

Biogeochemical reaction and transport within hydrologic landscapes: crossing disciplinary and ecosystem boundaries

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Abstract

Delivery of materials from catchments to coasts constitutes a significant flux within many global elemental cycles. However, large uncertainties bracket estimates of land-sea fluxes, due to limited understanding of interactions among material retention, transport, and transformation within hydrologic landscapes. Freshwater ecosystems facilitate biogeochemical reaction by bringing reactants together in complex physico-chemical environments. Further, they comprise the transport network by which materials move from catchments to coasts. Whereas there have been significant gains in understanding and quantifying hydrologic transport (HT) and biogeochemical reaction (BR) within specific types of freshwater ecosystems (e.g., nutrient spiraling in streams), disparate methodologies and approaches among ecosystems hinder synthesis efforts across the hydrologic landscape. Our goal is to increase the potential for synthesis of HT and BR across traditional ecosystem boundaries. We review the methods and metrics for quantifying HT and BR for the major ecosystems within hydrologic landscapes: lakes, rivers, wetlands, and groundwater. We then identify the research challenges that currently limit integration of HTBR across hydrologic landscapes and discuss the potential for a common set of metrics and approaches to represent HT and BR across multiple freshwater ecosystems. We advocate an approach that ties distribution functions of water residence time explicitly with retention efficiency of materials and nutrients. Such an approach reduces the impact of ecosystem-specific complexities that confound scaling exercises, avoids the assumption of steady-state, and provides a means for direct comparison of material dynamics across the hydrologic landscape.

Quantifying the flux of nutrients and materials from land to sea remains an important research challenge in global biogeochemistry. Recent estimates of global land-sea fluxes indicate that 367 Tg organic C, 65.9 Tg N, and 10.8 Tg P enter oceans from land each year (Seitzinger et al. 2005). However large uncertainties bracket such estimates, stemming from limited understanding of interactions among material retention, transport, and effects of anthropogenic activities in

freshwater ecosystems (Dumont et al. 2005; Harrison et al. 2005; Jenerette and Lal 2005; Cole et al. 2007). Improved estimates of hydrologic transport and biogeochemical reaction in freshwater ecosystems would contribute to mechanistic understanding and reduce uncertainties associated with material fluxes from land to sea.

Freshwater ecosystems, including streams, wetlands, lakes, and groundwaters, comprise the transport network by which materials and nutrients move from continents to the coasts. In addition to material transport, biogeochemical reactions within these diverse ecosystems change the abundance and form of materials delivered to downstream ecosystems. Ecosystems characterized by surface waters and saturated sediments may be conceptualized together as *hydrologic landscapes*. Many authors have advocated for application of a landscape ecological approach to stream ecosystems (Poole 2002; Ward et al. 2002; Wiens 2002; Fisher et al. 2007; Johnson and

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Host 2010). We extend the approach to other freshwater ecosystems and define the hydrologic landscape as patches distinguished by hydrologic characteristics including water residence time, the ratio of surface area to volume, and connectivity with bordering ecosystems (Fig. 1). Landscape ecology emphasizes the influences of spatial pattern on ecological processes and views landscapes as mosaics of patches that are

embedded in a surrounding matrix, and connected via corridors (Turner et al. 2001). Importantly, hydrologic flows provide the medium connecting patches within hydrologic landscapes, resulting in repeated recycling of reaction products and substrates as they are transported down-gradient. We recognize the importance of connections between terrestrial and aquatic portions of catchments, but the domain of this review

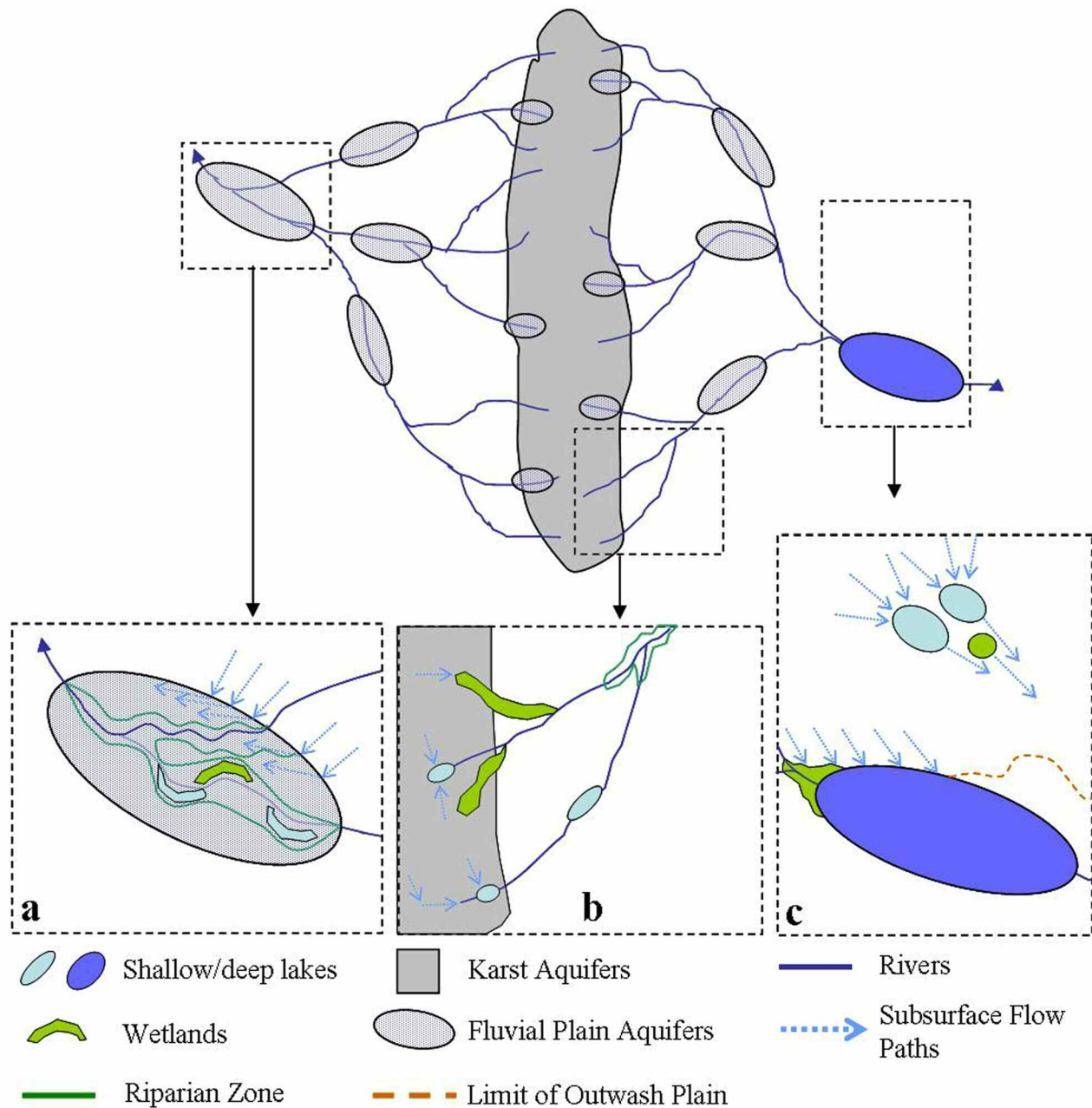


Fig. 1. Aquatic ecosystems within the hydrologic landscape. Fluvial plains (a) may include riparian zones, wetlands, and lakes embedded within a matrix of transmissive groundwater. “Refraction” of flow lines may occur at the interface between the hillslope and the fluvial plain (Woessner 2000). High elevation landscapes (b) may be strongly influenced by the effects of glaciations and resulting geomorphology and topography. The river network downstream may include lake chains, sloping wetlands or fens, and nonuniform groundwater flow lines in areas of karst and fractured rock. Large flow-through lake ecosystems, and coastal plain landscapes (c) may include lake-delta wetlands and lake complexes that have a focusing effect on shallow groundwater flowpaths.

is limited to freshwater ecosystems, the most hydrologically integrated components of catchments.

The diversity of freshwater ecosystems within hydrologic landscapes has yielded a similarly diverse suite of metrics available for quantifying hydrologic transport and biogeochemical reactions. Disparate objectives and methodologies across ecosystem types have limited the potential for syntheses across the hydrologic landscape (Grimm et al. 2003). For example, attempts to estimate the contribution of aquatic ecosystems to global material budgets incorporate simplifying assumptions, which usually introduce more uncertainty for some patches within the hydrologic landscape than others. Wetlands or groundwaters are often under-represented in such syntheses, due to sparse data or a mismatch in the scale of analysis with other ecosystems (Seitzinger et al. 2006; Cardille et al. 2007; Cole et al. 2007; Battin et al. 2008). Enhanced mechanistic understanding of material reaction and transport in hydrologic landscapes would therefore increase the confidence in estimates of land-sea fluxes. A key issue is disentangling the relative effects of hydrologic and biological mechanisms influencing material retention (Ocampo et al. 2006; Wollheim et al. 2006).

