An efficient method to estimate processing rates in streams

Ricardo González-Pinzón[1,2] and Roy Haggerty[1]

[1] We provide an efficient method to estimate processing rates through simple algebraic relationships derived from the transient storage model equations. The method is based on the transport equations, but eliminates the need to calibrate highly uncertain (and intermediate) parameters. We demonstrate that under some common stream transport conditions dispersion does not play an important role in the estimation of processing rates and, therefore, can be neglected. Under such conditions, no computer modeling is needed to estimate processing rates. We also derive algebraic equations to estimate processing rates of target solutes (such as dissolved oxygen) with proxy-tracers (such as resazurin), and show that even if both the target and proxy reactions happen in exactly the same locations at rates that are linearly proportional, the exact relationship between the two volume-averaged rates can be nonlinear and a function of transport. However, the uncertainty in the estimation of the target processing rate is linearly proportional to the proxy-tracer processing rate.

1. Introduction

[2] Processing rates (broadly defined as reaction, decay, or uptake rates) in streams contain information about physicochemical and biological interactions and are used in mass balances (e.g., carbon and nitrogen budgets) and environmental impact assessments (e.g., toxicity levels, (bio)accumulation, (bio)remediation). Furthermore, these rates can be used to directly compare processing within and across stream ecosystems. Processing rates are conventionally estimated through the calibration of transport models, and the uncertainty in their estimates is a function of the uncertainty in the rest of the model parameters. Because most physically based transport models are poorly constrained, the parameters are usually nonunique, interact with each other, and yield equifinal representations of the system, even when the observed data are high quality [*Wagner and Harvey*, 1997; *Wagener et al.*, 2002; *Camacho and González-Pinzón*, 2008; *González-Pinzón et al.*, 2013; *Kelleher et al.*, 2013]. Therefore, current methods to calculate processing rates might yield highly uncertain estimates.

[3] In this technical note, we derive (1) an efficient method to estimate processing rates in streams and (2) the relationship between the processing rate of one solute to the processing rate of another solute in streams. Our method simplifies the estimation of such rates to a point where only algebraic equations and experimental data are needed.

[1]College of Earth, Ocean, and Atmospheric Sciences, Oregon University, Corvallis, Oregon, USA.
[2]Now at Department of Civil Engineering, University of New Mexico, Albuquerque, New Mexico, USA.

Corresponding author: R. González-Pinzón, Department of Civil Engineering, University of New Mexico, MSC01 1070, Albuquerque, NM 87131, USA. (gonzaric@unm.edu)

2. Processing Rates in Streams

[4] The lumped transport equations describing advection, dispersion, transient storage, and first-order irreversible processing in a transient storage compartment are:

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - \beta\alpha_2(C - S) - \lambda_{mc}C, \quad (1)$$

$$\frac{\partial S}{\partial t} = \alpha_2(C - S) - \lambda_{sz}S, \quad (2)$$

where C and S (M L^{-3}) are the concentrations of the reactive solute in the main channel and transient storage zone; Q (L^{3}T^{-1}) is the discharge; D (LT^{-2}) is the dispersion coefficient; $\beta = A_s/A$; A (L^2) is the cross-sectional area of the main channel; A_s (L^2) is the cross-sectional area of the storage zone; α_2 (T^{-1}) is the mass-transfer rate between the main channel and transient storage zones (or $\alpha A/A_s$ as described by *Runkel* [2007]); x (L) is the longitudinal distance; t (T) is the time; λ_{mc} (T^{-1}) is the reactive rate in the main channel; and λ_{sz} (T^{-1}) is the reactive rate in the lumped transient storage zone.

