

Using multi-tracer inference to move beyond single-catchment ecohydrology

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Invited review

Using multi-tracer inference to move beyond single-catchment ecohydrology

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ABSTRACT

Protecting or restoring aquatic ecosystems in the face of growing anthropogenic pressures requires an understanding of hydrological and biogeochemical functioning across multiple spatial and temporal scales. Recent technological and methodological advances have vastly increased the number and diversity of hydrological, biogeochemical, and ecological tracers available, providing potentially powerful tools to improve understanding of fundamental problems in ecohydrology, notably: 1. Identifying spatially explicit flowpaths, 2. Quantifying water residence time, and 3. Quantifying and localizing biogeochemical transformation. In this review, we synthesize the history of hydrological and biogeochemical theory, summarize modern tracer methods, and discuss how improved understanding of flowpath, residence time, and biogeochemical transformation can help ecohydrology move beyond description of site-specific heterogeneity. We focus on using multiple tracers with contrasting characteristics (crossing proxies) to infer ecosystem functioning across multiple scales. Specifically, we present how crossed proxies could test recent ecohydrological theory, combining the concepts of hotspots and hot moments with the Damköhler number in what we call the HotDam framework.

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1. Introduction

> "*The waters of springs taste according to the juice they contain, and they differ greatly in that respect. There are six kinds of these tastes which the worker usually observes and examines: there is the salty, the nitrous, the aluminous, the vitrioline, the sulfurous and the bituminous…Therefore the industrious and diligent man observes and makes use of these things and thus contributes to the common welfare.*"
>
> [Georgius Agricola, *De Re Metallica* (1556)]

The central concerns of ecohydrology can be summarized in three basic questions: where does water go, how long does it stay, and what happens along the way (Fig. 1). Answering these questions at multiple spatial and temporal scales is necessary to quantify human impacts on aquatic ecosystems, evaluate effectiveness of restoration efforts, and detect environmental change (Kasahara et al., 2009; Krause et al., 2011; McDonnell and Beven, 2014; Spencer et al., 2015). Despite a proliferation of catchment-specific studies, numerical models, and theoretical frameworks (many of which are detailed and innovative) predicting biogeochemical and hydrological behavior remains exceedingly difficult, largely limiting ecohydrology to single-catchment science (Krause et al., 2011; McDonnell et al., 2007; Pinay et al., 2015).

A major challenge of characterizing watershed functioning is that many hydrological and biogeochemical processes are not directly observable due to long timescales or inaccessibility (e.g. groundwater

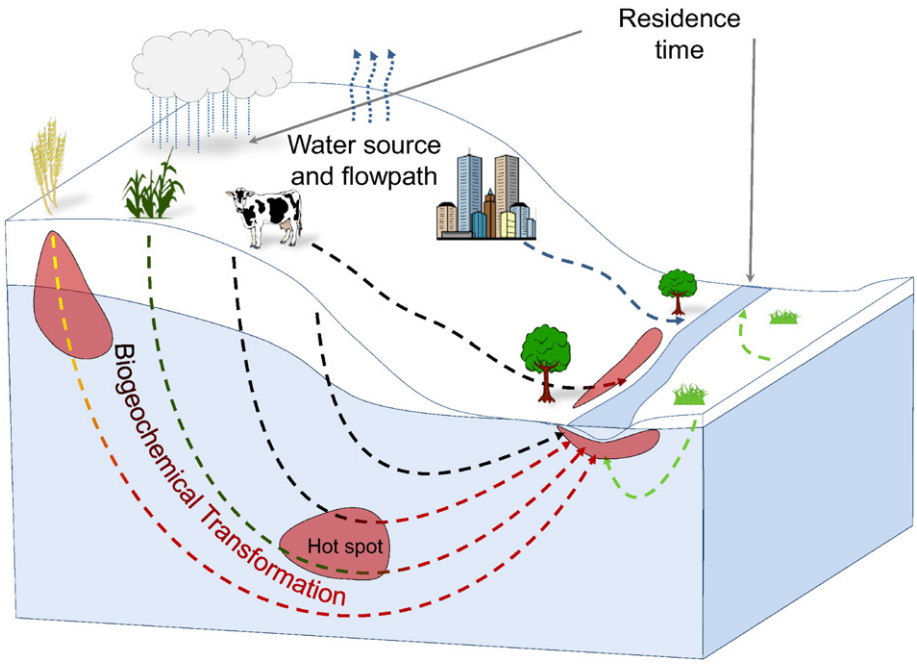


Fig. 1. Conceptual model of a catchment showing the three basic questions of ecohydrology: where does water go, how long does it stay there, and what happens along the way? Dashed lines represent hydrological flowpaths whose color indicates water source and degree of biogeochemical transformation of transported solutes and particulates. The proportion of residence time spent in biogeochemical hot spots where conditions are favorable for a process of interest (McClain et al., 2003) is defined as the exposure time, which determines the retention and removal capacity of the catchment in the HotDam framework (Oldham et al., 2013; Pinay et al., 2015).

