Combining Empirical Relationships with Data-Based Mechanistic Modeling to Inform Solute Tracer Investigations across Stream Orders

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Introduction

Solute transport studies in streams and rivers often begin with the introduction of conservative and reactive tracers into the water column. Information on the transport of these substances is then captured within tracer breakthrough curves (BTCs) and used to estimate, for instance, travel times and dissolved nutrient and carbon dynamics. Traditionally, these investigations have been limited to systems with small discharges (< 200 L/s) (but see Tank et al. 2008) and with small reach lengths (< 500 m), partly due to the need for a priori information of the reach’s hydraulic characteristics (e.g., channel geometry, resistance and dispersion coefficients) to predict arrival times, times to peak concentrations of the solute and mean travel times. Current techniques to acquire these channel characteristics through preliminary tracer injections become cost prohibitive at higher stream orders and the use of semi-continuous water quality sensors for collecting real-time information may be affected from erroneous readings that are masked by high turbidity (e.g., nitrate signals from Submersible Ultraviolet Nitrate Analyzer (SUNA) instruments) and/or high total dissolved solids (e.g., making the use of salt tracers such as sodium chloride [NaCl]) in larger systems prohibitively expensive). Additionally, a successful time-of-travel study is valuable for only a single river discharge. This research seeks to develop a hydrologic toolbox to predict solute transport and to inform sampling frequencies at small and large stream orders using empirical relationships developed from multiple tracer injections spanning several orders of magnitude in discharge and reach length, and data-based mechanistic transport models.

The objective of the research is to create a user-friendly computational toolbox capable of: 1) estimating injection mass needed to properly characterize a tracer BTC as a function of river discharge and longitudinal sampling distance, 2) predicting arrival time, time-to-peak concentration and mean travel time of a solute BTC as a function of longitudinal distance and discharge, 3) analyzing nutrient uptake kinetics along river reaches from short-term and plateau tracer injections, and 4) characterizing expected concentrations of contaminants in rivers as a function of observed upstream BTCs or known contaminant mass from short-term spills. This study focuses on predicting tracer signals (arrival times and peak concentrations) and in-stream nutrient processing varying spatially along a river continuum. We tested the methods in a 1st – 8th order continuum (Jemez River – Rio Grande) in New Mexico.

Methods

Site description

The Rio Grande (RG) system spans 1st – 8th stream orders with discharge ranging $10^0$ – $10^3$ L/s (Figure 1). The Jemez river, a tributary to the Middle Rio Grande, is a 5th order stream with flows dominated by snowmelt and summer monsoons and with headwaters originating in the Valles Caldera National Park (VCNP), a montane region in north-central New Mexico. Stream orders 6th, 7th and 8th fall along the Rio Grande (Taos, Albuquerque, Elephant Butte) with dam controlled river flow. Land use and land cover vary along the river continuum from managed forests, irrigated agriculture and metropolitan areas.
Figure 1. The Rio Grande (RG) system spans 1st – 8th stream orders with discharge ranging $10^6$ – $10^3$ L/s. Stream order boundary is marked with a red line and has a corresponding number. Sites where tracer experiments were performed are marked with a yellow circle.

Solute transport Excel toolbox

The Excel toolbox was developed from the unit concentration concept (Jobson 1983) and the Aggregated Dead Zone (ADZ) (Beer and Young 1983) solute transport model to predict tracer BTCs and inform sampling frequencies at small and large stream orders. Specifically, information from a highly parsimonious, data-based mechanistic ADZ transport model (Beer and Young 1983), which has 2 identifiable and sensitive parameters, and from the USGS meta-analysis on mass injected, river discharge and tracer BTCs from 60 rivers of varying discharges and sizes across the U.S. (Jobson 1997) were coupled to model arrival times and peak concentrations of solutes.