[5] Departing from the work by *Das et al.* [2002] and *Argerich et al.* [2011], the zeroth temporal moment (m_0 (ML^{-3}T)) describing the breakthrough curve (BTC) of a reactive solute, subject to the transport equations (1) and (2), is:

$$m_0^{dn} = m_0^{up}\exp\left[\frac{1}{2}\left(Pe - \left[Pe\left(4\tau\beta\left(\frac{\alpha_2\lambda_{sz}}{\alpha_2 + \lambda_{sz}}\right) + 4\lambda_{mc}\tau + Pe\right)\right]^{1/2}\right)\right], \quad (3)$$

where superscript *up* indicates an upstream measurement, superscript *dn* indicates a downstream measurement, $Pe = Lu/D$ is the Peclet number, which describes the relative importance of advection and dispersion in the system,

L (L) is the length of the reach, u (LT^{-1}) is the mean velocity in the reach ($u = Q/A$), and $\tau = L/u$ (T) is the mean travel time of a conservative solute in the reach.

[6] Let us define effective processing rates ($\lambda_{eff,sz}$ (T^{-1})) and volume-averaged processing rates ($\lambda_{\theta,sz}$ (T^{-1})) in the storage zone as:

$$\lambda_{\theta,sz} = \beta \left(\frac{\alpha_2 \lambda_{sz}}{\alpha_2 + \lambda_{sz}} \right) = \beta \, \lambda_{eff,sz}. \qquad (4)$$

[7] Combining equations (3) and (4) and rearranging, we obtain the total effective processing rate (λ_T (T^{-1})) in the stream reach:

$$\lambda_T = \lambda_{\theta,sz} + \lambda_{mc} = \frac{\ln\left[m_o^{up}/m_o^{dn}\right]}{\tau} \left(1 + \overbrace{\frac{\ln\left[m_o^{up}/m_o^{dn}\right]}{Pe}}^{\text{dispersive term } \Phi} \right). \qquad (5)$$

[8] Note that dilution effects from lateral inputs can be accounted for through $m_o^{dn\bullet} = m_o^{dn}\left(m_{o,cons}^{up}/m_{o,cons}^{dn}\right)$, where $m_o^{dn\bullet}$ is the dilution-corrected zeroth temporal moment downstream, and $m_{o,cons}^{up}$ and $m_{o,cons}^{dn}$ are the upstream and downstream zeroth temporal moments of a conservative tracer. Because $\ln\left[m_o^{up}/m_o^{dn}\right]$ is generally less than 5 (e.g., $\ln\left[m_o^{up}/m_o^{dn}\right] = 4.6$ for a 99% total processing), and Pe is typically 10 or larger in advection-dominated systems ($Pe > 100$ is a common condition; cf. *Bencala and Walters* [1983], *Gooseff et al.* [2003], and *O'Connor et al.* [2010]), the magnitude of the dispersive term Φ can be relatively small. For example, $\Phi < 0.1$ for $Pe > 100$, which makes Φ effectively negligible. If the dispersive term Φ and reactions in the main channel are negligible (most reactions happen in the sediment), λ^T simplifies to:

$$\lambda_{T_{(D \to 0; \lambda_{mc} \to 0)}} = \lambda_{\theta,sz_{(D \to 0)}} = \frac{\ln\left[m_o^{up}/m_o^{dn}\right]}{\tau}. \qquad (6)$$

[9] This assumption was made by *Argerich et al.* [2011] and implicitly by *Tank et al.* [2008]. Note that in equations (5) and (6), plateau (steady-state) concentrations can be substituted for the zeroth temporal moments (see, for example, equations related to equation (6) in *Runkel* [2007]).

[10] Normalized central moments of order n (m_n) can be estimated from experimental BTCs as [*Das et al.*, 2002]:

$$m_n = \sum_{k=1}^{r} \left(\frac{t_k + t_{k+1}}{2} \right)^n \left(\frac{C_k + C_{k+1}}{2} \right)(t_{k+1} - t_k), \qquad (7)$$

where $C(t)$ (ML^{-3}) is the measured concentration at time t (T); k is an index, and r is the total number of observations. The mean travel time τ between two sampling locations can be estimated with the conservative tracer BTCs as:

$$\tau = \frac{m_{1,cons}^{dn}}{m_{o,cons}^{dn}} - \frac{m_{1,cons}^{up}}{m_{o,cons}^{up}}. \qquad (8)$$

3. Relationship Between Processing Rates of Two Solutes

[11] We derive how a reactive solute (referred to as "proxy-tracer" from here on) can be used to estimate processing rates of another solute of interest (referred to as "target" from here on). We consider proxy-tracers that decay (are transformed) linearly proportional to the target. We assume that reactivity preferentially takes place in transient storage zones, where processing rates are significantly higher due to enhanced redox gradients and/or larger volume of colonized sediments (e.g., the hyporheic zone). Furthermore, we analyze a system where the dispersive term is negligible.