circulation or chemical weathering). Consequently, our understanding of many processes depends on how tightly an intermediate, observable parameter (i.e. a tracer or proxy) is associated with the phenomenon of interest. Naturally occurring and injected tracers have been used as proxies of hydrological, ecological, and biogeochemical processes since the founding of those fields (Dole, 1906; Kaufman and Orlob, 1956), and likely since the emergence of thirsty *Homo sapiens* (Agricola, 1556). Methodological advances in ecology, biogeochemistry, hydrology, and other fields including medicine and industry have vastly increased the number of tracers available (Bertrand et al., 2014), and theoretical and computational advances have improved our ability to interpret these chemical and hydrometric proxy data to infer catchment functioning and quantify uncertainty (Beven and Smith, 2015; Davies et al., 2013; Tetzlaff et al., 2015). Multi-tracer approaches have been developed to investigate ecohydrological and biogeochemical functioning unattainable with single proxies (Ettayfi et al., 2012; González-Pinzón et al., 2013; Urresti-Estala et al., 2015). Multi-tracer methods provide tools to address the three fundamental questions in ecohydrology by: 1. Identifying spatially explicit flowpaths, 2. Determining water residence time, and 3. Quantifying and localizing biogeochemical transformation (Fig. 1; Kirchner, 2016a; McDonnell and Beven, 2014; Oldham et al., 2013; Payn et al., 2008; Pinay et al., 2002).

While the diversity and number of tracers applied in different disciplines provide opportunities (Krause et al., 2011), they also represents a logistical and technological challenge for researchers trying to identify optimal methods to test their hypotheses or managers trying to assess ecosystem functioning. Although converging techniques have reduced the methodological distance between hydrological, biogeochemical, and ecological approaches (Frei et al., 2012; Haggerty et al., 2008; McKnight et al., 2015), most work remains discipline specific, particularly in regards to theoretical frameworks (Hrachowitz et al., 2016; Kirchner, 2016a; McDonnell et al., 2007; Rempe and Dietrich, 2014). Furthermore, excitement about what can be measured sometimes eclipses focus on generating general system understanding or testing theoretical frameworks to move beyond description of site-specific heterogeneity (Dooge, 1986; McDonnell et al., 2007).

Several review papers and books have summarized the use of tracers in quantifying hydrological processes, particularly groundwater-surface water exchange (Cook, 2013; Bertrand et al., 2014; Kalbus et al., 2006; Kendall and McDonnell, 2012; Leibundgut et al., 2011; Lu et al., 2014). Here, we expand on this work by exploring how tracers and combinations of tracers (crossed proxies) can reveal ecological, biogeochemical, and hydrological functioning at multiple scales to test general ecohydrological theory and to improve ecosystem management and restoration. Throughout this review we build on an interdisciplinary theoretical framework proposed by Oldham et al. (2013) and Pinay et al. (2015), which combines the ecological concept of hotspots and hot moments (McClain et al., 2003) with the generalized Damköhler number (the ratio of transport and reaction times; Ocampo et al., 2006) in what we call the HotDam framework (Fig. 1). In Section 2, we provide a brief historical perspective on the development of ecohydrological theory. In Section 3, we explore how crossed proxies can be used to better constrain flowpath, residence time, and biogeochemical transformation. Finally, in Section 4, we discuss how ecological and hydrological tracer methods can be applied to generate and test hypotheses of ecohydrological dynamics across scales.

2. A brief history of theories in ecohydrology and watershed hydrology

Over the past 150 years, numerous frameworks and theories have been proposed to conceptualize the transport, transformation, and retention of water and elements in coupled terrestrial-aquatic ecosystems. These frameworks are the basis of our current beliefs about ecohydrological systems and an improved understanding of the historical context of these ideas could illuminate pathways forward (Fisher et al., 2004; McDonnell and Beven, 2014; Pinay et al., 2015). In this section we trace the independent beginnings of catchment hydrology and aquatic ecology in the 19th and 20th centuries followed by a discussion of how increasing overlap and exchange between these fields is contributing to current methodological and conceptual advances.

One of the fundamental goals of catchment hydrology is to quantify catchment water balance, including accounting for inputs from precipitation, internal redistribution and storage, and outputs via flow and evapotranspiration. Early paradigms of catchment hydrology were focused on large river systems or were limited to single components of catchment water balance (e.g. non-saturated flow, in-stream dynamics, overland flow; Darcy, 1856; Horton, 1945; Mulvany, 1851; Sherman, 1932). Computational advances in the mid-20th century allowed more complex mathematical models of watershed hydrology, including the variable source area concept, which replaced the idea of static, distinct flowpaths with the concept of a dynamic terrestrial-aquatic nexus, growing and shrinking based on precipitation inputs and antecedent moisture conditions (Hewlett and Hibbert, 1967). Analysis of catchment hydrographs and water isotopes resolved the apparent paradox between the rapid response of stream discharge to changes in water input (celerity) and the relatively long residence time of stream water, by demonstrating that most of the water mobilized during storms is years or even decades old (Martinec, 1975). Further modeling and experimental work investigating heterogeneity in hydraulic conductivity (preferential flow) and transient storage allowed more realistic simulation of flowpaths at point and catchment scales, providing a scaling framework for predicting temporally-variant flow (Bencala and Walters, 1983; Beven and Germann, 1982; McDonnell, 1990). We note, however, that characterizing preferential flow at multiple scales remains an active subject of research and a major challenge (Beven and Germann, 2013).