A common language of metrics that can accurately represent biogeochemical reaction (BR) and hydrologic transport (HT) across multiple ecosystems would improve our ability to examine and identify important mechanisms of biogeochemical reaction and hydrologic transport (HTBR), improve frame-

works for scaling up from ecosystems or patches to the hydrologic landscape, and allow for more accurate estimates of material transport and retention within the landscape (Table 1). Our goal in this chapter is to provide a foundation for synthesizing HTBR across hydrologic landscapes. We first outline the theory and mechanics underlying metrics of HTBR. Next, we summarize common practices for estimating HTBR within major ecosystem types: lakes, rivers, wetlands, and groundwater. We then discuss appropriate metrics and potential approaches for comparing HTBR among ecosystems and across scales. Our aim is to contribute to a framework that facilitates cross-ecosystem comparisons. Such a framework would aid in identifying the contributions of various components of hydrologic landscapes to material retention, better predict how material retention will be altered by changes in climate and land use, and increase accuracy in estimating fluxes of materials from catchments to coasts.

Approaches to quantifying hydrologic transport and biogeochemical reaction in aquatic ecosystems

In this section, we introduce terms and models for examining hydrologic transport (HT) and biogeochemical reaction (BR) in aquatic ecosystems. All metrics of HTBR originate from a measure of change in mass over time and thereby provide an index of material movement, processing, and transformation in aquatic ecosystems. Metrics of HTBR consist of three components: 1) mass of the constituent of interest (e.g., H₂O, C, N,

Table 1. Current issues in biogeochemistry that may be improved by an integrated approach to hydrologic transport and biogeochemical reaction applied across the hydrologic landscape.

Problem	Issues	Analyses required
Scaling	Scale compatibility and detecting scale breaks	Develop comparable measures for a range of scopes (spatial and temporal extent of the study divided by the grain size of the measurement)
	Estimating contribution of hydrologic landscapes to global material budgets	Obtain accurate estimates for all ecosystems within hydrologic landscapes
	Dimensional constraints	Development and comparison of metrics that adequately address the relevant spatial dimensions of ecosystems within hydrologic landscapes
	Selecting a method of standardizing metrics	Comparison of the performance of metrics of efficiency and measures of process rates
	Encompassing temporal variability	Collection of temporally intensive datasets, followed by analysis of distribution functions Comparison of distributions to mean or absolute measures
Mechanisms	Contrasting biogeochemical and hydrologic contributions to material retention	Analysis of the interdependent nature of metrics of hydrologic transport and biogeochemical reaction
	Identifying contributions of individual processes to material retention	Simultaneous measures of gross rates of various processes Flowpath-specific analyses of HT
Prediction and forecasting	Identifying configurations of ecosystems that most efficiently retain or transport materials	Generate estimates of reaction and transport for suites of hydrologically connected ecosystems Construct models of relevant scenarios
	Non-steady-state conditions in HT or BR	Development and application of dynamic models

P), 2) a geometric normalizing term (e.g., area, mass, or volume), and 3) a temporal normalizing term. These three components can be re-arranged in multiple ways to provide insight into dynamics within a specific ecosystem or to compare dynamics across systems.

Metrics of HT quantify the movement of materials within or across ecosystems whereas BR reflects retention or removal of materials within ecosystems. Metrics of HT and BR may represent gross or net rates. These are common distinctions for biogeochemists; gross rates refer to unidirectional flows from a single pool, whereas net rates reflect the balance of production and consumption. Throughout the rest of the chapter, we will refer to HT and BR individually or in combination (HTBR) when describing material dynamics.

Quantifying hydrologic transport (HT)—Metrics of HT quantify the flow of water, standardized for one, two, or three spatial dimensions. For example, flow may be characterized in one dimension, as specific discharge, q [L^3T^{-1}], in groundwater by dividing Q [L^3T^{-1}] by the cross-sectional area of the aquifer (Table 2). Placing metrics of flow in the context of time, rather than space, is often important for comparing ecosystems of disparate hydrologic characteristics. Mean water residence time, τ , accomplishes this by describing the average time water spends in an ecosystem or portion of an ecosystem, and is quantified as the volume of the ecosystem, V [L^3], divided by the rate of input or output of water, Q [$L^3 T^{-1}$] (Table 2). Dividing mean water depth by residence time yields the hydraulic load, H_L [$L T^{-1}$], a metric of hydrologic flux normalized to surface area [L^2] that describes the volume of water accumulated

Table 2. Metrics of hydrologic transport (HT).

Metric	Units	Derivation	Description and methods	Ecosystems	References
Discharge (Q)	$[L^3 T^{-1}]$	streams: vA groundwater: $-KA_{dh}/dl$	v , water velocity [$L T^{-1}$] determined by conservative tracer dilution or float method; A , stream or aquifer cross-sectional area [L^2]; K , intrinsic permeability of aquifer sediments [$L T^{-1}$] estimated by falling head parameter or grain size distribution; dh/dl , hydraulic gradient [unitless] estimated from interpolation across a well grid	streams, groundwater	Fetter 2001; Gore 2007
Specific discharge (q)	$[L T^{-1}]$	groundwater: $q = Q/A$	A , cross-sectional area of the aquifer or stream [L^2];	groundwater,	Fetter 2001;
Hydraulic load (H_L)	$[L T^{-1}]$	streams: $H_L = Q/A$ lakes: $H_L = h/\tau$	h , mean depth [L]; τ , mean water residence time	lakes, streams;	Wollheim et al. 2006
Water residence time (τ)	$[T]$	V/Q	V , volume [L^3]; Q , discharge (inflow or outflow) [$L^3 T^{-1}$] Whole-system estimate of mean residence time; assumes steady state and complete mixing. Also referred to as global residence time or flushing time.	lakes, streams, wetlands, groundwater	Wetzel and Likens 2000; Monsen et al. 2002
Péclet number (P or P_d)	unitless	$v_x d/D_d$	v_x , advective velocity [$L T^{-1}$]; d , average grain diameter [L]; D_d , coefficient for molecular diffusion [unitless] Alternate forms for the Péclet equation may include flowpath length in place of d , dispersion coefficients D_L or D_T in place of D_d or a porosity term	groundwater, lakes, streams, wetlands	Fetter 1999; Huysmans and Dassargues 2005
Transient storage zone exchange coefficient (α)	$[T^{-1}]$	$\frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} + u_L (C_L - C) + \alpha (C_s - C)$ $\frac{\partial C_s}{\partial t} = -\alpha \frac{A}{A_s} (C_s - C)$	u , velocity [$L T^{-1}$]; C , concentration of conservative solute [$M T^{-1}$]; A , cross-sectional area [L^2]; subscripts L and s refer to lateral inflow to the channel and the transient storage zone, respectively Exchange coefficients and other parameters are estimated using inverse modeling of conservative solute breakthrough curve.	streams	Stream Solute Workshop 1990

over a standardized area for a unit of time (Table 2). This is similar to how precipitation and runoff are quantified in watershed studies, and can be used to compare the flux of water within and among different aquatic ecosystems (Wollheim et al. 2008; Harrison et al. 2009).

In many aquatic ecosystems, HT is represented by average values for simplicity. For example, the majority of downstream flow often occurs within the thalweg of a stream channel. However, an average value may poorly represent the hydrology of most ecosystems, especially groundwaters and wetlands, which are characterized by a broad array of flowpaths, each of which are defined by distinct flow rates or volumes. Even streams are comprised of myriad flowpaths that contribute to overall downstream flux of water (Poole et al. 2008). Thus, a frequency distribution describing observed or modeled estimates of a particular metric of HT may best describe the hydrologic flux within or between aquatic ecosystems. For example, residence time distributions (RTD) provide a frequency distribution of residence times and may more accurately represent the hydrology of an ecosystem than mean water residence time (Levenspiel 1972; Monsen et al. 2002). Deviation from the mean is quantified by skewness and kurtosis of the distribution (Fig. 2a) and is a function of the spatial scale of mixing (Holland et al. 2004). RTDs may also be represented spatially, within linear systems like streams (Monsen et al. 2002), or among ecosystems connected in the hydrologic landscape (Fig. 2b).

Quantifying biogeochemical reaction (BR)—The basic models for BR follow chemical kinetics:

$$\frac{dC}{dt} = -kC^n \quad (1)$$

where change in mass over time is modeled as the product of a rate constant k (units depend on the order of the equation) and concentration C [ML^{-3}] to the power of n (where $n \geq 0$). Analytical solutions and units for the most common forms, zero-order ($n = 0$) and first order ($n = 1$), are shown in Table 2. A more comprehensive overview of reactions involving multiple species, higher orders, or back reactions can be found in Stumm and Morgan (1996). The first-order reaction constant, k [T^{-1}], is frequently calculated because it can be estimated by observation of changes in solute concentration over time or along hydrologic flow paths (Table 2; note that this is a net rate of change, with many assumptions of mixing and steady state conditions, discussed in more detail below). k may be standardized by surface area, volume, or rate.