To model solute transport, the toolbox uses information from four components: 1) river basin information, 2) simulation parameters, 3) estimating injection mass for conservative and reactive tracer and 4) solute transport parameters (Table 1). Site specific inputs are modified by the user while other information is assumed to be constant across sites. Solute transport parameters are used to predict mean arrival time, time of peak concentration and peak concentration of the solute while also providing uncertainty which is represented as 80% and 120% of the predicted mean at two downstream sampling stations. The solute transport parameters (Table 1) are determined from stream velocity, sampling location and the dispersive fraction (DF).
Table 1. Solute transport toolbox components and associated parameters used to predict solute arrival time, arrival of peak concentration and peak concentration.

<table>
<thead>
<tr>
<th>Component</th>
<th>Parameter</th>
<th>Equation or values</th>
<th>Input/Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>River basin information</td>
<td>Discharge (m³/s)</td>
<td>modified by user</td>
<td>Input</td>
</tr>
<tr>
<td></td>
<td>Velocity, v (m/s)</td>
<td>modified by user</td>
<td>Input</td>
</tr>
<tr>
<td></td>
<td>Stream width</td>
<td>modified by user</td>
<td>Input</td>
</tr>
<tr>
<td></td>
<td>Disp. coeff (m²/s)</td>
<td>modified by user</td>
<td>Input</td>
</tr>
<tr>
<td></td>
<td>Mixing length (m)</td>
<td>modified by user</td>
<td>Input</td>
</tr>
<tr>
<td>Simulation parameters</td>
<td>Duration of injection (h)</td>
<td>modified by user</td>
<td>Input</td>
</tr>
<tr>
<td></td>
<td>Time intervals (h)</td>
<td>modified by user</td>
<td>Input</td>
</tr>
<tr>
<td></td>
<td>Time end of simulation (h)</td>
<td>modified by user</td>
<td>Input</td>
</tr>
<tr>
<td></td>
<td>sampling location, station A (km)</td>
<td>modified by user</td>
<td>Input</td>
</tr>
<tr>
<td></td>
<td>sampling location, station B (km)</td>
<td>modified by user</td>
<td>Input</td>
</tr>
<tr>
<td>Estimating injection mass</td>
<td>C_{max} of target tracer (ug/L)</td>
<td>modified by user</td>
<td>Input</td>
</tr>
<tr>
<td></td>
<td>Commercial tracer solubility (g/100 mL)</td>
<td>modified by user</td>
<td>Input</td>
</tr>
<tr>
<td></td>
<td>Molecular weight (MW) commercial tracer (g)</td>
<td>modified by user</td>
<td>Input</td>
</tr>
<tr>
<td></td>
<td>MW target tracer (g)</td>
<td>modified by user</td>
<td>Input</td>
</tr>
<tr>
<td></td>
<td>MW target:commercial ratio (-)</td>
<td>modified by user</td>
<td>Input</td>
</tr>
<tr>
<td></td>
<td>Estimated tracer decay (%)</td>
<td>modified by user</td>
<td>Input</td>
</tr>
<tr>
<td>Solute transport parameters</td>
<td>Delay time, τ (h)</td>
<td>(1-DF)*t_{mean}</td>
<td>Output</td>
</tr>
<tr>
<td></td>
<td>Mean travel time, t_{mean} (h)</td>
<td>station/v*0.277</td>
<td>Output</td>
</tr>
<tr>
<td></td>
<td>ADZ residence time, T (h)</td>
<td>t_{mean} - τ</td>
<td>Output</td>
</tr>
<tr>
<td></td>
<td>Dispersive Fraction, DF (-)</td>
<td>0.25 (can be modified by user)</td>
<td>Input</td>
</tr>
</tbody>
</table>

The unit concentration concept was used to estimate peak concentrations as a function of travel time (Figure 2) (Jobson 1997). This relationship derived from a USGS meta-analysis of tracer BTCs can be described empirically, where C_{up} is the unit-peak concentration and is a function of time-to-peak concentration (T_p).

\[
C_{up} = 1025 \times T_p^{-0.887}
\]  
Eq. 1

Time-of-travel of leading edge of the BTC is directly related to T_p and is described as,

\[
τ = 0.890 \times T_p
\]  
Eq. 2
where $\tau$ is also the delay time described in the ADZ model below and in Table 1.

