as measures of central tendency. The \( n \)th absolute moment (also referred to as the \( n \)th raw moment or \( n \)th normalized moment about 0), \( \mu_n \), of a concentration time series, \( C(t) \), is defined as

\[
\mu_n = \int_0^\infty t^n C(t) dt
\]

The \( n \)th normalized absolute moment (also referred to as the \( n \)th raw moment or \( n \)th normalized moment about 0), \( \mu_n' \), is defined as

\[
\mu_n' = \frac{\mu_n}{\mu_0}
\]

and the \( n \)th normalized central moment (also referred to as the \( n \)th normalized moment about the mean), \( m_n \), is defined as

\[
m_n = \frac{1}{\mu_0} \int_0^\infty (t - \mu_1')^n C(t) dt
\]

where \( i \) is an index. Note that (4) is an inverse binomial transform that can be easily used to calculate the normalized central moments of order 1 (mean travel time), 2 (variance), and 3 (skewness):

\[
\begin{align*}
m_1 & = \mu_1' \\
m_2 & = \mu_2' - \mu_1'^2 \\
m_3 & = \mu_3' - 3\mu_1'\mu_2' + 2\mu_1'^3
\end{align*}
\]

Temporal moments are also related to residence time distributions and transfer functions of linear dynamic systems [Jury and Roth, 1990; Sardin et al., 1991]. Aris [1958] developed a method to compute the theoretical temporal moments of linear functions, thus allowing the use of experimental temporal moments (i.e., those estimated from observed time series) to estimate the parameters of linear dynamic models, i.e.,

\[
\mu_n = (-1)^n \lim_{s \to 0} \left[ \frac{d^n}{dt^n} \mathcal{C}(x, s) \right]
\]

where \( \mathcal{C}(x, s) \) is the Laplace transform of \( C(x, t) \) and \( x \) is the longitudinal distance in one-dimensional approximations.

Theoretical temporal moments for most solute transport models have been estimated for different types of boundary conditions. A few examples of the progress on
this topic are the development of temporal moment-generating equations to model transport and mass transfer [Harvey and Gorelick, 1995; Luo et al., 2008], and the calculation of temporal moments for the TS model [Czernuszenko and Rowinski, 1997; Schmid, 2002], equilibrium and nonequilibrium sorption models [Goltz and Roberts, 1987; Cunningham and Roberts, 1998], the aggregated dead zone model [Lees et al., 2000], and the metabolically active TS model [Argerich et al., 2011].

[14] Matching (or equating) experimental and theoretical temporal moments is a useful technique to parameterize linear models [Nash, 1959]. The advantages of using experimental moments to match theoretical moments come with the challenge to completely recover the tracer experiment signals, as it has been shown that truncation errors affect the estimation of higher-order temporal moments. Using experimental data, Das et al. [2002] and Govindaraju and Das [2007] showed that when the error in mass recovery is 16%, the errors in absolute nth moments can be as high as approximately \((n + 1) \cdot 16\%\) for \(n = 0\) through \(n = 4\). This problem is related to the early cutoff of data measurement or the lack of instrumental resolution to detect low concentrations of tracers, and is not related to the apparent incomplete mass recovery due to dilution effects (e.g., groundwater contributions). Note that correcting the observed breakthrough curves (BTCs) uniformly (with a steady-state gain factor) for dilution only affects the magnitude of the absolute moments but does not modify the magnitude of the normalized absolute moments or that of the normalized central moments.

2.2. Experimental Database

[15] We created a database that includes 384 concentration time series, or BTCs, from 98 conservative tracer experiments conducted in 44 streams under different quasi-steady hydrologic conditions (10^{-3} to 10^3 m^3/s), different experimental conditions (BTCs observed from 10^1 to 10^5 m downstream the injection point), and different types of lotic environments (Table 1). We grouped the database by the orders of magnitude of discharge (Table 2) to facilitate the analysis and presentation of the statistical regressions in Figures 1 and 2. All BTCs were zeroed to background concentrations and corrected by discharge changes during the experiments as specified in the references or recorded in experimental notes.

3. Results and Discussion

3.1. Statistical Relationships Derived From Temporal Moment Analysis

[16] Information regarding longitudinal mixing and exchange processes can be found in the normalized central moments (moments about the mean). Figure 1a shows that the variance scales in a nonlinear (non-Fickian) form with the mean travel time. If dispersion processes in streams were Fickian, the regression presented in Figure 1a would have a slope of \(-1.0\), still preserving a scatter pattern that would be associated with the magnitudes of the dispersion coefficient for each experiment (i.e., different intercepts). Non-Fickian dispersion processes have been widely observed in stream ecosystems [e.g., Fischer, 1967; Nordin and Sabol, 1974; Nordin and Troutman, 1980; Bencala and Walters, 1983, and references therein], and in heterogeneous porous media [e.g., Rao et al., 1980; Haggerty and Gorelick, 1995; Dent and Tartakovsky, 2006]. A non-Fickian behavior is, broadly defined, the result of the presence of multiscale heterogeneities that cannot be integrated into a singular dispersion coefficient [Neuman and Tartakovsky, 2009]. To date, several approaches have been proposed to better represent non-Fickian transport, which are largely based on the conceptualization of TS processes and/or the definition of smaller representative elementary volumes, where local homogeneities can be integrated in space and time.

[17] We also correlated \(m_1\) versus \(m_2\) and \(m_3\) versus \(f(m_1, m_2)\). Figure 2a suggests that solute transport data have a small range in their coefficient of skewness (CSK, equation (7)). The coefficient of skewness is a measure of asymmetry, i.e., when CSK = 0 the data is perfectly symmetrical (no tailing), but it is known that solute transport experiences tailing effects due to surface and hyporheic TS, regardless of the type of stream ecosystem. For the 98 tracer tests (384 BTCs), CSK = 1.18±0.08 (95% confidence bounds). In Figure 2b, we show that the product \(m_1 \cdot m_2\) is a quasi-linear estimator of \(m_3\) (\(R^2 = 0.96\)). This result, although not representing a predefined statistical descriptor on its own, will be later used to define objective functions for predictive solute transport models (see section 3.3.). Not unexpectedly, based on the results from Figure 1, \(m_1\) is a much weaker predictor of the ratio \(m_3/m_2\) (\(R^2 = 0.66\), results not shown), suggesting that a satisfactory bottom-up estimation of normalized central moments is restricted to one level at most.

\[
\text{CSK} = \frac{m_3}{(m_2)^{3/2}} \quad \ln(m_3) = \frac{3}{2} \ln(m_2) + \ln(\text{CSK}) \quad (7)
\]

3.2. Observed Scale Invariance in Streams and Solute Transport Models

[18] Nordin and Sabol [1974] first reported observations revealing persistent skewness (longitudinally) from Eulerian observations of solute transport time distributions. Nordin and Troutman [1980] investigated the performance of the Fickian-type diffusion equation (advection dispersion equation (ADE)), and the inclusion of dead zone processes (i.e., TS model (TSM)) to account for the persistence of skewness, concluding that \(\ldots\) the observed data deviate consistently from the theory in that the skewness of the observed concentration distributions decreases much more slowly than the Fickian theory predicts, and that although the inclusion of dead zones \(\ldots\) yields a theoretical skewness coefficient [CSK] considerably larger than that given by the ordinary Fickian diffusion equation, \(\ldots\) the skewness of the observed concentrations does not appear to be decreasing as rapidly as the theory predicts.\] The skewness of BTCs also do not begin with values as high as those predicted by the TSM (cf. Nordin and Troutman, 1980, Figure 3).