Multiplying k by water depth yields a mass transfer coefficient, v_f [L T^{-1}] (Table 2). This metric is also referred to as uptake or piston velocity, and can be visualized as the vertical movement of the solute across the stream benthic-water interface. Although v_f is sometimes viewed as a metric of efficiency in the literature, we refer to v_f as a pseudo-efficiency, because true efficiencies are expressed as the fraction or percent of export relative to import. Comparisons of v_f among multiple

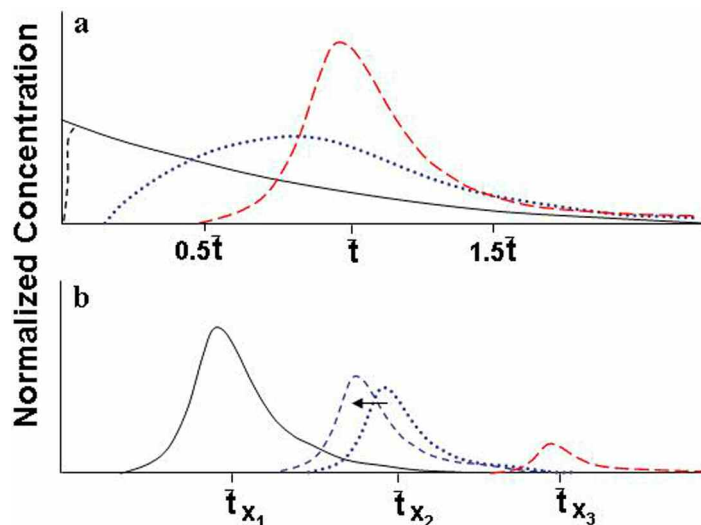


Fig. 2. Residence time distribution (RTD) for water or materials within an ecosystem. RTD is a function of the spatial scale of mixing. The theoretical RTD (a) for a continuously stirred tank reactor (black solid line) assumes instantaneous mixing, whereas most ecosystems have a ramping up period (black dashed line). As the scale of mixing decreases (less efficient mixing – blue dotted line), the RTD resembles a less skewed distribution, approaching a unimodal plug flow in less mixed systems (red dashed line). RTDs may also be represented spatially (b), within ecosystems such as streams (Monsen et al. 2002), or among systems connected in the hydrologic landscape. As a tracer plume or natural solute moves down gradient, the residence time distribution is thus a function of distance (\bar{t}_{x1} , \bar{t}_{x2} , \bar{t}_{x3} , etc.). If the solute is not conservative, a decrease in area under the RTD with distance indicates net uptake of solute, whereas a change in shape of the RTD (e.g., longer tail) would reflect transient storage. Short circuiting (blue dashed line) would shift the RTD such that it would be less than the theoretical residence time, τ , (adapted from Holland et al. 2004 and Monsen et al. 2002).

ecosystems are needed to evaluate the relationship between v_f and true efficiencies of material processing. Multiplying v_f by solute concentration yields an areal expression of retention or removal of materials, termed the areal uptake rate U [$\text{ML}^{-2} \text{T}^{-1}$] (Table 2). v_f and U are important metrics for comparing across ecosystems because they can be related to environmental characteristics. For example, the response of U to changing nutrient concentrations is often modeled using Michaelis–Menten kinetics or the Monod function (Table 2). This model is used when reactions are biologically mediated, and where reaction rate rises sharply with concentration but approaches an asymptote (V_{max}).

Estimating the effects of hydrologic transport and biogeochemical reaction (HTBR) on material retention—The combined effects of HT and BR on material retention may be expressed by the simple mass balance model:

$$E = I - H(B + C) \quad (2)$$

where E is gross material export from the ecosystem [M] for a given period, I is import over the same time period [M], H is

hydrologic retention, and B and C are biotic and chemical retention or removal processes [$M T^{-1}$] (modified from Valett et al. 1996). This simple mass balance approach is important because it partitions the effects of both HT and BR, and has straightforward data requirements such that it may be applied to many existing datasets.

Another common representation of HTBR, conducive to comparing across the hydrologic landscape and to scaling, is in the form of a partial differential equation, rearranging to solve for concentration C [$M L^{-3}$]. The following is a common model describing linear solute dynamics in stream ecosystems:

$$\frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} - kC + \frac{1}{h} k_b C_b \quad (3)$$

where HT is represented by coefficients for stream velocity u [$L T^{-1}$] and dispersion D [$L^2 T^{-1}$]. BR is represented by combined biological and chemical uptake processes k [T^{-1}] and solute release back to the water column k_b [T^{-1}]; physico-chemical conditions are described by solute concentration in the water column C [$M L^{-3}$], areal concentration of the solute on the stream bed C_b [$M L^{-2}$], length of the stream reach x [L], and stream depth h [L] (Stream Solute Workshop 1990). The first two terms on the righthand side of Eq. 3 represent physical movement of solutes within the reach (HT terms), whereas the last two terms represent a net quantification of HTBR (the term $H(B + C)$ in Eq. 2). The term $-kC$ represents a gross retention/removal of solute from the water column whereas the term $(1/h)k_b C_b$ represents the gross input/release, or back reaction, of solute back to the water column (Stream Solute Workshop 1990). Here we use first-order rate constants (kC and $k_b C_b$) to represent these hydrologic and biogeochemical processes, but they can be easily modified to represent zero-order or higher order kinetics (shown in Table 2). Additional terms can be added to this equation for two and three dimensional systems (i.e., lakes, wetlands, and groundwater). Transient storage zones can be represented in this model as well (Stream Solute Workshop 1990; Runkel 2007). This model and its two- and three-dimensional forms provides a basis for examining HTBR across multiple aquatic ecosystems.

Key considerations for cross-ecosystem comparisons—Several key assumptions and details of underlying mechanics must be addressed before applying relationships described by Eqs. 2 and 3 across ecosystems. First, metrics of HT quantify the movement of materials within or across ecosystems, whereas BR reflects removal (uptake, sorption, transient storage) or gain (synthesis/metabolite, desorption, release from storage) of materials within systems. As previously discussed, metrics of HT and BR may be represented by gross or net rates, and the outcome of any synthesis of HTBR will depend upon which is considered. Another consideration is that the relative importance of BR is directly dependent on the magnitude of H , as clarified by Eq. 2. Rates of BR may covary with HT or both may be influenced by a common physical mechanism (e.g., sediment grain size distribution). Finally, Eqs. 2 and 3 are formu-

lated here to represent rates of processes, but these relationships can also be reorganized to represent efficiencies by dividing both sides of the equation by I (Fig. 3).

It is perhaps best to view terms of basic mass balance relationships as distribution functions, rather than average or absolute rates. For example, when considering H as a Residence Time Distribution (RTD), thresholds for B and C may result, in turn producing a distribution of E that may be substantially different from average or system values (Monsen et al. 2002). Such a distribution may better represent temporal or spatial heterogeneity of ecosystems. Non-steady-state conditions in HT (e.g., flashy hydrograph) or BR (e.g., seasonal or diel variation) may also result in more complicated dynamics within ecosystems and the hydrologic landscape.

Aligning appropriate spatial and temporal scales, or identi-

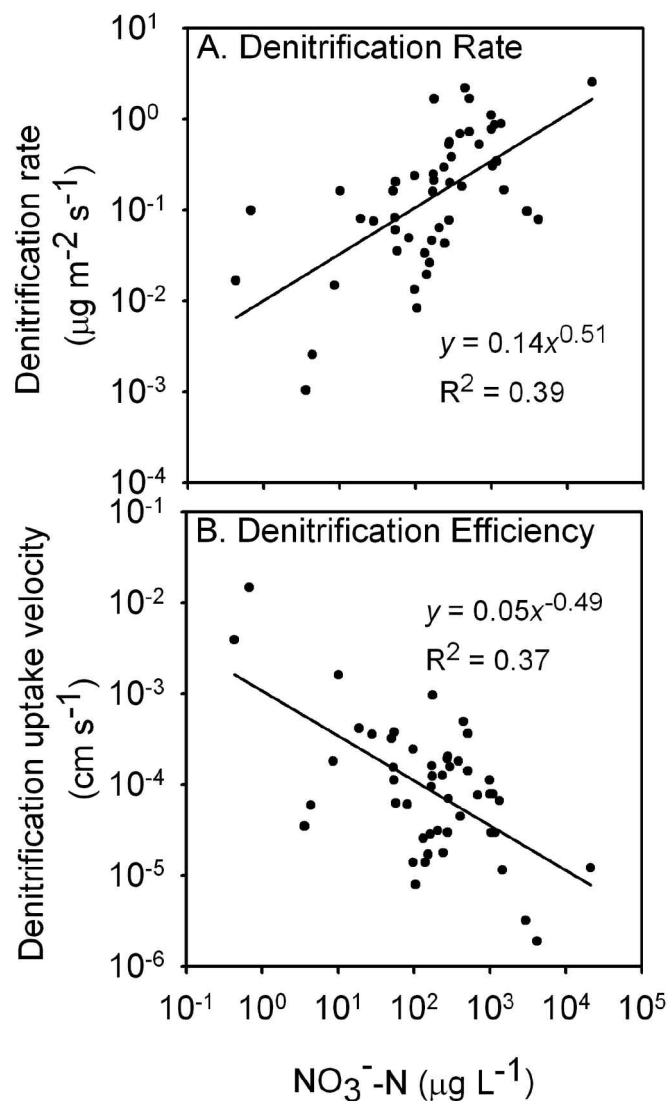


Fig. 3. Whole-stream rates of denitrification increase in a nonlinear fashion with increases in NO_3^- concentration (a), while rates become less efficient in response to NO_3^- loading at high concentrations (b). Adapted from Mulholland et al. (2008).