Solute transport processes were estimated from the ADZ model (Beer and Young 1983) by using two solute transport parameters ($T$ and $\tau$) that are defined by input information in the toolbox.

$$\frac{dC(t)}{dt} = \frac{1}{T} [C_u(t - \tau) - C(t)]$$

Eq. 3

Where the output concentration $C(t)$ is related to the known concentration upstream, $C_u$, and by the lumped ADZ residence time parameter, $T$,

$$T = \bar{t} - \tau$$

Eq. 4

where $\tau$ is the delay time of injection to arrival of solute signal and $\bar{t}$ is the mean travel time of the solute that is being advected and dispersed in a reach.

$$DF = T / \bar{t}$$

Eq. 5

The DF parameter in the ADZ model accounts for mixing of the solute (Lees et al. 2000). One assumption is that the DF is relatively constant with discharge, given observations from multiple rivers (Wallis et al. 1989a; Young and Wallis 1993).

Figure 2. USGS meta-analysis of tracer BTCs from over 60 different streams shows A) travel time of the leading edge of tracer BTC and B) unit-peak concentration are a function of travel time of peak concentration. Taken from Jobson et al. (1997).
Performance of the Excel toolbox was evaluated in the field from a series of tracer experiments conducted in representative reaches of each of the eight stream orders of the Jemez River-Rio Grande continuum, between the Valles Caldera National Park and Elephant Butte. Stream characteristics (model inputs) were measured the day of experiments to estimate arrival times and peak concentrations at two Stations (A and B) downstream of the Injection site. An instantaneous injection of tracer was applied upstream of Stations A and B. Each sampling station received grab samples of surface water and were equipped with automated sensors to monitor water quality along with a Submersible Ultraviolet Nitrate Analyzer V1 (SUNA) to capture NO$_3$ as a semi-continuous signal during the experiment (Figure 3). Grab samples were analyzed using Ion Chromatography to estimate the concentration of the conservative and reactive tracers (Br and NO$_3$) immediately following collection in the field. BTC were corrected for ambient concentrations of Br and NO$_3$.

![Image](73x278 to 541x539)

**Figure 3.** Solutes were injected at the Injection station and monitored at two separate downstream locations, Station A and Station B. Each station received grab samples of surface water and was equipped with automated sensors.

**In-stream nutrient spiraling**

The Tracer Additions for Spiraling Curve Characterization (TASCC) method (Covino et al. 2010) estimates uptake kinetics from ambient to saturated conditions, which increases the information of nutrient processing for one tracer experiment. This method was applied using grab samples collected during tracer experiments at stream orders 1$^{st}$ – 6$^{th}$ and 8$^{th}$. The 7$^{th}$ stream order was removed due to poor resolution in NO$_3$ collected in both grab samples and SUNA instruments. TASCC calculates the dynamic longitudinal uptake rate ($k_{w-add-dyn}$) from each background corrected grab sample along the tracer BTC. The negative inverse of $k_{w-add-dyn}$ provides estimates of uptake length of added nutrients ($S_{w-add-dyn}$) which is then used to quantify additional nutrient spiraling metrics; dynamic areal uptake ($U_{add-dyn}$), dynamic uptake velocity ($V_{add-dyn}$) and NO$_3$-$N_{add-dyn}$ of added nutrients.

$$U_{add-dyn} = Q \times \frac{[NO_3^*-N_{add-dyn}]}{S_{w-add-dyn}} \times w$$ \hspace{1cm} \text{Eq. 6}

$$V_{add-dyn} = \frac{U_{add-dyn}}{[NO_3^*-N_{add-dyn}]}$$ \hspace{1cm} \text{Eq. 7}

$$[NO_3^*-N_{add-dyn}] = \sqrt{[NO_3^*-N_{add-obs}] \times [NO_3^*-N_{cons}]}$$ \hspace{1cm} \text{Eq. 8}
where $Q$ is stream discharge, $w$ is stream width and $NO_3-N_{cons}$ is background removed [Br] multiplied by the N:Br ratio.