[19] The work by van Mazijk [2002] reported that tracer experiments conducted to develop the River Rhine alarm model also showed time distributions with persistent CSK along the extensive reach studied (100 km < L < 1000 km; \(Q = 1170\text{m}^3/\text{s}\); cf. van Mazijk, 2002, Figure 6), i.e., \(0.93 \leq \text{CSK} \leq 1.24\). These observations justified the use of the Chatwin-approximation (Edgeworth series) [Chatwin, 1980] to predict solute concentrations in space and time, by fixing CSK = 1 for the whole river. Further tracer experiments in the River Rhine (\(Q = 663\text{m}^3/\text{s}, Q = 1820\text{m}^3/\text{s}\)) supported the existence of a persistent CSK [van Mazijk and Veling, 2005].
Schmid [2002] investigated the conditions under which the TSM could represent the persistence of skewness in solute transport processes. Schmid [2002] examined the case of a slug injection into a uniform channel and concluded that a small parametric region (a loop right bounded by $A_s/A < 0.008$; cf. Schmid [2002, Figure 1]) could generate a nondecreasing CSK. However, this condition was hypothetical and does not play a major role in practice. Such conditions, if they exist, would be logically inconsistent because tailing effects would be inversely proportional to TS. Schmid [2002] also examined a more general scenario with a time-varying concentration distribution as an upstream boundary condition, the division of long reaches into hydraulically uniform subreaches and a routing procedure to link temporal moments at both ends of the subreaches. This analysis suggested that “...the TS model has the potential to explain persistent or growing temporal skewness coefficients, if applied to a sequence of subreaches with respective parameter sets different from each other.” However, predicting solute transport meeting these conditions is rather impractical.

Table 1. Conservative Solute Transport Database

<table>
<thead>
<tr>
<th>Stream</th>
<th>Reach Length (km)</th>
<th>Discharge (m$^3$/s)</th>
<th>State, Country, (Continent$^b$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canal Molinos</td>
<td>0.2</td>
<td>0.2–0.4</td>
<td>Colombia (SA)</td>
<td>As referenced by González-Pinzón [2008]</td>
</tr>
<tr>
<td>Quebrada Lejía</td>
<td>0.3</td>
<td>0.1–0.5</td>
<td>Colombia (SA)</td>
<td></td>
</tr>
<tr>
<td>Subachaco 1</td>
<td>0.3–0.4</td>
<td>0.2–1.3</td>
<td>Colombia (SA)</td>
<td>González-Pinzón [2008] and Camacho and González-Pinzón [2008]</td>
</tr>
<tr>
<td>Subachaco 2</td>
<td>0.1–0.2</td>
<td>0.3–1.9</td>
<td>Colombia (SA)</td>
<td></td>
</tr>
<tr>
<td>Teusacá 1</td>
<td>0.1–0.2</td>
<td>0.3–0.4</td>
<td>Colombia (SA)</td>
<td></td>
</tr>
<tr>
<td>Teusacá 2</td>
<td>0.3–0.4</td>
<td>0.2–1.4</td>
<td>Colombia (SA)</td>
<td></td>
</tr>
<tr>
<td>Rio Magdalena</td>
<td>36–207</td>
<td>1200–1390</td>
<td>Colombia (SA)</td>
<td>Torres-Quintiero et al. [2006]</td>
</tr>
<tr>
<td>Shaver’s Cr.</td>
<td>0.1–0.4</td>
<td>0.2</td>
<td>PA, USA (NA)</td>
<td>Unpublished data</td>
</tr>
<tr>
<td>Cherry Cr.</td>
<td>0.7–1.3</td>
<td>0.2</td>
<td>WY, USA (NA)</td>
<td>Briggs et al. [2013]</td>
</tr>
<tr>
<td>Oak Cr.</td>
<td>0.04–0.3</td>
<td>0.02</td>
<td>OR, USA (NA)</td>
<td></td>
</tr>
<tr>
<td>Fuirosos 1</td>
<td>0.2–0.3</td>
<td>0.01</td>
<td>Spain (EU)</td>
<td></td>
</tr>
<tr>
<td>Fuirosos 2</td>
<td>0.2–0.3</td>
<td>0.01</td>
<td>Spain (EU)</td>
<td></td>
</tr>
<tr>
<td>Antietam Cr.</td>
<td>2.6–67</td>
<td>1.2–12.7</td>
<td>MD, USA (NA)</td>
<td></td>
</tr>
<tr>
<td>Monocacy River</td>
<td>7.5–34</td>
<td>12.7–22.1</td>
<td>MD, USA (NA)</td>
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<tr>
<td>Conocochaque Cr.</td>
<td>4.4–34</td>
<td>2.6–30.6</td>
<td>MD, USA (NA)</td>
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</tr>
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<td>Chattahoochee River</td>
<td>10.5–104</td>
<td>108–180</td>
<td>GA, USA (NA)</td>
<td></td>
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<tr>
<td>Salt Cr.</td>
<td>9.5–52</td>
<td>2.5–4.1</td>
<td>NE, USA (NA)</td>
<td></td>
</tr>
<tr>
<td>Difficult Run</td>
<td>0.6–2</td>
<td>0.9–1.1</td>
<td>VA, USA (NA)</td>
<td></td>
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<tr>
<td>Bear Cr.</td>
<td>1.1–10.9</td>
<td>10.2–10.5</td>
<td>CO, USA (NA)</td>
<td></td>
</tr>
<tr>
<td>Little Piny Cr.</td>
<td>0.6–7.3</td>
<td>1.4–1.6</td>
<td>MO, USA (NA)</td>
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<td>Bayou Anacoco</td>
<td>11–38</td>
<td>2.0–2.7</td>
<td>LA, USA (NA)</td>
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<tr>
<td>Comite River</td>
<td>6.8–79</td>
<td>0.8–1.0</td>
<td>LA, USA (NA)</td>
<td></td>
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<tr>
<td>Bayou Bartholomew</td>
<td>3.2–117</td>
<td>4.1–8.1</td>
<td>LA, USA (NA)</td>
<td></td>
</tr>
<tr>
<td>Amite River</td>
<td>10–148</td>
<td>5.7–8.9</td>
<td>LA, USA (NA)</td>
<td></td>
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<tr>
<td>Tieckau River</td>
<td>6.4–50</td>
<td>2.0–2.9</td>
<td>LA, USA (NA)</td>
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<td>Tangipahoa River</td>
<td>8.2–94</td>
<td>3.5–18.7</td>
<td>LA, USA (NA)</td>
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<td>Red River</td>
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<td>108–249</td>
<td>LA, USA (NA)</td>
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<tr>
<td>Sabine River</td>
<td>7.9–209</td>
<td>127–433</td>
<td>LA, USA (NA)</td>
<td></td>
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<tr>
<td>Sabine River</td>
<td>17–121</td>
<td>0.7–9.5</td>
<td>TX, USA (NA)</td>
<td></td>
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<td>Mississippi River</td>
<td>35–294</td>
<td>1495–6824</td>
<td>LA, USA (NA)</td>
<td></td>
</tr>
<tr>
<td>Wind/Bighorn River</td>
<td>9.1–181</td>
<td>55–255</td>
<td>WY, USA (NA)</td>
<td></td>
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<td>Copper Cr.</td>
<td>0.2–8.4</td>
<td>1.0–8.7</td>
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<td></td>
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<td>Clinch River</td>
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<td>5.7–110</td>
<td>VA, USA (NA)</td>
<td></td>
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<tr>
<td>Powell River</td>
<td>1.0–7.1</td>
<td>3.9–4.1</td>
<td>TN, USA (NA)</td>
<td></td>
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<td>Coachella Canal</td>
<td>0.3–5.5</td>
<td>25.4–26.9</td>
<td>CA, USA (NA)</td>
<td></td>
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<td>Missouri River</td>
<td>66–227</td>
<td>883–977</td>
<td>LA, USA (NA)</td>
<td></td>
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<tr>
<td>WSI</td>
<td>0.02–0.3</td>
<td>1.5–0.06</td>
<td>OR, USA (NA)</td>
<td>Gooseff et al. [2003, 2005]; Haggerty et al. [2002], unpublished</td>
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<td>WS3</td>
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<td>1.5–0.03</td>
<td>OR, USA (NA)</td>
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<td>Lookout Cr.</td>
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<td>OR, USA (NA)</td>
<td>Gooseff et al. [2003]</td>
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<td>Huey Cr.</td>
<td>0.5–1.0</td>
<td>0.1</td>
<td>AN</td>
<td>Runkel et al. [1998]</td>
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<td>AUS</td>
<td>Lamontagne and Cook [2007]</td>
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<td>Clackamas River</td>
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<td>36.8</td>
<td>OR, USA (NA)</td>
<td>Lee [1995]</td>
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<tr>
<td>Uvas Cr.</td>
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<td>CA, USA (NA)</td>
<td>Bencala and Walters [1983]</td>
</tr>
<tr>
<td>River Mimram</td>
<td>0.1–0.2</td>
<td>0.3</td>
<td>UK (EU)</td>
<td>Lees et al. [2000]</td>
</tr>
</tbody>
</table>