[12] An example of these conditions is the use of resazurin in headwater streams [*Argerich et al.*, 2011]. Resazurin is a bioreactive compound that can be used as a proxy-tracer to quantify oxygen (target) consumption in stream ecosystems [*Haggerty et al.*, 2008, 2009; *Argerich et al.*, 2011; *González-Pinzón et al.*, 2012; *Stanaway et al.*, 2012; *Lemke et al.*, 2013]. Resazurin is a proxy-tracer because it has been found that there is a nearly perfect linear relationship between oxygen consumption and resazurin uptake [*González-Pinzón et al.*, 2012]. However, this relationship has to be found via calibration, i.e., it is ecosystem dependent. Other examples are the use of CO_2 production rates to estimate respiration rates (or vice versa), the use of partitioning tracers to assess NAPL distribution rates, and the use of proxy-tracers to assess environmental impacts of hazardous or emerging contaminants [*Sabatini and Austin*, 1991; *Morel and Hering*, 1993; *Rao et al.*, 2000; *Kunkel and Radke*, 2011].

[13] We want to know the volume-averaged processing rate of the target, $\lambda_{\theta,sz}^{target}$ (T^{-1}). This rate is related to the volume-averaged processing rate of the proxy-tracer in the storage zone ($\lambda_{\theta,sz}^{proxy}$ (T^{-1})) (cf. equation (4)):

$$\lambda_{\theta,sz}^{target} = \beta \left(\frac{\alpha_2 \left(K_{target}^{proxy} \lambda_{sz}^{proxy}\right)}{\alpha_2 + \left(K_{target}^{proxy} \lambda_{sz}^{proxy}\right)} \right) = \omega \beta \, \lambda_{eff,sz}^{proxy} = \omega \lambda_{\theta,sz}^{proxy}. \qquad (9)$$

$$\omega = \frac{K_{target}^{proxy} \left(\lambda_{sz}^{proxy} + \alpha_2\right)}{K_{target}^{proxy} \lambda_{sz}^{proxy} + \alpha_2}, \qquad (10)$$
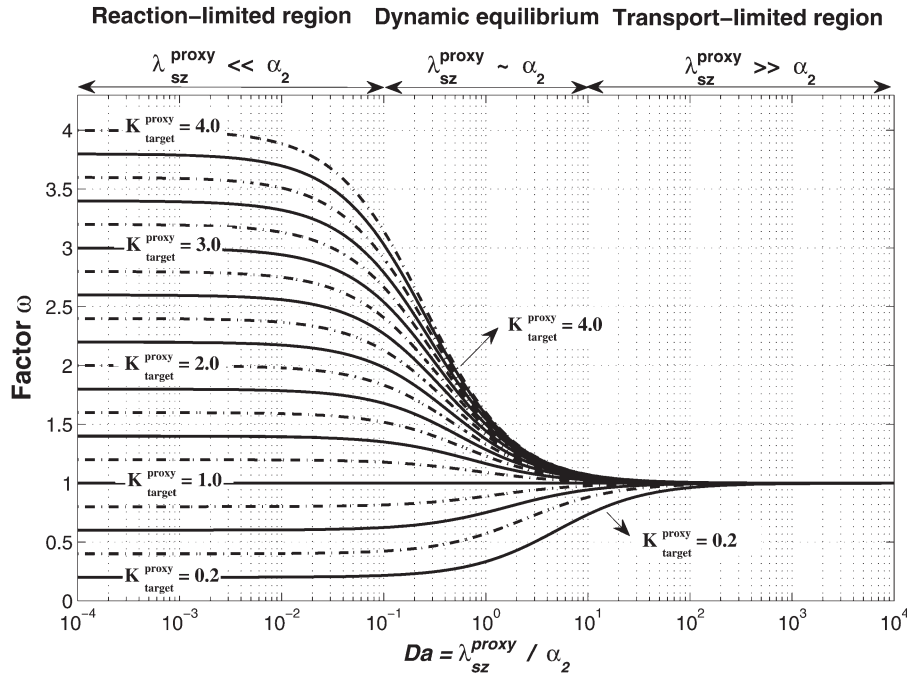
where K_{target}^{proxy} is the molar processing ratio of the target to the proxy-tracer, i.e., $K_{target}^{proxy} =$ (moles of target processed/moles proxy-tracer processed); and ω is a scaling factor between the volume-averaged processing rate of the proxy-tracer and the volume-averaged rate of the target, both in the storage zone.