Ambient stream spiraling parameters were estimated from dynamic spiraling metrics described above. Where ambient $NO_3$ ($NO_3-N_{amb}$) is background concentration without the added nutrient, ambient uptake length ($S_{w-amb}$) is found from the linear relationship between $S_{w-add-dyn}$ and total $NO_3-N (NO_3-N_{tot})$, ambient areal uptake is $U_{amb}$, and ambient uptake velocity is $V_{amb}$.

$$U_{amb} = Q \times \frac{[NO_3-N_{amb}]}{S_{w-amb}} \times w$$ \hspace{1cm} \text{Eq. 9}

$$V_{amb} = \frac{U_{amb}}{[NO_3-N_{amb}]}$$ \hspace{1cm} \text{Eq. 10}

Total dynamic spiraling metrics are then calculated by combing added nutrients spiraling metrics with ambient nutrient spiraling metrics.

$$U_{tot} = U_{amb} + U_{add-dyn}$$ \hspace{1cm} \text{Eq. 11}

$$V_{f-tot} = U_{tot}/[NO_3-N_{tot-dyn}]$$ \hspace{1cm} \text{Eq. 12}

$$[NO_3-N_{tot}] = \sqrt{[NO_3-N_{add-obs}] \times [NO_3-N_{cons}] + [NO_3-N_{amb}]}$$ \hspace{1cm} \text{Eq. 13}

**Results**

*Solute transport Excel toolbox*

Arrival time of conservative and reactive solutes were accurately predicted for Stations A and B for 1st through 6th stream orders using the Excel toolbox. For example, Figure 4 shows predicted Bromide concentration ([Br]) to arrive at Station A approximately an hour from time of injection and subsequently, arrives at Station B ~1 hr from Station A at the 3rd stream order. Time of arrival of solutes was less accurate for larger river reaches (7th – 8th stream order). Similarly, time of peak concentration was accurately predicted for Stations A and B for 1st through 6th stream orders. When comparing concentrations between the actual and predicted, reactive tracer signals are smaller and shorter than the predicted [Br] for the conservative tracer, as expected.
Figure 4. A third-order stream with two downstream stations for sampling tracer signal. A) Prediction of peak concentration and time of arrival for the conservative tracer signal at two stations. The Excel toolbox provides 80% and 120% from predicted mean signal. B) Actual tracer signal measured shows timing is accurately predicted; note that, as it is expected reactive tracer signals are smaller and shorter than those predicted for the conservative tracer.

**In-stream nutrient spiraling**

Total dynamic areal uptake ($U_{tot}$) was highest at site 4 (12.52 – 15.59 mg m$^{-2}$ min$^{-1}$) and lowest at site 5 (0.4 – 0.61 mg m$^{-2}$ min$^{-1}$) (Figure 5A). $U_{tot}$ did not vary substantially with total [NO$_3$], suggesting saturation at low to moderate concentrations within sites. Total dynamic velocity ($V_{tot}$) was highest at site 4 (3.995 – 19.414 mm min$^{-1}$) and lowest at site 5 (0.524 – 0.718 mm min$^{-1}$) (Figure 5B). $V_{tot}$ did not vary substantially with total [NO$_3$], suggesting saturation at low to moderate concentrations within sites. Ambient values of NO$_3$ were common across stream order (~0.5 mg L$^{-1}$) except site 6 where ambient NO$_3$ was higher (1.0 mg L$^{-1}$)
Conclusions