$^a$A total of 98 tracer experiments with 384 BTCs were used in this meta-analysis.
$^b$SA: South America; NA: North America; EU: Europe; AUS: Australia; AN: Antarctica.

[20] Schmid [2002] investigated the conditions under which the TSM could represent the persistence of skewness in solute transport processes. Schmid [2002] examined the case of a slug injection into a uniform channel and concluded that a small parametric region (a loop right bounded by $A_s/A < 0.008$; cf. Schmid [2002, Figure 1]) could generate a nondecreasing CSK. However, this condition was hypothetical and does not play a major role in practice. Such conditions, if they exist, would be logically inconsistent because tailing effects would be inversely proportional to TS. Schmid [2002] also examined a more general scenario with a time-varying concentration distribution as an upstream boundary condition, the division of long reaches into hydraulically uniform subreaches and a routing procedure to link temporal moments at both ends of the subreaches. This analysis suggested that “...the TS model has the potential to explain persistent or growing temporal skewness coefficients, if applied to a sequence of subreaches with respective parameter sets different from each other.” However, predicting solute transport meeting these conditions is rather impractical.

[21] If a transport theory is to be capable of scaling and predicting solute transport processes, it will have a
persistent and statistically constant CSK. Our observations of CSK being statistically constant for widely different hydrodynamic conditions suggest that CSK is not only persistent for a given stream (with distance traveled downstream), but can also be used to scale and predict solute transport processes across ecosystems. At a minimum, a persistent value of CSK is a test that a theory of solute transport must pass.

We used the theoretical temporal moments of three models commonly used for the analysis of in-stream solute transport (ADE, TSM, and the aggregated dead zone model (ADZM)) to calculate their theoretical CSK. If these models were systematically capable of representing the

[22] We used the theoretical temporal moments of three models commonly used for the analysis of in-stream solute transport (ADE, TSM, and the aggregated dead zone model (ADZM)) to calculate their theoretical CSK. If these models were systematically capable of representing the

Table 2. Conservative Solute Transport Database Grouped by the Orders of Magnitude of Discharge

<table>
<thead>
<tr>
<th>Discharge Group Q Gr.</th>
<th>Discharge Order of Magnitude (m³/s)</th>
<th>Number of Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10⁻³</td>
<td>19</td>
</tr>
<tr>
<td>2</td>
<td>10⁻²</td>
<td>37</td>
</tr>
<tr>
<td>3</td>
<td>10⁻¹</td>
<td>68</td>
</tr>
<tr>
<td>4</td>
<td>10⁰</td>
<td>131</td>
</tr>
<tr>
<td>5</td>
<td>10¹</td>
<td>59</td>
</tr>
<tr>
<td>6</td>
<td>10²</td>
<td>53</td>
</tr>
<tr>
<td>7</td>
<td>10³</td>
<td>17</td>
</tr>
</tbody>
</table>

*The regressions presented in Figures 1 and 2 were labeled as described hereafter.

Figure 1. Meta-analysis (n = 384 BTCs) of conservative solute transport experiments in streams demonstrates the general occurrence of non-Fickian dispersion processes. (a) The growth rate of the variance is nonlinear (therefore non-Fickian) with respect to the mean travel time; the thick dashed line represents the slope pattern of Fickian dispersion. (b) Skewness as a function of the mean travel time. Coefficients were fitted with 95% confidence bounds. Thin dashed lines represent 95% prediction bounds.
scale-invariant patterns observed in our meta-analysis, the
parameters would be self-consistent when describing CSK.
The model equations and the theoretical temporal moments
and CSKs (calculated for an impulse-type boundary condi-
tion, e.g., Cunningham and Roberts [1998]) are shown
below, along with the consequences of the invariance of
CSK on the model parameters. We also included in our
analysis (see section 3.2.4) three additional transport mod-
els less commonly used to describe solute transport in
streams, but that have been used in groundwater systems.

3.2.1. Advection Dispersion Equation

\[
\frac{dC}{dt} = -\frac{Q}{A} \frac{dC}{dx} + D \frac{d^2C}{dx^2}
\]

\[m_1 = \tau\]

\[m_2 = 2\tau^2 / Pe\]

\[m_3 = 12\tau^3 / Pe^2\]

\[CSK_{ADE} = 3\sqrt{2}/\sqrt{Pe}\]

Figure 2. (a) Meta-analysis (n = 384 BTCs) of conservative solute transport experiments from con-
trasting stream ecosystems suggests that the coefficient of skewness holds statistically constant. Fitted
coefficients defined CSK = 1.18 ± 0.08. (b) The factor \([m_1/m_2]\) is a quasi-linear estimator of \(m_3\). How-
ever, using \(m_1\) to define the ratio \([m_3/m_2]\) yields an \(R^2 = 0.66\), showing that a satisfactory bottom-up
estimation of normalized central moments is restricted to one level, at most. Coefficients were fitted with
95% confidence bounds. Thin dashed lines represent 95% prediction bounds.
where \( C \) \([ML^{-1}]\) is the concentration of the solute in the main channel; \( Q \) \([L^3T^{-1}]\) the discharge; \( A \) \([L^2]\) the cross-sectional area of the main channel; \( D \) \([LT^{-2}]\) the dispersion coefficient; \( x \) \([L]\) the reach length; \( t \) \([T]\) time; \( \tau = x/u \) \([T]\) is the conservative mean travel time; \( Pe = Xu/D \) the Peclet number; and \( u = Q/A \) the mean velocity in the main channel \([LT^{-1}]\).