[14] Equations (9) and (10) are interesting. Even if both the target and proxy reactions happen in exactly the same locations at rates that are linearly proportional, the relationship between the two volume-averaged rates can be nonlinear and a function of transport.

[15] K_{target}^{proxy} can be experimentally estimated, whereas λ_{sz}^{proxy} and α_2 need to be estimated through the calibration of the transport model described by equations (1) and (2). Estimating these parameters might be expensive. Therefore, we investigated convenient simplifications of the scaling factor ω for a range of K_{target}^{proxy}, α_2, and λ_{sz}^{proxy}. To do so, we used the ratio of the characteristic transient storage residence time τ_{sz} ($\tau_{sz} = 1/\alpha_2$) to the characteristic reaction time of the proxy-tracer τ_{sz}^{proxy} ($\tau_{sz}^{proxy} = 1/\lambda_{sz}^{proxy}$), i.e., the Dahmköhler number (Da):

$$Da = \lambda_{sz}^{proxy}/\alpha_2. \qquad (11)$$

[16] Da reflects the relative importance of reactive and hydrological processes (cf. equation (4)). *González-Pinzón*

Figure 1. The scaling factor ω to estimate processing rates of a target solute $(\lambda_{\theta,sz}^{target})$ from a proxy-tracer $(\lambda_{\theta,sz}^{proxy})$ is a function of the molar uptake ratio K_{target}^{proxy} and the Da. The Da defines three characteristic regions under which solute transport and processing reactions operate. When the system is transport-limited, $\omega \rightarrow 1$, and $\lambda_{\theta,sz}^{target} \approx \lambda_{\theta,sz}^{proxy}$. When the system is reaction-limited, $\omega \rightarrow K_{target}^{proxy}$, and $\lambda_{\theta,sz}^{target} \approx \lambda_{\theta,sz}^{proxy} K_{target}^{proxy}$. Under "dynamic-equilibrium" conditions, both hydrology and reactivity define the scaling factor ω, and $\lambda_{\theta,sz}^{target} \approx \lambda_{\theta,sz}^{proxy} \omega$.

et al. [2012] showed that when $Da > 10$, α_2 controls the effective processing rate λ_{eff}^{proxy} and the processing rate is transport-limited. Conversely, when $Da < 0.1$, λ_{sz}^{proxy} controls λ_{eff}^{proxy}, and the processing rate is reaction-limited. Reaction-limited conditions mean that the reaction rate is much slower than the exchange of mass between the main channel and transient storage zones. Transport-limited conditions mean the reverse.

[17] We let Da span nine orders of magnitude (10^{-4} to 10^4) to encompass mass transfer and processing rates observed in field experiments [e.g., *Hall et al.*, 2002; *Runkel*, 2007; *Haggerty et al.*, 2008, 2009; *Zarnetske et al.*, 2012; *Briggs et al.*, 2013]. We also bounded $K_{target}^{proxy} = [0.2, 4.0]$ to encompass expected values (cf. *González-Pinzón et al.* [2012] for an example of molar uptake ratios observed for resazurin and dissolved oxygen; note that $K_{DO}^{Raz} = 1/K_{Raz}^{DO}$).