fying scale breaks within or across ecosystems, remains one of the greatest challenges for considering HTBR in the hydrologic landscape. In Eq. 2, H , B , and C may not necessarily operate on similar spatial or temporal scales, neither with respect to each other nor with respect to the magnitude of E and I . For example, the first-order reaction rate constant k is scale-dependent, and sensitive to discharge, solute concentration, or relative abundance of solutes (Stream Solute Workshop 1990). Use of the piston velocity (v_p) in place of k provides a potential remedy to these issues (Wollheim et al. 2006). For some types of aquatic systems (e.g., lakes and wetlands), v_f appears to be insensitive to nutrient concentration and hydrology, making it scale-independent (Harrison et al. 2009). However, this may not be the case for stream ecosystems where v_p appears to depend on solute concentration (Mulholland et al. 2008). Spatial and temporal scales require explicit consideration because 1) fluxes of water and nutrients occur at different rates across ecosystems (Wagener et al. 1998; Fisher et al. 1998; Fisher et al. 2004), and 2) the scope of a metric (spatial and temporal extent of the study divided by the grain size of the measurement) in one ecosystem may not adequately capture spatial and/or temporal heterogeneity in another (Wagener et al. 1998). Considering multiple spatial and temporal scales may therefore yield relevant insights in cross-ecosystem comparisons (e.g., Essington and Carpenter 2000).

Estimating metrics of HTBR within ecosystems

In this section, we discuss how metrics of HTBR are applied to particular aquatic ecosystems including streams, lakes, wetlands, and groundwater ecosystems. We describe the key attributes of each ecosystem that require attention when estimating HT and BR. These attributes guide selection of appropriate metrics, and we identify metrics typically applied to each aquatic ecosystem.

Fluvial ecosystems

Dominance of advective flow in streams results in significant transport of water and materials to downstream ecosystems within the hydrologic landscape and eventually to coastal ecosystems (Gruber and Galloway 2008; Seitzinger et al. 2005). Less obvious is the role of streams and rivers in transformation, retention, and removal of materials. However, biogeochemical reaction is fostered by large benthic surface area:water volume ratios (Alexander et al. 2000) and hydrologic connections with stream sediments and riparian soils (Dahm et al. 1998). Identifying the relative importance of hydrologic transport and biogeochemical reaction remains an important research challenge in stream ecology.

Hydrologic transport (HT)—Transmission of water downstream is measured as discharge (Q ; $L^3 T^{-1}$) in streams. Total discharge may, in large part, determine the mass of materials transported to downstream ecosystems. However, stream water may be conveyed downvalley via subsurface flowpaths, termed the hyporheic zone, in addition to surface flow (Ben-

cala 1993). In ephemeral or intermittent streams, hyporheic flows may account for a large fraction of the downstream flux of materials (Dahm et al. 1998). At larger spatial scales, changes in stream discharge also occur via exchanges with the aquifer, resulting in reaches that gain or lose water as they flow downstream. Finally, tributaries transport water from distant locations within catchments, and may have significant influences on both water and elemental budgets of stream ecosystems (Fisher et al. 2004).

Transient storage in the hyporheic zone, eddies, and pools result in longer water residence times and broader RTDs (Fig. 2). Metrics of HT in streams include terms for transient storage and are based on a 1-dimensional transport model that characterizes advection and diffusion, including terms for the cross-sectional area of storage zones (A_s), rate of exchange between the main channel and storage zones (α), and lateral inflows (Table 2; Bencala and Walters 1983; Harvey and Wagner 2000). Size of transient storage zones relative to the main channel can be estimated by A_s/A . Many other metrics of transient storage are described in the literature, but these are specific to streams and less amenable to cross-system comparison, so we do not discuss them here.

Biogeochemical reaction (BR)—Uptake and release of dissolved and particulate materials by biogeochemical processes occurs primarily in the benthos of streams, carried out by chemical reaction with sediments or biota anchored to the streambed. BR occurs simultaneously with downstream transport in the water column, and thus nutrient cycles in streams resemble spirals (Webster and Patten 1979; Newbold et al. 1981). A series of metrics describes nutrient spirals, and estimates of these metrics are typically derived from solute addition or isotope tracer experiments at the reach scale (10^2 m), followed by modeling of downstream tracer or solute concentrations (e.g., Webster and Valett 2007). An entire cycle, from a unit of material in the water column, to biota, followed by return to the water column, is termed spiraling length. Uptake length, S_w [L], is typically derived from k , the first-order reaction constant, and describes the average distance traveled by a unit of material before it is removed from the water column (Newbold et al. 1981; Stream Solute Workshop 1990). Describing stream nutrient cycles in terms of uptake length is conceptually advantageous because it encompasses both hydrologic and biological processes. However, uptake length is not comparable across streams of varying discharge, and is therefore not appropriate for use in scaling exercises (Wollheim et al. 2002; Wollheim et al. 2006).

Estimates of uptake velocity, v_f [$L T^{-1}$], are more suited to moving across scales because this metric removes the effect of downstream transport and describes only the effects of biological processes on nutrient availability (Wollheim et al. 2006). v_f can be calculated as the areal uptake rate, U [$M L^{-2} T^{-1}$] standardized by solute concentration. However, analogues have not yet been applied to other ecosystem types (except for lakes, see Lentic ecosystems), limiting direct application of v_f

to cross-ecosystem comparisons. Finally, the areal uptake rate, U , is advantageous because it is equivalent to uptake rates commonly reported for terrestrial ecosystems. However U does not convey information about transport, and budgets based on uptake rate are sensitive to ecosystem boundaries.

Lentic ecosystems

Whereas fluvial ecosystems are predominantly characterized by advective flow and transport of materials, lentic ecosystems—lakes, ponds, and reservoirs—are viewed as diffusion-dominated systems (e.g., Seitzinger et al. 2006). Thus, whereas lotic ecosystems are typically studied within a defined reach of the whole stream, lentic systems have distinct spatial boundaries and are much more amenable to whole-ecosystem studies.

Hydrologic transport (HT)—Numerous metrics quantify internal water movement in lentic ecosystems (e.g., stratification index, Osgood index, Richardson number), but these metrics have limited applicability to other aquatic ecosystems (Wetzel 2001). The most relevant metrics of HT for cross-system comparisons describe flushing rates, residence time τ , or water renewal rates. Water residence time in lakes may be estimated by a landscape budgeting approach incorporating precipitation, evaporation, and thermal stratification of the water column (Rousseau et al. 2004). A critical assumption is that τ is steady-state both with respect to lake volume and the water flux term. This assumption is almost never met (Rueda et al. 2006), and hence τ represents an approximation in all but a few systems near steady-state (e.g., small glacial lakes that receive consistent precipitation; Wetzel 2001). Larger lakes tend to have longer τ due to disproportionate changes between volume and water flux; hence, τ is scale-dependent (Wetzel 2001). A key exception, however, is reservoirs, for which τ depends strongly on landscape position in addition to spatial dimensions (e.g., systems on minor headwater tributaries versus systems on large rivers). Hydraulic load, H_L [$L T^{-1}$], provides an estimate of relative flux of water through the ecosystem by removing system-specific spatial dependency and provides a useful metric for comparison among ecosystems.

Biogeochemical reaction (BR)—Lakes have a long history as model biogeochemical systems (e.g., Forbes 1887). Their relatively closed structure, accessibility, and propensity for experimental manipulation have allowed for numerous mass balance studies that have quantified dynamics of various materials (Wetzel 2001). Specific approaches include long-term monitoring of lake or reservoir inflow-outflow, nutrient additions (Schindler et al. 2008), water column mesocosm studies (Wetzel 2001), and isotope tracer experiments (Mengis et al. 1997).

Vertical and horizontal water movement in lentic ecosystems largely determines biogeochemical reaction rates, both within the water column and at the sediment-water interface (Wetzel 2001). A uniformly mixed water column continuously

replenishes nutrients and oxygen to the entire ecosystem. Seasonal stratification in some lentic ecosystems creates strong reductive-oxidative gradients within the water column, typically producing an oxic epilimnion overlying a hypoxic hypo- or chemolimnion, and characteristic chemical profiles (Wetzel 2001).

Common metrics of BR include areal uptake rate (applied both to the water body surface and benthic sediments), volumetric uptake rate (applied to lake volume and/or volume of planktonic cells), and mass-specific uptake rate (Currie and Kalff 1984; Wetzel 2001; Harrison et al. 2009). At regional and global scales, a metric of efficiency may be applied by scaling relationships to surface area, volume, or hydraulic load, thus removing the complexities of water movement or residence (e.g., Seitzinger et al. 2002; Dumont et al. 2005; Harrison et al. 2005; Harrison et al. 2009). Correlation of nutrient removal with size of lentic ecosystems makes this scaling possible and local nuances (e.g., seasonality, morphology) are not relevant for network- or global-level predictions. For example, Seitzinger et al. (2002) used statistical relationships between nutrient removal, water depth, and/or water residence time to predict N retention in reservoirs. Similarly, Harrison et al. (2009) developed a global model of N retention in lakes and reservoirs based on H_L and v_r .