**Figure 3.** Predicted results using empirical relationships derived from normalized central moment meta-analysis \((n = 384 \text{ BTCs})\) and the moment-matching technique for the TSM. The known variables were \( L, Q \) and \( m_{\text{est}} \), and all others were predicted from 1000 Monte Carlo simulations. The effects of uncertainty in estimating \( m_1 \) \((i.e., m_{\text{est}} = \varphi m_{\text{obs}}, \text{with } \varphi = [0.8 - 1.2])\), the parameters of the TSM and the fitting coefficients from our meta-analysis are shown as uncertainty bounds. (a) River Brock, (b) River Conder, (c) River Dunsop, and (d) River Ou Beck. Experimental observations from Young and Wallis [1993]. The best parameter sets from the simulations are presented in Table 3. Goodness of fit was estimated with the Nash–Sutcliffe model efficiency coefficient \((E)\).

**Table 3.** Best Parameter Sets From 1000 Monte Carlo Simulations Using Empirical Relationships Derived From Normalized Central Moment Meta-Analysis \((n = 384 \text{ BTCs})\) and the Moment-Matching Technique\(^a\)

<table>
<thead>
<tr>
<th>River</th>
<th>( Q ) (m(^3)/s)</th>
<th>( L ) (m)</th>
<th>( D ) (m(^2)/s)</th>
<th>( \beta )</th>
<th>( \alpha \times 10^5 ) (s(^{-1}))</th>
<th>( E )</th>
<th>( \tau_{\text{ADZ}} ) (s)</th>
<th>( E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brock</td>
<td>( 4.5 \times 10^{-4} )</td>
<td>128</td>
<td>2.33</td>
<td>1.31 \times 10^{-2}</td>
<td>9.77</td>
<td>0.96</td>
<td>218.01</td>
<td>0.98</td>
</tr>
<tr>
<td>Conder</td>
<td>( 1.0 )</td>
<td>116</td>
<td>2.20</td>
<td>8.12 \times 10^{-3}</td>
<td>8.08</td>
<td>0.99</td>
<td>151.95</td>
<td>0.97</td>
</tr>
<tr>
<td>Dunsop</td>
<td>( 5.4 \times 10^{-3} )</td>
<td>130</td>
<td>1.33</td>
<td>1.45 \times 10^{-2}</td>
<td>7.89</td>
<td>0.98</td>
<td>332.55</td>
<td>1.00</td>
</tr>
<tr>
<td>Ou Beck</td>
<td>( 3.5 \times 10^{-2} )</td>
<td>127</td>
<td>0.67</td>
<td>4.40 \times 10^{-3}</td>
<td>8.92</td>
<td>1.00</td>
<td>135.95</td>
<td>0.76</td>
</tr>
</tbody>
</table>

\( ^a \text{Study case of four rivers located in the United Kingdom [Young and Wallis, 1993; pp. 160–165]. Goodness of fit was estimated with the Nash–Sutcliffe model efficiency coefficient (E).} \)
[24] Equation (9) suggests that if CSK$_{ADE}$ is constant, the Pecllet number should also be constant. This implies that, under steady-state flow conditions, the dispersion coefficient must scale linearly with the distance traveled. This violates the assumption of spatially uniform coefficients. Therefore, the ADE with spatially uniform coefficients is incapable of representing the experimental observations. Dispersion coefficients scaling with distance have been widely observed in porous media [e.g., Pickens and Grisak, 1981; Silliman and Simpson, 1987, Pachepsky et al., 2000, and references therein]. Note that the ADE with constant coefficients predicts BTCs with longitudinally decreasing skewness (CSK$_{ADE} \sim x^{-1/2}$), becoming asymptotically Gaussian (i.e., CSK$_{ADE}(x \rightarrow \infty) = 0$).

3.2.2. Transient Storage Model

\[ \frac{\partial C}{\partial t} = -\frac{Q}{A} \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} - A_4 \frac{\partial C}{\partial A} (C - C_t) \]  

(10a)

\[ \frac{\partial C_t}{\partial t} = \alpha_2 (C - C_t) \]  

(10b)

\[ m_1 = \frac{\tau (1 + \beta)}{\beta} \]  

\[ m_2 = \frac{2(1 + \beta)^2 r^2 + 2 \beta r}{Pe} \]  

\[ m_3 = \frac{12(1 + \beta)^3 r^3}{Pe^2} + \frac{12 \beta (1 + \beta)}{\alpha_2^2} + \frac{6 \beta r}{\alpha_2^2} \]  

CSK$_{TSM}$ = \[ \sqrt{2 \alpha_2^2 Pe^2 \left( \frac{\beta r}{\alpha_2} + \frac{(1 + \beta)^2 r^2}{Pe} \right)^{3/2}} \]  

(11)

where $C_t [ML^{-3}]$ is the concentration of the solute in the storage zone; $A_4 [L^2]$ is the cross-sectional area of the storage zone; $\alpha_2 [T^{-1}]$ is the mass-exchange rate coefficient between the main channel and the storage zone; and $\beta = A_4 / A$. Other variables as are defined for the ADE. The TSM in equation (10a) is the same presented by Bencala and Walters [1983] and Rukeyl [1998] for a reach without lateral inputs, with a slightly different definition of $\alpha_2 = \alpha / \beta$. Note that CSK$_{TSM} = CSK_{ADE}$ when $\beta = 0$.

[26] If dispersion effects were assumed negligible [e.g., Wörman, 2000; Schmid, 2002], CSK$_{TSM}$ in equation (11) would simplify to

\[ CSK_{TSM}(D=0) = \frac{3}{\sqrt{2 \alpha_2^2 r^2}} = \frac{3}{\sqrt{2 \alpha_2^2 \tau}} \]  

(12)

[27] Using the CSK value found in our meta-analysis, the mean residence time in the storage zones ($t_0 = 1 / \alpha_2$) normalized by $\beta$ scale linearly with travel time ($\tau$), i.e.,

\[ \frac{t_0}{\beta} = \frac{2}{9} (CSK)^2 \Rightarrow \frac{t_0}{\beta} \approx \frac{\tau}{(3.23 \pm 0.4)} \]  

(13)

[28] Equations (11) and (12) suggest that the standard TSM generates BTCs with longitudinally decreasing skewness (CSK$_{TSM} \sim x^{-1/2}$), becoming asymptotically Gaussian (i.e., CSK$_{TSM}(x \rightarrow \infty) = 0$). The physical meaning of the parameters describing CSK$_{TSM}$ is constant is unclear unless dispersion is assumed negligible ($D = 0$). In this case, equation (13) suggests that the TSM model parameters are not independent and that their ratio grows with distance traveled. This analysis supports the results of other studies showing problems of equifinality for the TSM [e.g., Wagener and Harvey, 1997; Wagener et al., 2002; Camacho and González-Pinzón, 2008; C. Kelleher et al., 2012]. Equations (11) and (13) suggest that the physical meaning of the TSM parameters is limited, and that relationships between TSM parameters and biogeochemical processing may be site dependent (as was discussed in section 1) or even experiment dependent.