[18] Figure 1 shows that when streams are transport-limited, the scaling factor $\omega \rightarrow 1$, regardless of the magnitude of K_{target}^{proxy}. Conversely, when the system is reaction-limited, the scaling factor $\omega \rightarrow K_{target}^{proxy}$. A detailed analysis shows that when transport-limited conditions are assumed to occur at $Da > 10$, only values of $K_{target}^{proxy} < 0.2$ yield $\omega < 0.8$. On the other end, when reaction-limited conditions are assumed to occur at $Da < 0.1$, only values of $K_{target}^{proxy} > 3.8$ yield $\omega/K_{target}^{proxy} < 0.8$.

[19] The behavior of the scaling factor ω as a function of Da constrains the estimation of $\lambda_{\theta,sz}^{target}$ with $\lambda_{\theta,sz}^{proxy}$. Also, equations (9) and (10) show that when $K_{target}^{proxy} = 1$, $\omega = 1$, and $\lambda_{\theta,sz}^{target} = \lambda_{\theta,sz}^{proxy}$. Altogether, these conditions bracket the estimation of $\lambda_{\theta,sz}^{target}$, allowing an explicit estimate of the

uncertainty propagated from the estimation of the transport parameters.

[20] These simplifications can be summarized as:

$$\lambda_{\theta,sz}^{target} = \begin{cases} \lambda_{\theta,sz}^{proxy}, & \text{if } Da > 10 : \text{transport-limited system} \\ \lambda_{\theta,sz}^{proxy} \omega, & \text{if } 0.1 < Da < 10 : \text{dynamic equilibrium} \\ \lambda_{\theta,sz}^{proxy} K_{target}^{proxy}, & \text{if } Da < 0.1 : \text{reaction-limited system} \end{cases}$$

(12)

[21] Note that equations (9), (10), and (12) suggest that K_{target}^{proxy} defines at least one of the two uncertainty bounds when estimating $\lambda_{\theta,sz}^{target}$ from $\lambda_{\theta,sz}^{proxy}$. Because ω converges to either 1 (one) or to K_{target}^{proxy}, when estimations of K_{target}^{proxy} yield magnitudes that are both less than 1 (one) and larger than 1 (one) (e.g., $K_{target}^{proxy} = 0.9 \pm 0.3$), such values will bound the estimation of $\lambda_{\theta,sz}^{target}$, i.e., $\lambda_{\theta,sz}^{proxy} K_{target\ min}^{proxy} \leq \lambda_{\theta,sz}^{target} \leq \lambda_{\theta,sz}^{proxy} K_{target\ max}^{proxy}$. Otherwise, $\lambda_{\theta,sz}^{proxy} \leq \lambda_{\theta,sz}^{target} \leq \lambda_{\theta,sz}^{proxy} K_{target\ max}^{proxy}$ or $\lambda_{\theta,sz}^{proxy} K_{target\ min}^{proxy} \leq \lambda_{\theta,sz}^{target} \leq \lambda_{\theta,sz}^{proxy}$. Describing the uncertainty in $\lambda_{\theta,sz}^{target}$ as a function of K_{target}^{proxy}, and using square brackets to indicate parameter ranges [min, max], the previous analysis can be summarized as:

$$\lambda_{\theta,sz}^{target} = \begin{cases} \left[\lambda_{\theta,sz}^{proxy} K_{target\ min}^{proxy}, \ \lambda_{\theta,sz}^{proxy}\right], & \text{if } K_{target}^{proxy} = [<1, <1] \\ \left[\lambda_{\theta,sz}^{proxy} K_{target\ min}^{proxy}, \ \lambda_{\theta,sz}^{proxy} K_{target\ max}^{proxy}\right], & \text{if } K_{target}^{proxy} = [<1, >1] \\ \left[\lambda_{\theta,sz}^{proxy}, \ \lambda_{\theta,sz}^{proxy} K_{target\ max}^{proxy}\right], & \text{if } K_{target}^{proxy} = [>1, >1] \end{cases}$$

(13)

[22] Put in words, equations (12) and (13) show that the uncertainty in the estimation of $\lambda_{\theta,sz}^{target}$ is proportional to the uncertainty in the estimation of K_{target}^{proxy}. Also, the uncertainty in the transport conditions (i.e., model-based estimation of λ_{sz}^{proxy}, β and α_2) is less significant than (or bracketed by) the uncertainty in K_{target}^{proxy}.