Wetland ecosystems

Neither fully terrestrial nor completely aquatic, wetlands have less discrete boundaries than streams and lakes and are among the most difficult ecosystems to classify, describe, and study. Wetlands contribute over \$13 billion USD in ecosystem services annually (Costanza et al. 1997), and increasing the number and areal extent of these biogeochemical heavyweights is a major policy priority in developed regions of the world. Wetlands show wide morphological diversity; therefore, we limit our discussion to ecosystems connected within the hydrologic landscape (i.e., at the groundwater interface, or riparian wetlands). Some wetlands are not immediately distinguished as aquatic ecosystems, due to ephemeral appearance of surface water, but may be recognized on the basis of distinctive plant communities, soil type, or hydrologic regimes.

Hydrologic transport (HT)—Geomorphic setting, water source and transport, and hydrodynamics (i.e., direction and strength of water flow) characterize the form and function of wetlands (Brinson 1993). In particular, wetlands are differentiated by source water, water table depth, water residence time, hydroperiod, hydroperiod, and connectivity to other surface waters. Water source divides wetlands into broad categories defining ecosystems receiving primarily precipitation (bogs), groundwater (fens), or surface water (riparian zones and bordering wetlands). In practice, wetlands rarely belong to just one category, but rather are comprised of a mixture of water sources (Fig. 1).

Quantifying HT of wetlands is complicated by their complex hydrology. If a water balance can be constructed, various

metrics of HTBR common to other aquatic ecosystems can be estimated, including τ (also called detention time in wetland literature), retention efficiency, and H_L . The use of mean water residence time in wetlands is problematic due to “short-circuiting” or creation of preferential flowpaths (Fig. 2b) that may have significant effects on the biogeochemical cycling of wetland ecosystems (Lightbody et al. 2008). Therefore, more than any other ecosystem type, HT is best characterized by a RTD, rather than mean values (Kadlec 1994).

Biogeochemical reaction (BR)—In addition to hydrologic transport of materials, wetland hydrology determines soil saturation, which in turn, controls oxygen availability and oxidation-reduction status, a key determinant of dominant biogeochemical processes. For example, fens have a strong connection to groundwater and exposure of hydrologic flowpaths to soil minerals results in higher pH, nutrient, and ion concentrations (Mitsch and Gosselink 2007). Ecosystems connected to surface-water (riparian wetlands, swamps, and marshes) are also often influenced by groundwater and precipitation, the relative importance of which may vary seasonally (Mitsch and Gosselink 2007), resulting in dynamic and variable biogeochemical regimes.

Due to the hydrologic complexity of many wetlands, mass balance approaches vastly outnumber other methodologies for measuring BR. For example, the seminal studies on retentive capacity of riparian zones were based on mass balance (Peterjohn and Correll 1984; Lowrance et al. 1984). As in other ecosystems, mass balance measurements must be made for all of the inputs and outputs, and in the simplest hydrologic cases (flow-through wetlands or floodplains), monitoring nutrient loads up and downstream of the wetland may be sufficient to estimate material retention (Valett et al. 2005). However, it is often impossible to measure all of the inputs and outputs in wetlands. In contrast to lakes or streams, wetlands may contain long-lived biota and developed soils that contribute to long-term storage of materials. Hence mass balance approaches must be applied at appropriate time scales. For example, significant fractions of N become incorporated into stable soil organic matter pools of floodplains over successional time (Kaye et al. 2003), and nutrients are taken up and stored by growing vegetation (Harner and Stanford 2003; Drake et al. 2006).

Mass balance methods are often extrapolated to first-order models of BR (Table 2), which calculate changes in concentrations of outputs relative to inputs (Eq. 2) on an areal or volumetric basis (Kadlec and Knight 1996). These first-order rate constants are typically used to determine the areal or volumetric extent needed for constructed treatment wetlands (Kadlec 2000; Goulet et al. 2001; Braskerud 2002), and thus rate constants have been calculated for many biogeochemical parameters in wetlands (Rousseau et al. 2004).

The steady-state assumptions of mass balance techniques are rarely met when calculating BR in wetland soils (Kadlec et al. 2005), in part because nutrients can be recycled many

times as they traverse a wetland (similar to nutrient spiraling in streams). Nutrient spiraling metrics have been applied to wetlands (Kadlec et al. 2005), and the well-recognized capacity to assimilate nutrients is a function of their large storage reservoirs and short spiral lengths (Howard-Williams 1985). For example, using a $^{15}\text{NH}_4$ addition experiment and a two compartment model, Kadlec et al. (2005) found that plants and the biotic fraction of soils could “park” large amounts of N before releasing it to hydrologic flow pathways, where it could be subsequently detected by mass balance approaches. They concluded that better metrics are needed to delineate the effects of hydrology and biology on nutrient retention in wetlands.

Groundwater ecosystems

The bulk of liquid water on Earth is stored as groundwater—within unconsolidated sediments, fractured or porous rock, or dissolution cavities—and the flow of groundwater has been the purview of hydrogeology for more than 150 years (Fetter 2001). Meanwhile, the hyporheic zone of river-groundwater interaction (*sensu* Brunke and Gonser 1997) has only more recently attracted the attention of limnologists and ecologists (Findlay 1995), whom have borrowed some of the tools and concepts from hydrogeology (Dahm et al. 2007). The spatial extent of the hyporheic zone varies depending on biological, chemical, or physical criteria, and instead we use the more inclusive term “fluvial plain” (Woessner 2000), as it reflects a distinct facies change between hillslopes (which are usually characterized by unsaturated zone processes), to the generally more transmissive alluvial sediments (Fig. 1). Not all groundwaters of interest are directly linked to the fluvial network; also important are lake ecosystems connected by subsurface waters via glacial outwash plains (Magnusen et al. 2006), or topography-driven groundwater flow or Tóth flow (Tóth 1963; Fetter 2001). Fractured rock and karst ecosystems may provide a very important contribution to water-sediment interaction (Cardenas and Gooseff 2008), although they are difficult to map and their contribution to HT and BR is very poorly understood.

Hydrologic transport (HT)—Water velocities are generally orders of magnitude smaller in groundwaters compared with surface waters, rarely exceeding 3 m d^{-1} in alluvial aquifers (Davis et al. 1980), but as high as 600 m d^{-1} in well-sorted gravels (Woessner et al. 2001). Flow velocities in groundwater are measured using a wide variety of approaches (Davis et al. 1980). Salt tracers are the most common method used at larger scales (Harvey and Wagner 2000); however the method is cumbersome, limited in spatial application, and frequently unsuccessful. As an alternative to velocity, subsurface residence time can be measured directly based on naturally occurring tracers such as radon (Hoehn and von Gunten 1989), or by interpreting the phase velocity of the temperature pulse from recharge water (Hoehn and Cirpka 2006).

HT in groundwater is usually estimated with numerical models (e.g., MODFLOW, McDonald and Harbaugh 1983). Solutions to these problems in two or three dimensions are based on differential equations governing the flow through porous materials (Darcy's Law, Table 2). The modeled area is segmented into a regular grid or irregular cells, with boundaries defined as no-flow (impermeable bedrock) or constant head (surface water), and the model is run for either steady state or transient conditions. Model output consists of a mass balance for the model domain, as well as mass balances and estimates of flow rate and flow vector for every cell. A graphical interface allows visualization of the potentiometric surface and the spatial distribution of flow lines (Poole et al. 2008). Particle tracking may be used to estimate the route traveled by hypothetical particles and hence simulate the residence time distribution. Numerical model simulations predict residence time distributions following a power law function (e.g., black line in Fig. 2a) at regional scales (Cardenas 2007), for individual gravel bars (Cardenas et al. 2004), or for subsurface flowpaths within a fluvial plain (Poole et al. 2008).

The advection-dispersion-diffusion transport equation (Darcian flow combined with terms for diffusion and dispersion) represents species-specific solute transport. Diffusive transport may dominate in aquifers with very fine sediments and/or at the interface with reactive aquitards that are the source of organic matter storage (e.g., Chapelle and Lovley 1990). Along longer flowpaths or higher water velocities, dispersion will dominate the non-advective flux. The relative contribution of advection versus diffusion or dispersion can be determined via the Péclet number (Table 2), which may take a variety of forms (Huysmans and Dassargues 2005), allowing model simplification by elimination of unnecessary terms (Huysmans and Dassargues 2005).

Biogeochemical reaction (BR)—Biogeochemical transformation of solutes in groundwater is estimated using a three-dimensional version of Eq. 3, adding terms for retardation (e.g., sorption) and reaction rates (e.g., biological uptake) (Fetter 1999). This approach is applied to understanding the behavior of solute plumes in the field, with laboratory-based estimates of uptake. This is the opposite of the approach taken in streams, where dynamics of solutes in situ are modeled to estimate parameters of transport and uptake.