3.2.3. Aggregated Dead Zone Model

\[ \frac{dC}{dt} = \frac{1}{T_r} [C_s (t - \tau_{ADZ}) - C(t)] \]  

(14)

\[ m_1 = \frac{n (\tau_{ADZ} + T_r)}{m_2} \]  

\[ T_{r,e} = 2nT_r^2 \]  

(15)

where $T_r [T]$ is the lumped ADZ residence time parameter representing the component of the overall travel time associated with dispersion; $C_s [ML^{-3}]$ is the known concentration at the input or upstream location; and $\tau_{ADZ} [T]$ is the time delay describing solute advection due to bulk flow movement.

[29] Equation (14) describes the mass balance of an imperfectly mixed system (ADZ representative volume), where a solute undergoes pure advection, followed by dispersion in a lumped active mixing volume [Lees et al., 2000]. In the ADZM, the distance $x$ implicitly appears in the model description through the time parameters. Note that when $n = 1$, the mean travel time ($m_1$) could be written as $m_1 = x / u$. In equation (15), the parameter $n$ represents the number of identical ADZ elements serially connected ($n = 1$ for a single ADZ representative volume) to route the upstream boundary condition. The serial ADZM, although capable of representing a persistent CSK, would require the specification of the nonphysical parameter $n$. More complex ADZM structures can be defined under the database mechanistic approach [e.g., Young, 1998], but we restricted our discussion in those that have been more commonly used in stream solute transport modeling [Young and Wallis, 1993; Lees et al., 2000; Camacho and González-Pinzón, 2008; Romanowicz et al., 2013].

3.2.4. Alternative Solute Transport Models

[31] Similar sets of calculations also show that the multi-rate mass transfer (MRMT) model [Haggerty and Gorelick, 1995; Haggerty et al., 2002] (Appendix A) and a decoupled continuous time random walk (dCTRWF) model [e.g., Dentz and Berkowitz, 2003; Dentz et al., 2004; Boano et al., 2007] (Appendix B) are equally incompatible with observations of persistent skewness. The CSK in both of these models also scales as CSK$_{TSM} \sim x^{-1/2}$.

[32] We also explored a Lévy-flight dynamics model (LFDM) (Appendix C) [e.g., Slésinèr et al., 1982; Pachepsky et al., 1997, 2000; Sokolov, 2000], which describes the motion of particles behaving similarly to Brownian motion, but allowing occasional clusters of large jumps (significant deviations from the mean). Lévy-flight
models have constant transition times, combined with transition length distributions that are characterized by power-law behaviors for large distances. Therefore, such models represent processes characterized by large velocities for long transitions and low velocities for short transitions, and would account for transport in the continuum of river and storage, with the high velocities present in the stream. We were able to generate an LDFM with persistent CSK for a storage, with the high velocities present in the stream. We would account for transport in the continuum of river and represent processes characterized by large velocities for large at large velocities, which does not appear realistic.

3.2.5. Remarks on Existent Solute Transport Models

[33] To preserve CSK, the parameters in the solute transport models, including common versions of the CTRW and MRMT model, must change with travel distance. Solute transport parameters therefore have some degree of scale dependence (and arbitrariness) imposed by the constant CSK. Furthermore, these parameters have scaling patterns that are unrelated to anything that can currently be measured in the field. These inconsistencies might be because (1) the common solute transport models and assumptions are partly incorrect or (2) we (the stream research community) have collected erroneous observations for decades. The latter condition is possible, but is not likely the explanation for a problem that has been observed across so many data sets. The worst-case scenario in our meta-analysis is that all BTCs were truncated prematurely, due to lack of instrument sensitivity or other reasons. However, this would generate BTCs with larger CSK and would contradict the asymptotic behavior shown for CSK in the transport models discussed above. Consequently, we suspect that our models do not correctly represent one or more aspects of solute transport processes from the field.

3.3. Use of Moments Scaling Properties to Predict Solute Transport

[34] While the models contain an error that needs correction, it may be possible (in the meantime) to adjust the parameters in a way that is predictive of field behavior. In this section, we use the regressions from the temporal moment analysis (section 3.1) to predict solute transport. We provide the parameterization of the TSM, ADZM, and two probability distributions. We then provide an example using data from tracer experiments that were conducted in the River Brock, River Conder, River Dunsop, and River Ou Beck in the United Kingdom [Young and Wallis, 1993; Wallis et al., 1989; Pilgrim, 1977; Calkins and Dunne, 1970]. The first three rivers are natural, and River Ou Beck is a concrete urban channel.

[35] The methodology requires an independent estimation of the mean travel time ($m_1$). One way to do this is to regress $m_1$ against discharge ($Q$) using a power law or an inverse relationship in $Q$ [Young and Wallis, 1993; Wallis et al., 1989; Pilgrim, 1977; Calkins and Dunne, 1970]. Once $m_1$ is estimated, the results from our temporal moment analysis can be used to constrain predictive (forward) simulations of solute transport models. We exemplify this methodology using the experiments by Young and Wallis [1993], which were not used in the previous moment analysis, because they show the technique to estimate mean travel times from discharge.

3.3.1. Predicted Solute Transport With Classic Solute Transport Models

[36] The parameters of solute transport models can be determined by matching theoretical and experimental moments. Here, we show how the empirical scaling relationships described in section 3.1 can be used to direct the search of the parameters of the TSM and the ADZM in predictive simulations.

3.3.1.1. Predicted Solute Transport With TSM

[37] We used the empirical relationships derived for $m_1$ versus $m_2$ and $m_1$ versus $f(m_1, m_2)$ (Figure 2) to match the theoretical moment equations presented by Czernuszenko and Rowinski [1997]. These theoretical equations have been developed for a general upstream boundary condition with tracer distribution $C(t)$. The parameters for the TSM are those defined by Bencala and Walters [1983] and Runkel [1998].

$$m_1 = 2D \frac{u}{u^2} + L (1 + \beta)$$

$$m_2 = 8D^2 \frac{u}{u^2} + \frac{2L}{u} (1 + \beta) + \frac{2L \beta^2}{u^2}$$

$$m_3 = \frac{2L^2 D}{u^2} (1 + \beta)^2 \beta + 64D^3 \left[ \frac{12D^2}{u^2} (1 + \beta)^2 + \frac{4D \beta^2}{u^2} (\beta + 2) + \frac{6\beta^3}{\alpha^2} \right]$$