4. Conclusions

[23] We present an efficient method to estimate processing rates in streams that incorporates transport theory. The method consists of algebraic equations that can be easily implemented by researchers and practitioners in routine investigations of (bio)reactivity in stream ecosystems. The method requires estimates or measurements of the zeroth temporal moments of the upstream and downstream BTCs of a reactive solute (or plateau concentrations), the mean travel time in the stream reach (which is estimated with first temporal moments of a conservative solute), and an estimate of the Peclet number. However, the Peclet number is not needed (dispersion can be assumed effectively negligible) under some common transport conditions and, therefore, no computer modeling would be needed to estimate processing rates. The method is efficient because it does not require the calibration of other intermediate transport parameters, thus reducing the uncertainty in the estimated processing rates.

[24] We also derived algebraic equations to estimate processing rates from one solute (proxy-tracer, $\lambda_{\theta,sz}^{proxy}$) to another (target, $\lambda_{\theta,sz}^{target}$). We showed that the relationship between the two rates is a function of the molar processing ratio of the target to the proxy-tracer $\left(K_{target}^{proxy}\right)$ and the Dahmköhler number (Da). We analyzed the coupling between solute transport and in-stream processing within the three characteristic transport conditions defined by Da and showed that the uncertainty in the estimation of $\lambda_{\theta,sz}^{target}$ is linearly proportional to the uncertainty in the estimation of K_{target}^{proxy}. Furthermore, the uncertainty in the transport parameters is less significant than the uncertainty in K_{target}^{proxy}. Altogether, our results show that only algebraic equations are needed to estimate processing rates in streams.

References

Argerich, A., R. Haggerty, E. Martí, F. Sabater, and J. Zarnetske (2011), Quantification of metabolically active transient storage (MATS) in two reaches with contrasting transient storage and ecosystem respiration, *J. Geophys. Res.*, 116, G03034, doi:10.1029/2010JG001379.

Bencala, K. E., and R. A. Walters (1983), Simulation of solute transport in a mountain pool-and-riffle stream: A transient storage model, *Water Resour. Res.*, 19(3), 718–724, doi:10.1029/WR019i003p00718.

Briggs, M. A., L. K. Lautz, D. K. Hare, and R. González-Pinzón (2013), Relating hyporheic fluxes, residence times, and redox-sensitive biogeochemical processes upstream of beaver dams, *Freshwater Sci.*, 32, 622–641, doi:10.1899/12-110.1.

Camacho, L. A., and R. González-Pinzón (2008), Calibration and prediction ability analysis of longitudinal solute transport models in mountain streams, *J. Environ. Fluid Mech.*, 8(5), 597–604.

Das, B. S., R. S. Govindaraju, G. J. Kluitenberg, A. J. Valocchi, and J. M. Wraith (2002), Theory and applications of time moment analysis to study the fate of reactive solutes in soil, in *Stochastic Methods in Subsurface Contaminant Hydrology*, edited by R. S. Govindaraju, pp. 239–279, ASCE Press, Reston, Va.

González-Pinzón, R., R. Haggerty, and D. D. Myrold (2012), Measuring aerobic respiration in stream ecosystems using the resazurin-resorufin system, *J. Geophys. Res.*, 117, G00N06, doi:10.1029/2012JG001965.

González-Pinzón, R., R. Haggerty, and M. Dentz (2013), Scaling and predicting solute transport in streams, *Water Resour. Res.*, 49, 6096–6099, doi:10.1002/wrcr.20280, in press.

Gooseff, M. N., S. M. Wondzell, R. Haggerty, and J. Anderson (2003), Comparing transient storage modeling and residence time distribution (RTD) analysis in geomorphically varied reaches in the Lookout Creek basin, Oregon, USA, *Adv. Water Resour.*, 26, 925–937.