Laboratory-based rates of BR are modeled as zero-order, first order, or following Michaelis-Menten kinetics (Table 2; note that reaction rates may be expressed per volume of water, whereas rates per volume of sediment must be corrected for sediment porosity). The most commonly used laboratory microcosms for hyporheic studies include batch reactors (e.g., flask incubations), packed bed reactors in closed recirculation (Baker et al. 2000; Craft et al. 2002; Marshall and Hall 2004), or larger, above-ground flow-through chambers (Sobczak and Findlay 2002). Correction factors adjust laboratory-derived rates where experimental substrates do not represent the full range of substrates in situ (Naegeli and Uehlinger 1997).

At small spatial scales, where subsurface flowpaths have been identified, hydrologic transport and uptake along flow paths can be determined by addition of both reactive and conservative solutes (Baker et al. 1999; Duvall and Hill 2007). Tracer addition experiments may be conducted in an individual groundwater well (push-pull technique; Addy et al. 2002; Burgin and Hamilton 2008; Kaushal et al. 2008), or using a chamber driven into the aquifer (Korom et al. 2005). This approach yields rate constants that approximate areal rates over a larger scale. Whereas these in situ methods are more realistic than laboratory rates, they require replication across multiple sites to represent spatial variability. BR at medium to larger spatial scales may be estimated based on mass balance, such as the change in oxygen over a flowpath (Chapelle 1993; Table 1). This approach assumes steady state conditions, an assumption that probably does not hold in many ecosystems within the hydrologic landscape, where groundwater is strongly coupled to dynamic forcing from surface water. Another assumption of this method is that sampling stations are oriented along flow lines, and estimates represent net change rather than gross rates (i.e., competing effect of re-supply of oxygen from aeration or mixing are ignored).

Challenges and considerations for cross-ecosystem comparisons

Despite significant gains in understanding and quantifying HTBR within individual freshwater ecosystems, disparate methodologies and approaches hinder synthesis efforts across hydrologic landscapes. Here we discuss key considerations for implementing metrics of HTBR in cross-ecosystem comparisons and propose several approaches for synthesis. Cross-ecosystem comparisons depend foremost upon an appropriate match of spatial and temporal grain and extent, and we begin with a discussion of scale. Second, syntheses of HTBR across hydrologic landscapes may seek mechanistic explanation of patterns in material retention, and in particular, may address the relative contributions of HT and BR. We address the interdependence of HT and BR, and how such relationships influence interpretation of metrics quantifying HT or BR.

Spatial and temporal dynamics—Comparing HTBR across hydrologic landscapes is difficult because metrics of HTBR are estimated across a wide range of spatial and temporal scales. For example, nutrient uptake rates in streams are generally measured at a spatial extent of a reach (e.g., 50–500 m) and a temporal extent of hours (Ensign and Doyle 2006; Mulholland et al. 2008). In contrast, nutrient uptake rates in lakes and reservoirs are quantified at larger spatial extents (m to km) and temporal extents from months to years (Harrison et al. 2009; Schindler et al. 2008). These contrasts are largely due to differences in the rates at which water and nutrients enter and move through different ecosystems (Wagener et al. 1998; Fisher et al. 2004).

Spatial and temporal heterogeneity present another prominent challenge for cross-ecosystem comparisons. Assessment

of spatial heterogeneity is particularly important in ecosystems for which metrics of HTBR are typically applied to sub-systems. Extrapolation procedures are commonly applied in stream or groundwater ecosystems, where estimates of HTBR are made at sub-system (e.g., stream reach) or point (e.g., piezometer) scales, and then extrapolated to the ecosystem as a whole. Methods are under development in streams for improving the accuracy of scaling experimental estimates of HTBR to whole stream networks (Wollheim et al. 2006; Ensign and Doyle 2006), but these approaches have not been widely applied. In contrast, modeling approaches have been applied extensively to account for spatial heterogeneity of residence time, sediment structure, or flow paths in groundwater ecosystems (Weissmann et al. 2002; Fleckenstein et al. 2006; Gauthier et al. 2009), with less uncertainty regarding the performance of these methods, despite limited empirical data on internal variability.

Temporal variation occurs at myriad scales in aquatic ecosystems. Normalizing metrics of HTBR relative to water residence time addresses variation due to hydrologic inputs, such as ENSO or PDO cycles, or seasonal flood regime. Accurately accounting for temporal heterogeneity introduced by factors other than hydrologic input often requires an experimental approach. For example, pulsed input of terrestrial materials or light due to seasonal dynamics can increase biological demand for N in stream ecosystems (Valett et al. 2008). In contrast, cold temperatures can depress rates of nutrient removal in rivers and lakes to values below the annual mean (Piña-Ochoa and Álvarez-Cobelas 2006). Quantitative relationships between reaction rates and these environmental factors are needed to account for cross-ecosystem comparisons. In many cases, the challenge of appropriately matching scales across ecosystems is complicated by methodological obstacles or data limitations. For example, capturing temporal dynamics may be critical for understanding material retention, but the highest flows in many aquatic ecosystems are short-lived and difficult to predict.

Normalization of metrics for cross-ecosystem comparisons—Choosing a normalizing term for metrics is a crucial first step in comparing HTBR across ecosystems. Normalizing by spatial units may be appropriate for comparisons among a subset of ecosystems, but substantial differences in spatial dimensions and hydro-dynamics of individual sites makes it nearly impossible to implement a single spatial normalization term for all relevant comparisons. For example, uptake rates expressed per unit area are commonly employed for streams and lakes (Harrison et al. 2009; Wollheim et al. 2006), but applying areal uptake rate to hyporheic zones and groundwater is problematic since water interacts with sediments in three dimensions (as opposed to the simplified two-dimensional interaction assumed for streams and lakes). Normalizing by water residence time or residence time of the solute of interest provides a more promising approach to cross-ecosystem comparisons. For example, Essington and Carpenter (2000) identified simi-

larities and differences in nutrient cycles of lakes and streams by comparing a metric of phosphorus cycling normalized to residence time of water versus residence time of phosphorus.

Metrics quantifying rates of BR or HT are useful for understanding overall flux of materials through ecosystems, but do not link pools and fluxes of materials in individual ecosystems. We propose that metrics describing *efficiency* of material retention hold greater promise in evaluating overall capacity of an ecosystem to influence HTBR (Fig. 3). Relative retention, R [unitless], describes the fractional retention of a material relative to hydrologic inputs and provides a promising metric of efficiency for cross-ecosystem comparisons (Table 3). Thus, R describes the effects of both hydrologic transport and biogeochemical reaction on material retention, and is straightforward to calculate using either material fluxes or direct measures of HTBR (Table 3). Application of R to river networks and lakes has allowed separation of the effects of HT and BR on material retention (Dillon and Molot 1990; Wollheim et al. 2006), and we recommend a similar approach be applied across aquatic ecosystems. Because concentration and discharge data are usually available, in most ecosystems material inputs and outputs combined with estimates of hydraulic load can be used to calculate uptake velocity (e.g., Harrison et al. 2009).

Several caveats must be considered when applying R across multiple ecosystem types. The approach assumes that systems are well-mixed, which is unlikely met in most ecosystems, especially since sub-surface processes likely account for much of the biogeochemical reaction in aquatic ecosystems. Specifically, this limits the direct applicability of R to groundwater and many wetland ecosystems. Second, calculation of H_L from physical parameters may be problematic in ecosystems with temporally variable boundaries or spatially heterogeneous patterns of inundation. Sensitivity analysis of input parameters should therefore accompany calculation of R .

Interdependence of HT and BR—Although we have examined them separately, HT and BR are often interdependent (Eq. 2). Interdependence of HT and BR is a function of the reaction rate (Table 3) and the RTD. Fast reaction rates are transport-limited, whereas reaction rates that are slow relative to encounter rate or loading rate are governed by the rate of chemical reaction (Stumm and Morgan 1996; Seitzinger et al. 2006). If the residence time of the chemical species or particle is short relative to rates of reaction or biological processes (e.g., for flow-through lakes and lower-order rivers), then the reaction may be insignificant or may appear very low on a per-area basis ($\tau \ll k$; see Stumm and Morgan 1996 for a more detailed treatment).

The interaction between HT and BR may also be driven by the spatial distribution of reaction substrates on the landscape. For example, the River Continuum Concept (Vannote et al. 1980) states the relationship between materials produced or entering headwater streams and the eventual recycling of those materials as substrates for processes occurring further

Table 3. Metrics of biogeochemical reaction (BR).