[38] We have eight variables, i.e., the dispersion coefficient $D$, $\beta$ ($\beta = A_1/A_2$), the mass-transfer rate $\alpha$, the length of the reach $L$, the discharge $Q$ ($u = Q/A$), and the normalized central moments $m_1$, $m_2$, $m_3$. We have five equations: three for the theoretical moments (equations (16)–(18)) and two empirical relationships (derived from Figure 2). To balance the degrees of freedom ($n = 8$), we therefore need to specify three ($3 = 8 - 5$) variables, namely $L$, $Q$, and $m_1$. We used a Newton-Raphson algorithm to solve for the five unknowns by minimizing the objective function (OF) shown in equation (19). We estimated the mean travel time as: $m_{1est} = \varphi m_{1obs}$, with $\varphi = [0.8 - 1.2]$, and randomly varied the regression coefficients of our meta-analysis within the 95% confidence bounds.

$$OF_1 = \left| \frac{1 - \text{CSK}_{\text{theor}}}{\text{CSK}_{\text{empirical}}} \right| = \left| \frac{1 - \text{CSK}_{\text{theor}}}{1.18(\pm 0.08)} \right|$$

$$OF_2 = \left| \frac{1 - \text{ln}[m_{1\text{theor}}]}{\text{ln}[m_{1\text{empirical}}]} \right| = \left| \frac{1 - \text{ln}[m_{1\text{theor}}]}{0.932(\pm 0.04)\text{ln}[m_{1\text{est}} / m_{2\text{est}}]} \right|$$

$$OF_3 = \left| \frac{1 - \text{m}_{1\text{theor}}}{\text{m}_{1\text{est}}} \right|$$

$$OF = OF_1 + OF_2 + OF_3$$

(19)

[39] In the optimization routine, we allowed the TSM parameters to vary within ranges typically found in similar streams, i.e., $D = [10^{-3}, 10^{-1}]$ (m$^2$/s), $A_1 = [10^{-2}, 10^1]$ (m$^2$), $A = [10^{-3}, 10^3]$ (m$^2$), $\alpha = [10^{-7}, 10^{-4}]$ (s$^{-1}$). Once the system of equations was optimized for each random set
of estimated mean travel time and fitting coefficients 
\( n = 1000 \), we ran a forward simulation using the optimum parameters. Results from the Monte Carlo simulations are presented in Figure 3 and Tables 3 and 4. We used the Nash–Sutcliffe model efficiency coefficient \((E) \) \cite{Nash1969} to estimate the goodness of fit of the predictions, i.e., how well the plot of observed versus simulated data fits a 1:1 line.

3.3.1.2. Predicted Solute Transport With ADZM

\cite{Gonzalez2021} The two parameters of this model are the advection time delay, \( \tau_{ADZ} \), and the residence time, \( \tau_{R} = \tau_{ADZ} \), where \( \tau_{ADZ} \) is the mean travel time \( \tau_{m} \). The theoretical moments of the ADZM for one first-order ADZ element \( n = 1 \) were presented in equation (15). Since the mean travel time is a measured or estimated quantity, we only need to solve for the advection time delay, \( \tau_{ADZ} \). We applied the same optimization routine described for the TSM, and the results obtained are presented in Figure 4 and Tables 3 and 4.

3.3.2. Predicted Solute Transport With Probability Distributions

\cite{Gonzalez2021} Time series described by probability distributions can be used to predict solute transport processes. Here, we show how the empirical scaling relationships described in section 3.1 can be used to estimate the temporal moments of two probability distributions and then to perform predictive simulations.

3.3.2.1. Predicted Solute Transport With Gumbel Distribution

\cite{Gonzalez2021} We chose the Gumbel (Extreme Value I) probability distribution because of its constant CSK Gumbel = 1.1395, which closely agrees with the empirical relationships derived from our meta-analysis \( \text{CSK} = 1.18 \pm 0.08 \). This distribution is typically used to describe hydrologic events pertaining to extremes \cite{Brutsaert2005}. The concentration distribution of a solute BTC using this distribution takes the form:

\[
C(t) = m_0 \exp \left(-\beta \cdot \exp\left(-\frac{t-\mu}{\beta}\right)\right)
\]

\[
z(t) = \frac{t-\mu}{\beta}
\]

\[
\mu = m_1 - \beta \cdot 0.5772
\]

\[
\beta = \sqrt{\frac{6m_2}{\pi^2}}
\]

where \( \mu \) and \( \beta \) are the location (mode) and scale parameters, respectively. Note that these parameters, and those of any other probability distribution, have no direct physical interpretation.

\cite{Gonzalez2021} The use of probability distributions requires the explicit definition of moments beyond the mean travel time, i.e., variance and in some cases the skewness. Therefore, we would need to use empirical relationships such as those derived in Figure 1, even though \( R^2 < 0.9 \). In our predictive analysis, we used \( m_{\text{test}} = \varphi m_{\text{obs}} \), with \( \varphi = [0.8 - 1.2] \) to estimate the uncertainty of \( m_{\text{test}} \), and \( m_{\text{test}} = (m_{\text{test}})^\theta \), with \( \theta = [1.601 - 1.629] \), as it was suggested by our meta-analysis \( \text{(i.e.,} \ln m_2 = 1.615(1.601, 1.629) \cdot \ln m_1, \ R^2 = 0.86, \text{regression not shown in Figure 1)} \). The results obtained are presented in Figure 5 and Table 4.

3.3.2.2. Predicted Solute Transport With Lognormal Distribution

\cite{Gonzalez2021} A random variable described by a lognormal distribution comes from the product of \( n \) variables, each with its own arbitrary density function with finite mean and variance. This distribution has been widely used in hydrologic modeling of flood volumes and peak discharges, duration curves for daily streamflow, and rainfall intensity-duration data \cite{Chow1954, Stendininger1980}. Applications in solute transport suggested that the solute velocity, saturated hydraulic conductivity, and dispersion coefficient are logarithmically distributed \cite{Rogowski1972, VanDePol1977, Russo1981}. The concentration distribution of a solute BTC with this distribution takes the form:

\[
C(t) = m_0 \exp \left(-\frac{1}{2\sigma_n^2} \ln^2 \left(\frac{t-\mu_n}{\sigma_n}\right)\right)
\]

\[
m_1 = \mu_n + \frac{\sigma_n^2}{2}
\]

\[
m_2 = m_1^2 \exp \left(\frac{\sigma_n^4}{2}\right)
\]

where \( \mu_n \) and \( \sigma_n \) are the mean and the standard deviation of \( \ln(t) \). In our predictive analysis, we followed the same procedure described for the Gumbel distribution. The results obtained are presented in Figure 6 and Table 4.

3.3.3. Analysis of Predictive Solute Transport Modeling

\cite{Gonzalez2021} In our predictive analyses, we used two classic models (TSM and ADZM) and hypothesized that these models could adequately predict solute transport if the results of our meta-analysis were defined as objective functions to minimize the differences between the theoretical and empirical temporal moments. Our main goal therefore was...
to fix a constant CSK regardless of the longitudinal positioning. The predictive results presented in Figures 3 and 4 and Tables 3 and 4 show that this approach required only basic information (i.e., \( Q \), \( L \), and an estimation of the mean travel time) to adequately predict the behavior of the solute plumes traveling downstream. For the TSM (four parameters), the best predictions in the uncertainty analysis had \( E > 0.96 \) for the four rivers. For the ADZM (two parameters), the best predictions had \( E > 0.97 \) for all natural rivers, and \( E = 0.76 \) for the concrete channel. Although satisfactory results can be achieved with this predictive methodology, it is important to bear in mind that good fittings do not necessarily come from adequate interpretations of mechanistic processes and, therefore, the physical meaning of the parameters should not be taken literally in both inverse (used for calibration) and forward (predictive) simulations.