Haggerty, R., A. Argerich, and E. Marti (2008), Development of a "smart" tracer for the assessment of microbiological activity and sediment-water interaction in natural waters: The resazurin-resorufin system, *Water Resour. Res.*, 44, W00D01, doi:10.1029/2007WR006670.

Haggerty, R., E. Marti, A. Argerich, D. von Schiller, and N. Grimm (2009), Resazurin as a "smart" tracer for quantifying metabolically active transient storage in stream ecosystems, *J. Geophys. Res*, 114, G03014, doi:10.1029/2008JG000942.

Hall, R. O., E. S. Bernhardt, and G. E. Likens (2002), Relating nutrient uptake with transient storage in forested mountain streams, *Limnol. Oceanogr.*, 47, 255–265.

Kelleher, C., T. Wagener, B. McGlynn, A. S. Ward, M. N. Gooseff, and R. A. Payn (2013), Identifiability of transient storage model parameters along a mountain stream, *Water Resour. Res.*, 49, 6096–6099, doi:10.1002/wrcr.20413.

Kunkel, U., and M. Radke (2011), Reactive tracer test to evaluate the fate of pharmaceuticals in rivers, *Environ. Sci. Technol.*, 45(15), 6296–6302, doi:10.1021/es104320n.

Lemke, D., P.-A. Schnegg, M. Schwientek, K. Osenbrück, and O. A. Cirpka (2013), On-line fluorometry of multiple reactive and conservative tracers in streams, *Environ. Earth Sci.*, 69, 349–358, doi:10.1007/s12665-013-2305-3.

Morel, F. M. M., and J. G. Hering (1993), *Principles and Applications of Aquatic Chemistry*, John Wiley, New York.

O'Connor, B. L., M. Hondzo, and J. W. Harvey (2010), Predictive modeling of transient storage and nutrient uptake: Implications for stream restoration, *J. Hydraul. Eng.*, 136(12), 1018–1032.

Rao, P. S. C., M. D. Annable, and H. Kim (2000), NAPL source zone characterization and remediation technology performance assessment: Recent developments and applications of tracer techniques, *J. Contam. Hydrol.*, 45(1–2), 63–78, doi:10.1016/S0169-7722(00)00119-4.

Runkel, R. L. (2007), Toward a transport-based analysis of nutrient spiraling and uptake in streams, *Limnol. Oceanogr. Methods*, 5, 50–62.

Sabatini, D. A., and T. A. Austin (1991), Characteristics of Rhodamine WT and fluorescein as adsorbing ground-water tracers, *Ground Water*, 29(3), 341–349, doi:10.1111/j.1745-6584.1991.tb00524.x.

Stanaway, D., R. Haggerty, S. Benner, A. Flores, and K. Feris (2012), Persistent metal contamination limits lotic ecosystem heterotrophic metabolism after more than 100 years of exposure: A novel application of the resazurin resorufin smart tracer, *Environ. Sci. Technol.*, 46(18), 9862–9871, doi:10.1021/es3015666.

Tank, J. L., E. J. Rosi-Marshall, M. A. Baker, and J. Robert O. Hall (2008), Are rivers just big streams? A pulse method to quantify nitrogen demand in a large river, *Ecology*, 89(10), 2935–2945.

Wagner, B. J., and J. W. Harvey (1997), Experimental design for estimating parameters of rate-limited mass transfer: Analysis of stream tracer studies, *Water Resour. Res.*, 33(7), 1731–1741, doi:10.1029/97WR01067.

Wagener, T., L. A. Camacho, and H. S. Wheater (2002), Dynamic identifiability analysis of the transient storage model for solute transport in rivers, *J. Hydroinform.*, 4(3), 199–211.

Zarnetske, J. P., R. Haggerty, S. M. Wondzell, V. A. Bokil, and R. González-Pinzón (2012), Coupled transport and reaction kinetics control the nitrate source-sink function of hyporheic zones, *Water Resour. Res.*, 48, W11508, doi:10.1029/2012WR011894.