Metric	Units	Derivation	Description and methods	Ecosystems	References
Zero-order loss rate constant (k)	[M L ⁻³ T ⁻¹]	$\frac{-(C_1 - C_0)}{t}$	C_0 concentration [M L ⁻³]; t , time; C_0 initial concentration [M L ⁻³] Applied when the substrate is in excess of demand	lakes, streams, wetlands, groundwater	Fetter 1999; Stumm and Morgan 1996
First-order loss rate constant (k)	[T ⁻¹]	$\frac{-\ln(C_1 / C_0)}{t}$	Applied when the substrate is limiting to reaction processes	lakes, streams, wetlands, groundwater	Fetter 1999; Stumm and Morgan 1996; Newbold et al. 1981
Monod or Michaelis-Menton saturation kinetics (U_p , K_m)	[M L ⁻³ T ⁻¹] or [M L ⁻² T ⁻¹]	$\frac{U_{max} C_t}{K_m + C_t}$	U_{max} maximum reaction rate [M L ⁻³ T ⁻¹] or [M L ⁻² T ⁻¹]; K_m half-saturation constant [M L ⁻³] Applied to microbially mediated reactions	lakes, streams, wetlands, groundwater	Fetter 1999; Earl et al. 2006
Uptake length (S_w)	[L]	$\frac{-x}{\ln(C_x / C_0)}$	C_x concentration [M L ⁻³]; x , distance along flowpath [L] Equivalent to the inverse of a first-order loss rate constant when expressed as length-specific uptake [L ⁻¹]	streams	Stream Solute Workshop 1990
Mass transfer coefficient (v_f)	[L T ⁻¹]	h^*v / S_w	h , stream depth [L]; v , water velocity [L T ⁻¹]; S_w uptake length [L] Also referred to as settling velocity, piston velocity, vertical velocity	lakes, streams	Stream Solute Workshop 1990; Harrison et al. 2009
Areal uptake rate (U)	[M L ⁻² T ⁻¹]	$v_f C$	v_f mass transfer coefficient [L T ⁻¹]; C , concentration [M L ⁻³] Does not standardize for depth	lakes, streams, wetlands	Stream Solute Workshop 1990
Net uptake rate (k)	[M L ⁻³ T ⁻¹]	$\frac{(C_x - C_0)v}{x}$; $\frac{(C_x - C_0)vt}{x}$	x , distance [M]; v , water velocity [L T ⁻¹] Reaction rate along a flowpath, normalized to water volume Multiply by porosity (n) for rate per unit sediment	groundwater	Chapelle 1993; Malard and Hervant 1999
Specific uptake rate (U_p)	[M M ⁻¹ T ⁻¹]	U / C_0	U , areal uptake rate [M L ⁻² T ⁻¹]; C_0 concentration of solute on benthos [M L ⁻²]	lakes, streams	Dodds et al. 2004; Currie and Kalff 1984
Retention efficiency (R)	unitless	$1 - \exp(-v_f / H_L)$ $1 - \exp(-k\tau)$	Applied to individual taxa or biological communities in lentic systems; inverse used as the mass turnover time, assuming steady-state conditions H_L , hydraulic load [L T ⁻¹]; k , first-order loss rate [T ⁻¹]; τ , mean water residence time	lakes, streams, wetlands, groundwater	Wollheim et al. 2006
		$(M_{in} - M_{out}) / M_{in}$	[T ⁻¹]; M_{in} and M_{out} , mass of material entering and leaving study unit Relative efficiency of material processing in freshwater ecosystems		

downstream. Further, positive relationships between HT measured as flux and BR may occur when high flows result in hydrologic connection between the stream channel and transient storage zones or biogeochemically active patches in riparian zones, resulting in increased reaction rates or material retention (Fisher et al. 1998; Hall et al. 2009).

Interdependence of HT and BR occurs in saturated sediments or the water-sediment interface (benthic zone, wetlands, hyporheic zone, groundwater), due to sediment grain size distribution. Flow rate and total surface area of sediments combine to determine advective transport of water. Extremes in grain size may have high flow but low surface area, and vice versa. We predict that maximum efficiency of HTBR occurs at some intermediate grain size (e.g., sand), where relatively high hydraulic conductivity occurs with high sediment surface area.

Approaches to integrating HTBR across hydrologic landscapes

Selection of metrics for comparison of HTBR across hydrologic landscapes depends on the objectives of the comparison. Here we focus on the objective of improving estimates of material retention within hydrologic landscapes. Such estimates would improve our ability to quantify fluxes of materials from catchments to coasts. Specifically, we discuss potential approaches to improve temporal resolution of dynamics of HTBR, and to detect spatial and temporal locations of material retention.

Capturing temporal dynamics

Models of material retention in catchments typically capture average conditions, but infrequent events may result in export of a disproportionate fraction of materials (Brooks et al. 2007; Wollheim et al. 2008), or initiate new biogeochemical pathways (Otter and Scholes 2000; Bernhardt et al. 2003). A series of simple chemical reaction vessels (Fig. 4b-g) subject to a range of forcing functions (Fig. 4a) provides a qualitative comparison of potential temporal dynamics. The physical and biological properties of the respective systems define the outputs resulting from a given forcing function (Fig. 4h), which may be phase shifted, dampened, dispersed, and/or retained relative to inputs (e.g., Hoehn and Cirpka 2006; Fig. 4i). Beyond this, our interpretation of actual rates of uptake depends on improved parameterization of the competing processes—for example the “loading” indicated by i_3 may be solely due to dispersion of the previous wave peak. Net uptake at an annual time scale may be estimated as the difference between the mean annual concentrations for input and output, shown by Fig. 4i₄ and Fig. 4i₅, respectively. Hence, waveform analysis provides a method for comparing net uptake across complex transient systems.

Statistical methods can identify and quantify specific phases of the hydrologic cycle associated with retention and transport. For example, the ecological effective discharge in

stream ecosystems is defined as the discharge associated with the greatest ecological “work” (Doyle et al. 2005). Calculated using the frequency distributions of discharge and ecological variables of interest, effective discharges are unique to various ecological processes, such as nutrient transport and periphyton accrual. A similar value could be derived for other aquatic ecosystems by considering frequency distributions of hydraulic load or water residence time in concert with distributions of material export or reaction rates. Applied across ecosystems, such an approach would yield insight into the hydrologic events characteristic of material transport or retention, and increase ability to predict hot moments, times of extreme transport, or retention relative to the temporal extent under considerations (sensu McClain et al. 2003).

Sophisticated statistical tools for quantifying spectral attributes of time series, such as Fourier and wavelet analyses, offer potential to analyze the temporal patterns underlying average conditions. For example, using widely available stream discharge data, Sabo and Post (2008) applied spectral analysis to identify characteristic patterns of seasonal and interannual variation across a range of hydrologic regimes. Such analyses capture temporal trends at multiple scales, and produce statistics that summarize attributes of the hydrologic regime that could be regressed with metrics of biogeochemical reaction to evaluate key times of material retention and transport. Kirchner et al. (2000) used spectral characteristics of time series of chloride concentrations in rain and stream water to show that chemical inputs to catchments may persist over long time scales, an observation inconsistent with the notion of a single, characteristic flushing time. Applied across aquatic ecosystems, such approaches present the potential to uncover the similarities and contrasts in temporal patterns of HTBR among aquatic ecosystems.

Although analyses of temporal variation offer novel insights into HTBR, data limitations prevent widespread implementation. We advocate application of these methods where data are available. Initially, statistical distributions of metrics of HTBR could be examined using existing datasets and distribution forms (e.g., normal, gamma, uniform) compared among ecosystems. Statistical distributions provide insight into the factors (i.e., hydrologic, chemical, or biological) that influence HTBR in individual ecosystems and thus may guide comparisons across ecosystems. For application of the more sophisticated spectral and wavelet analyses, we suggest use of mass flux data, which are at present more abundant than process measures. This first step would quantify temporal patterns in material exports at multiple temporal scales. We also propose that data inputs for non-steady state models could be enhanced considerably through improvements in the design and implementation of in situ sensors (e.g., ion selective electrodes). Sensor networks offer potential for both a major research opportunity and a significant advance toward the synthesis we advocate in this paper.