Besides from predicting solute transport with classic models, we explored the use of probability distributions. We developed predictive models through the parameterization of the Gumbel and lognormal probability distributions, using the results from our meta-analyses and performing uncertainty estimations. The results of our predictive simulations can be summarized as (Table 4): (1) the Gumbel distribution (CSK\textsubscript{Gumbel} = 1.1395) yielded better predictions when the distributions were parameterized with the observed \( m_1 \) and \( m_2 \), suggesting that CSK = 1.18±0.08 is a consistent pattern derived from our meta-analysis and (2) estimating the variance (\( m_2 \)) of the distributions from the mean travel time (\( m_1 \)) can be highly uncertain, and it is explicitly required for using probability distributions in predictive mode; therefore, uncertainty analysis must be always included. Importantly, the parameters of these
distributions do not have direct physical meaning, and this has two main consequences: (1) solute transport understanding cannot be mechanistically advanced and (2) erroneous parametric interpretations from physically based, but poorly constrained models are explicitly avoided.

In summary, we found that the regressions from our meta-analysis can be used to adequately predict solute transport processes using either transport models (fixing CSK) or probability distributions. We consider this a transitional methodology (“a patch solution”) between our current understanding and an improved transport theory that better represents the experimental results.

3.4. Implications for Scale-Invariant Patterns

Other experimental findings reveal intriguing similarities to the scale-invariant patterns that we have highlighted here. These include the linear relationship between cross-sectional maximum and mean velocities [Chiu and Said, 1995; Xia, 1997; Chiu and Tung, 2002], and the relatively constant behavior of the dispersive fraction (a parameter derived from the ADZM) in alluvial and headwater streams [Young and Wallis, 1993; González-Pinzón, 2008]. These observations suggest that stream cross sections establish and tend to maintain a quasi-equilibrium entropic state by adjusting the channel characteristics, i.e., erodible channels adjust their geomorphic characteristics with discharge (bedform and type of sediment transported, slope, alignment, etc.) and nonerodible channels adjust their velocity distributions by changing the maximum velocity and flow depths [Chiu and Said, 1995; Chiu and Tung, 2002]. An improved solute transport theory should address these observed scale-invariant hydrodynamic patterns and explore the physical meaning of the
persistence of skewness, which perhaps could be based on principles of thermodynamics and fluid dynamics.

The coefficient of skewness of the classic solute transport models discussed in section 3.2 shows that Fickian dispersion is inconsistent with the experimental results. The inclusion of macroscopic Fickian dispersion generates a system where the variance of a dispersing solute grows linearly with the distance traveled, generating skewed distributions that later become asymptotically Gaussian [Fisher et al., 1979; Nordin and Troutman, 1980]. This behavior is independent of the assumption of hydraulically uniform stream reaches, suggesting that a revised dispersion approach would be needed unless other mechanisms included in the transport theory (e.g., TS) were capable of counteracting the ever decreasing skewness represented by Fickian dispersion.

Although we have not yet investigated scale-invariant behaviors of temporal distributions in processes other than solute transport, we predict that similar patterns can be derived from meta-analysis of flow routing BTCs. We ground this prediction in the fact that the conservative tracers used in our analyses have marked up how water flowed through the different stream ecosystems considered, experiencing similar physical characteristics and processes involved in flow routing (i.e., shear effects, heterogeneity and anisotropy, and dual-domain mass transfer). Regardless of the adequacy of current transport and flow routing modeling approaches, clear similarities appear when comparing the BTCs of these hydrologic processes, and the temporal moments of (for example) the ADZM and those of the Nash cascade [Nash, 1960] and the Linear (and Multilinear) Discrete (Lag) Cascade channel routing models.

Figure 6. Predicted results using empirical relationships derived from normalized central moment meta-analysis (n = 384 BTCs) and the lognormal distribution. Uncertainty bounds represent 1000 Monte Carlo simulations where $m_{\text{est}} = \varphi m_{\text{obs}} \theta$, with $\varphi \in [0.8 - 1.2]$, and $m_{\text{est}} = (m_{\text{est}})^\theta$, with $\theta \in [1.601 - 1.629]$. The “L-N=Q(Obs.)” simulation uses the actual $m_1$ and $m_2$ moments derived from the observed data. (a) River Brock, (b) River Conder, (c) River Dunsop, and (d) River Ou Beck. Experimental observations from Young and Wallis [1993]. Goodness of fit was estimated with the Nash–Sutcliffe model efficiency coefficient (E).
Appendix A: MRMT Model

\[
\frac{\partial C_a(\alpha_2)}{\partial t} = \alpha_2 (C_a - C_a(\alpha_2)), 0 < \alpha_2 < \infty \tag{A2}
\]

[54] The theoretical temporal moments were computed in a manner similar to Cunningham and Roberts [1998]:

\[
m_1 = \tau (1 + \beta)
\]
\[
m_2 = \frac{2 \tau^2 (1 + \beta)^2}{Pe^2} + 2 \tau \beta \mu
\]
\[
m_3 = \frac{12 \tau^3 (1 + \beta)^3}{Pe^3} + \frac{12 \tau^2 \beta (1 + \beta)}{Pe^2} \mu + 6 \tau \beta (\mu^2 + \sigma^2)
\]

\[
\text{CSK}_{\text{MRMT}} = \sqrt{2} \left( \frac{(1 + \beta)^2 \tau^2 + Pe \beta \mu}{Pe} \right)^{3/2}
\]

where \(C_a(\alpha_2) \ [ML^{-3}]\) is the concentration of the solute in the storage zone; \(p\) is the probability density function of mass transfer exchange rates; and \(\mu\) and \(\sigma^2\) are the mean and variance of the distribution of TS residence times [cf., Hoggerty and Gorelick; 1995; Cunningham and Roberts, 1998]. Other variables are as defined for the TSM. When \(\beta = 0\), \(\text{CSK}_{\text{MRMT}} = \text{CSK}_{\text{ADE}}\). If dispersion is negligible (\(D = 0\)):

\[
\text{CSK}_{\text{MRMT}} \ (D=0) = \frac{3 \tau \beta (\mu^2 + \sigma^2)}{\sqrt{2} (\beta \mu \tau)^{3/2}} \tag{A4}
\]

[55] If \(\text{CSK}_{\text{MRMT}}\) is not fixed, the MRMT model will represent BTCs with longitudinally decreasing skewness (\(\text{CSK}_{\text{MRMT}} \sim x^{-1/2}\)), becoming asymptotically Gaussian (i.e., \(\text{CSK}_{\text{MRMT}}(x \rightarrow \infty) = 0\)).