We performed solute tracer instantaneous injections along the Jemez River-Rio Grande continuum, which spans 1st – 8th stream orders with discharge ranging $10^0$ – $10^3$ L/s. For each stream order we tested the predictive capacity of our toolbox using easy-to-gather site characteristics (width, velocity and discharge), as well as the locations of the downstream sampling stations and the mass injected. These data were input into a user-friendly spreadsheet to generate predictions. Our tool predicts (within a 90-95% uncertainty bounds) arrival time, time to peak-concentration and mean travel time of a solute BTC as a function of longitudinal distance and discharge. With this information we were able to successfully plan all the logistics required to collect samples (~50) at each location. In other words, our sampling regimen did not miss any important information from the BTC. After comparing our conservative tracer BTC prediction with the experimental data, we found our tool worked reasonably well across stream orders. We found that for lower stream orders (1st-6th) the observations closely overlapped the predicted behavior; however, the observed data for higher stream orders (7th-8th) was located outside the uncertainty bounds of the predicted result. In order to address the underestimation of our predictive tool we need to come up with a methodology to ensure that there is good mixing and a better strategy to reduce systematic errors when estimating discharge in big rivers.

By using the Excel toolbox to capture solute concentrations, we used these data for estimating in-stream nutrient spiraling metrics by applying TASCC. Areal uptake and uptake velocity for total NO$_3$ shows saturation at low to moderate concentrations. Given these patterns, there is not a simple scaling up or down relationship for nutrient areal uptake or velocity by stream order. We do see clustering by stream order and intend to explore what is driving this
trend (i.e. water geochemistry). Because nutrient uptake and metabolism are interrelated fluxes that depend on external and internal factors, it is likely that nutrient stoichiometry is a strong control on these fluxes, but has not been extensively studied yet.

**Broader significance**

In our research lab, we are interested in moving our investigations beyond traditional approaches of studying transport/reaction processes mainly in headwater streams into larger river systems. In doing so we have identified a need to be able to predict BTCs when we are unable to inject inexpensive tracers such as NaCl due to high background levels (cost/logistically prohibitive), and/or when higher turbidity prevents the utilization of water quality sensors that rely on ultraviolet light emissions. Our work produced an integrated and easy-to-use computational tool that can be referenced by researchers and practitioners to design solute transport studies in rivers and to estimate the movement of dissolved constituents after unexpected contaminant spills in an emergency situation that threatens the public water supply, as recently occurred with the Animas River spill. In summary, this work provides a robust tool to predict BTC behavior and travel time when channel characteristics are either unknown or difficult to obtain.

**Budget**

Funds were spent on the following supplies:

- Travel to and from 8 field sites to perform tracer experiments in summer 2015 and spring 2016 (Valles Caldera National Park, Taos, Elephant Butte)
- Chemical supplies needed for tracer experiments (i.e. NaBr, NaNO₃, digitubes, vials and caps for Ion Chromatography)
- Travel to the Association for the Sciences of Limnology and Oceanography conference in Santa Fe, NM to present research results (see poster presentation)

**Poster presentation**

Summers, B.M., V. Garayburu-Caruso, C. Herrington, J. Mortensen, T.P. Covino, D.J. Van Horn, R. González-Pinzón. Quantifying and predicting in-stream nutrient processing using TASCC along a river continuum. Summer meeting for the Association for the Sciences of Limnology and Oceanography, Santa Fe, NM, 5-10 June 2016.

**People who have assisted with the project**

Vanessa Garayburu-Caruso (PhD student, Department of Civil Engineering, University of New Mexico – UNM)
Jacob Mortensen (M.S. student, Department of Civil Engineering, UNM)
Cameron Herrington (Engineer, Bohannan Huston Inc., Albuquerque)
Dave Van Horn (Assistant Research Professor, Department of Biology, UNM)
Tim Covino (Professor, Ecosystems Science and Sustainability, Colorado State University)

**References**