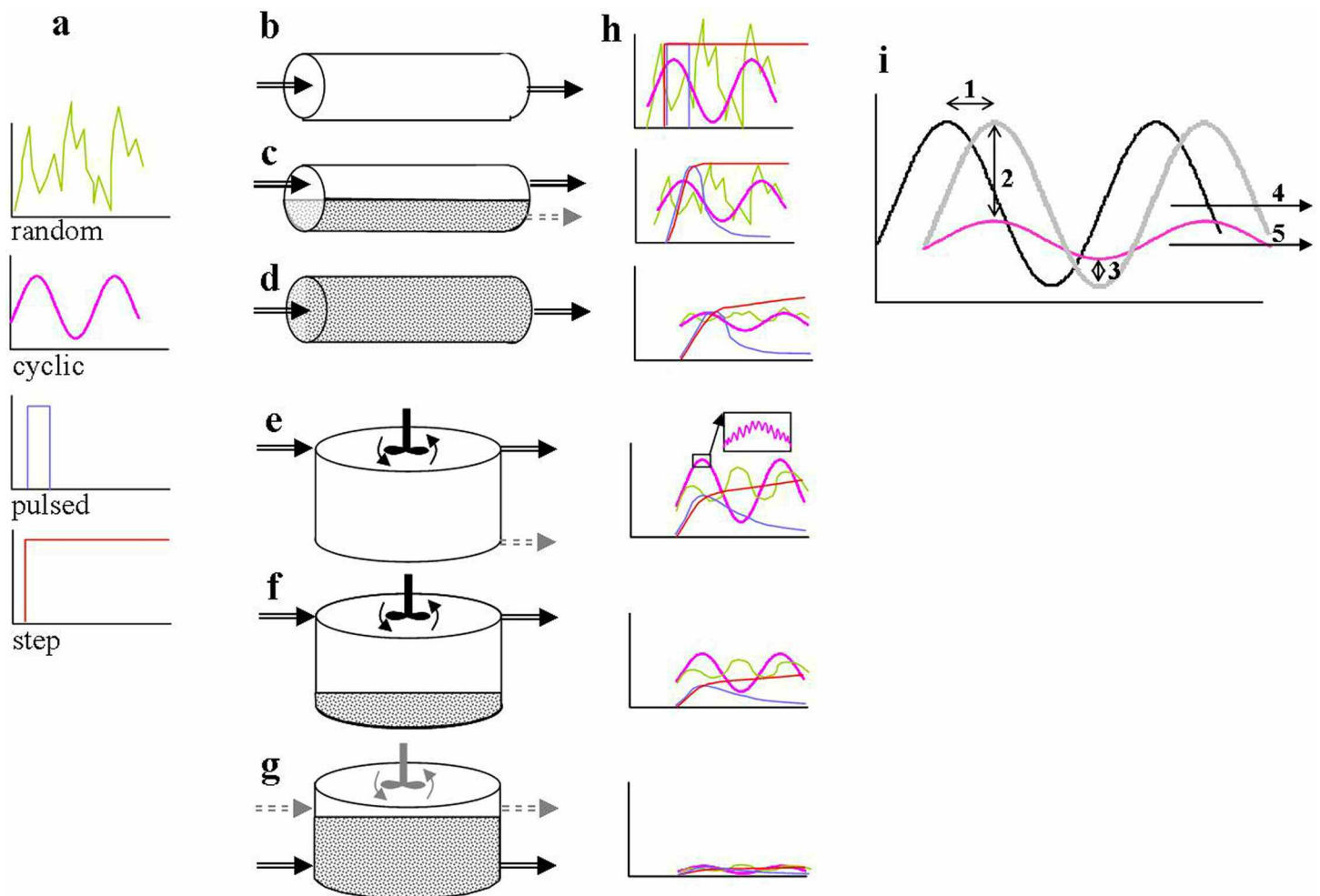


Fig. 4. Non-steady state dynamics of reaction and transport in ecosystems (adapted from Huggenberger et al. 1998). Forcing functions may be random, cyclic, pulsed, or step (a). Reactor vessels may be plug-flow (b-d) or mixed batch reactors (e-g), representing basic ecosystem types: river channel (b), coupled river and benthic zone (c), groundwater (d), and lacustrine ecosystems with either surface or sublittoral discharge (e), shallow lakes with benthic coupling (f), and wetlands with intermittent or seasonal flooding (g). The outputs (h) may be phase shifted, dampened, dispersed, and/or retained relative to inputs (i). In this example, a sine function (black) is the input waveform, the output waveform (red) is also a sine wave, but minimum and maximum values phase shifted (i_1). This shift represents the mean residence time of the chemical species in the reaction vessel. Assuming that residence time is constant over time, inputs and outputs can be directly compared by shifting forward the input wave form (gray). Differences between the two waveforms at any given point in time reflect the net uptake (i_2) or loading (i_3) as a function of time.

Estimating material fluxes and retention capacity of hydrologic landscapes

One of the major objectives of biogeochemical studies conducted at catchment and larger scales is to understand the absolute or relative amount of materials transferred from catchments to downstream ecosystems. This objective requires an estimate of mass flux, typically standardized by contributing area. Such estimates are obtained via stream discharge and water chemistry at the catchment outlet, providing an integrated, whole-catchment perspective. Thus, metrics for individual ecosystems are not needed to estimate catchment-scale fluxes in watersheds with gauges recording discharge. The temporal resolution of discharge and chemistry records determines

the accuracy and precision with which fluxes may be quantified and forecasted. However, most catchments are ungauged, and lack sufficient records of discharge and water chemistry to estimate flux, necessitating application of metrics of HTBR within the catchment. Further, estimates of material retention, in addition to export, are often of interest.

Mass balance approaches are commonly applied to estimate fluxes of materials from catchments when mass flux data are not available, or to estimate material retention within catchments. Net inputs are calculated based on literature values and land use/land cover data (e.g., fertilizer application rates and agricultural cover), or extrapolated from measured or modeled values (e.g., atmospheric deposition) (Boyer et al. 2002; Schaefer and Alber 2007; Sobota et al. 2009). However,

biogeochemical processes often contribute significantly to material retention, and this contribution is typically estimated by functions relating process rates to physical features of the catchment (Seitzinger et al. 2002) or to first-order drivers such as temperature (Whitehead et al. 1998; Green et al. 2004). Rate constants derived in this way often represent only a single ecosystem type (Band et al. 2001). Finally, although the most detailed models can explicitly include reaction and/or transport in groundwater (e.g., Hydrologic Simulation Program-Fortran [Whitehead et al. 1998]), most do not, and few explicitly represent the contributions of wetlands to material retention.

Models formulated without attention to reaction and transport that occur within specific ecosystem types perform reasonably well for estimating average annual flux of materials from large catchments to coasts (Dumont et al. 2005; Harrison et al. 2005; Alexander et al. 2002). However, catchment management often requires estimates of material flux at finer spatial and temporal scales to address specific water quality issues. Further, whole-catchment estimates of mass flux do not provide mechanistic understanding of HTBR within hydrologic landscapes. Here we outline approaches for improving understanding of spatial and temporal components of HTBR in hydrologic landscapes by incorporating ecosystem-specific metrics of HTBR.

Comparison of relative retention, R (Table 3), with uptake velocity, v_p and hydraulic load, H_L , across ecosystems allows assessment of the contributions of hydrologic transport and biogeochemical reaction to material retention. This would apply toward the objective of improving estimates of the retentive capacity of catchments by addressing the relative effects of reaction and transport. Assessing relationships among R , v_p and H_L across gradients such as climate or landscape position would provide further insights into the drivers underlying trends in HTBR. Within individual catchments, analyses based on R could provide information regarding locations and processes that contribute to hot spots of retention (McClain et al. 2003) providing foci for conservation and management actions.

Whole-ecosystem approaches, such as mass balance studies, provide a view of the average rate of material uptake over a given time period. However, smaller-scale estimates of material uptake and transformation may disentangle the mechanisms by which uptake occurs, identify spatial locations of material retention, or evaluate biota responsible for uptake. Sub-system metrics may provide useful information for scaling efforts because replicated estimates can be generated for distinct geomorphic forms, biotic communities, or substrate types. Patch- or habitat-specific estimates of material uptake may be generated by conducting solute or tracer addition within chambers (see groundwater section, and also Stanley and Ward 1997; O'Brien and Dodds 2008), intact sediment cores (Poe et al. 2003; Sheibley et al. 2003; Scott et al., 2008), or by incubating particular biotic communities (Baker et al.

2009). The distribution of these relatively easily measured biotic or geomorphic attributes can then be used to scale up patch-specific estimates (e.g., O'Connor et al. 2006).

Few studies have compared patch-specific estimates of HTBR to those generated from whole-ecosystem experiments. Some have found reasonable overlap (O'Brien and Dodds 2008), whereas others have measured considerable differences in whole-system compared with patch-scale estimates (Scott et al. 2008). Hybrid approaches being developed in streams combine whole-reach solute or tracer additions with detailed monitoring of conservative solute and water velocities in representative sub-reaches or storage zones (Briggs et al. 2009). Combined with information on reactive solute concentrations, these hybrid approaches will allow greater insight into the spatial locations and hydrologic mechanisms influencing transformation and retention of materials, and may be well-suited to poorly mixed aquatic ecosystems.

Recommendations for future research and method development

Research within individual ecosystems has resulted in tremendous gains in our understanding of hydrologic transport and biogeochemical reaction. The next stage of discovery will come from integrating our knowledge across hydrologic landscapes to understand the transport of materials between ecosystems as well as reactions occurring within them. To further aid in the development of this integrative framework, we encourage authors to report metrics of both reaction and transport. This combination of metrics can often be converted into metrics that are comparable between ecosystems (e.g., R , Table 3). Further, metrics of efficiency, rather than rates, offer greater potential for cross-ecosystem comparison because they are made in the context of mass balance, which considers both inputs and retention or removal of materials.

We have discussed examples of metrics that quantify rates of HT and BR, as well as retention efficiency. However, improved prospects for synthesis will require further assessment of the performance of particular metrics. Specifically, we need further examination of the sensitivity of various metrics to spatial and temporal heterogeneity, and the interdependence of various metrics of HT and BR. Given the uncertainties in each of the approaches to investigating rates of HT and BR, we advocate combined use of laboratory-based studies, modeling, and field studies to evaluate the performance of various metrics across hydrologic landscapes.

Finally, we emphasize that the simplifying assumptions of steady state hinder cross-ecosystem comparisons. We have highlighted both potential advances in analysis of existing data (i.e., statistical time series analyses), and a parallel opportunity from enhanced continuous time series datasets generated by emerging sensor networks. These tools will enhance opportunities for examining non-steady state conditions and comparing parameter distributions, both of which will contribute to a more synthetic view of hydrologic landscapes.

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