Appendix B: The dCTRW Model

[56] The Laplace transform (LT) of \(f(x, t)\) for a dCTRW model is given by Dentz et al. [2004]:

\[
\tilde{f}(x, s) = \exp \left[ -\frac{x}{2D} \left( 1 + \frac{4MsD}{a^2} - 1 \right) \right] \tag{B1}
\]

where \(s\) is the LT variable. Other variables have been defined previously in the ADE. The memory function \(M(s)\) is defined by

\[
M(s) = \frac{1 - \phi(s)}{\tau_1 \phi(s)} \tag{B2}
\]

where \(\phi(s) = \sum \phi(x, s)\) is the LT of the time transition probability density function; \(\phi(x, s) = p(x) \phi(s)\) is the LT of a joint space (\(p(x)\)) and time transition probability density function; and \(\tau_1\) is a median transition time. We estimated the temporal moments using the method by Aris [1958].
\[ m_1 = \frac{x}{u} \left| \frac{M(s)'}{\sqrt{1 + 4(M(s)D)} u^2} \right|_{s=0} \]

\[ m_2 = -\frac{x}{u} \left| \frac{M'(s)'' - 2xD}{\sqrt{1 + 4(M(s)D)} u^2} \right|_{s=0} \]

\[ m_3 = \frac{x}{u} \left| \frac{M(s)'}{\sqrt{1 + 4(M(s)D)} u^2} \right|_{s=0} \]

\[ \text{where } I(0 \leq x < \xi) \text{ is an indicator function that is 1 if the} \]

condition in its argument is true and 0 otherwise. The latter equation can be further developed as

\[ f(x,t) = \int_0^\xi \delta(t-t_n) \langle \delta(x'-x_n) \rangle I(0 \leq x < x' \leq \xi_n) dx' \]

[61] Computing the second average we get:

\[ f(x,t) = \int_0^\xi R(x',t) dx' \int_0^\infty p(\xi) d\xi \]

\[ R(x',t) = \sum_{n=0}^\infty \delta(t-t_n) \langle \delta(x' - x_n) \rangle \]

[62] The latter satisfies the Kolmogorov type equation:

\[ R(x,t) = \delta(x) \delta(t) + \int_0^\infty p(\xi) R(x, \xi, t - \tau_0) d\xi \]

[63] Combining equations (C8) and (C10) in Laplace space, we get

\[ \kappa \tilde{f}(\kappa, t) = \delta(t) + \frac{\mathcal{M}(\kappa)}{1 - p(\kappa)} \tilde{f}(\kappa, t) \]

\[ \mathcal{M}(\kappa) = \frac{\kappa \tilde{p}(\kappa)}{1 - p(\kappa)} \]

[64] The time increment \( \tau_0 \) is supposed to be small compared to the observation time, so that we can write (C11) as

\[ \kappa \tilde{f}(\kappa, t) = \delta(t) - \mathcal{M}(\kappa) \tau_0 \frac{d\tilde{f}(\kappa, t)}{dt} \]

[65] In real space, it reads as

\[ \frac{\partial f(x,t)}{\partial t} = - \int_0^\infty M(\xi) \tau_0 \frac{\partial f(x-\xi, t)}{\partial t} d\xi \]

[66] Defining the moments of \( f(x,t) \) by

\[ \mu_n(x) = \int_0^\infty t^n f(x,t) dt \]

[67] We obtain from equation (C14) the moment equations

\[ \frac{\partial \mu_n(x)}{\partial x} = \int_0^\infty M(\xi) \tau_0 \mu_{n-1}(x-\xi) d\xi \]

where \( \mu_n(x) = 0 \) for \( n < 0 \). This equation can, again, be solved in Laplace space:

\[ \kappa \mu_n(\kappa) = \delta_0(t) + \mathcal{M}(\kappa) \tau_0 \mu_{n-1}(\kappa) \]

[68] For \( n = 1 \) we obtain:

\[ \mu_1(\kappa) = \mathcal{M}(\kappa) \kappa^{-2} \]
because $\overline{p_0}(\kappa) = \kappa^{-1}$. We are interested in the behavior at large distances, which means at small $\kappa$. Inserting equation (C12) above gives

$$\overline{p_1}(\kappa) = \tau_0 \kappa^{-1} \left( 1 - \overline{p}(\kappa) \right)$$  \hspace{1cm} (C19)

[69] Inserting now equation (C3) and expanding up to leading order gives

$$\overline{p_1}(\kappa) = \tau_0 \kappa^{-1} \left( 1 - \frac{1}{a \kappa - b \kappa^alpha} \right) = \tau_0 \frac{\kappa^2}{a^2} + ...$$  \hspace{1cm} (C20)

[70] Thus, the first moment is given by

$$\mu_1(x) = \frac{x\tau_0}{a}$$ \hspace{1cm} (C21)

[71] For the second moment, we have

$$\overline{p_2}(\kappa) = 2\tau_0^2 \kappa^{-4} \left( 1 - \overline{p}(\kappa) \right)^2$$ \hspace{1cm} (C22)

[72] Inserting equation (C3) and expanding up to leading orders we have

$$\overline{p_2}(\kappa) = 2\tau_0^2 \kappa^{-4} + \frac{4\tau_0^2 b}{a^3} \kappa^{-4} + ...$$ \hspace{1cm} (C23)

[73] Inversion of this expression gives

$$\mu_2(x) = \frac{x^3}{a^2} + \frac{x^3}{a^2} \left( 4 - \alpha \right)$$ \hspace{1cm} (C24)

[74] The second normalized central moment is

$$m_2(x) = 4\tau_0^2 \frac{b}{a^3(4-\alpha)} x^{3-\alpha}$$ \hspace{1cm} (C25)

[75] For the third moment, we have

$$\overline{p_3}(\kappa) = 6\tau_0^3 \kappa^{-5} \left( 1 - \overline{p}(\kappa) \right)^3$$ \hspace{1cm} (C26)

[76] Inserting equation (C3) and expanding up to leading orders, we have

$$\overline{p_3}(\kappa) = 6\tau_0^3 \kappa^{-5} + 18\tau_0^3 \frac{b}{a^4} \kappa^{-5} + ...$$ \hspace{1cm} (C27)

[77] Inversion of this expression gives:

$$\mu_3(x) = \frac{x^4}{a^3} + \frac{18\tau_0^3 b}{a^4} \frac{1}{(5-\alpha)} x^{4-\alpha}$$ \hspace{1cm} (C28)

[78] The third normalized central moment is

$$m_3(x) = \frac{3\tau_0^3 b}{a^4} \left[ \frac{6}{15-\alpha} \right] x^{4-\alpha}$$ \hspace{1cm} (C29)

[79] We can now estimate the scaling of CSK as

$$\text{CSK}_{\text{LFDM}} = \frac{m_3(x)}{m_2(x)} \sim \frac{x^{4-\alpha}}{x^{3(1.5-\alpha)(1.5)}}$$ \hspace{1cm} (C30)

For CSK$_{\text{LFDM}}$ to be independent of $x$ (or persistent) we need:

$$\alpha = \frac{4 - 3 \cdot (1.5)}{1 - 1.5} = 1$$ \hspace{1cm} (C31)

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