Analogous to the hydrological goal of quantifying water balance, a major focus of ecohydrology is closing elemental budgets, including accounting for inputs from primary production, internal redistribution due to uptake and mineralization, and outputs via respiration and lateral export. Early descriptive work gave way to quantitative ecological modelling, using the concept of ecological stoichiometry to link energetic and elemental cycling (Lotka, 1925; Odum, 1957; Redfield, 1958). Work on trophic webs and ecosystem metabolism generated understanding of carbon and nutrient pathways within aquatic ecosystems (Lindeman, 1942) and across terrestrial-aquatic boundaries (Hynes, 1975; Likens and Bormann, 1974). The nutrient retention hypothesis related ecosystem nutrient demand to catchment-scale elemental flux in the context of disturbance and ecological succession (Vitousek and Reiners, 1975), and experimental watershed studies tested causal links between hydrology and biogeochemistry such as evapotranspiration and elemental export (Likens et al., 1970). A major conceptual and technical breakthrough was the concept of nutrient spiraling, which quantitatively linked biogeochemistry with hydrology, incorporating hydrological transport with nutrient turnover in streams (Newbold et al., 1981; Webster and Patten, 1979). In combination with the nutrient retention hypothesis, nutrient spiraling allowed consideration of temporal variability on event, seasonal, and interannual scales for coupled hydrological and biogeochemical dynamics (Mulholland et al., 1985), leading to its application in soil and groundwater systems (Wagener et al., 1998). The telescoping ecosystem model generalized the concept of nutrient spiraling to include any material (e.g. carbon, sediment, organisms), visualizing the stream corridor as a series of cylindrical vectors with varying connectivity depending on hydrological conditions and time since disturbance (Fisher et al., 1998). These hydrological and biogeochemical studies helped re-envision the watershed concept as a temporally dynamic network of vertical, lateral, and longitudinal exchanges, rather than discrete compartments or flowpaths.

The 21st century has seen a continuation of the methodological convergence of catchment hydrology and biogeochemistry (Godsey et al.,

2009; Oldham et al., 2013; Zarnetske et al., 2012). Specifically, two technological advances have strongly influenced the creation and testing of ecological and hydrological theory: 1. Hydrological and biogeochemical models have become vastly more powerful and complex (Davies et al., 2013; McDonnell et al., 2007; McDonnell and Beven, 2014), and 2. High frequency datasets of hydrological and biogeochemical parameters have come online thanks to advances in remote and environmental sensors (Kirchner et al., 2004; Krause et al., 2015; McKnight et al., 2015). Increased computing power has allowed the development of bottom-up, mechanistic models that simulate chemical reactions and water exchange based on realistic physics and biology (Beven and Freer, 2001; Frei et al., 2012; Trauth et al., 2014; Young, 2003). At the same time, more extensive and intensive datasets have allowed the development of top-down, black-box models based on empirical or theoretical relationships between catchment characteristics and biogeochemistry (Godsey et al., 2010; Jasechko et al., 2016; Kirchner, 2016b). While there has been a lively discussion of the merits and drawbacks of these approaches, developing models that are simultaneously physically realistic and capable of prediction remains difficult (Beven and Freer, 2001; Dooge, 1986; Ehret et al., 2014; Kirchner, 2006; Kumar, 2011; McDonnell et al., 2007).

Recently, several frameworks have been proposed to integrate biogeochemical and hydrological dynamics across temporal and spatial scales. Oldham et al. (2013) and Pinay et al. (2015) proposed complementary frameworks that combine the concept of temporally variable connectivity (hot spots and hot moments) with the Damköhler ratio of exposure to reaction times (Fig. 1; Detty and McGuire, 2010; McClain et al., 2003; Ocampo et al., 2006; Zarnetske et al., 2012). The hot spots and hot moments concept is based on the observation that biological activity is not uniformly distributed in natural systems, but that transformation tends to occur where convergent flowpaths bring together reactants or when isolated catchment compartments become reconnected hydrologically (Collins et al., 2014; McClain et al., 2003; Pringle, 2003). This concept has been demonstrated in terrestrial and aquatic ecosystems (Abbott and Jones, 2015; Harms and Grimm, 2008; Vidon et al., 2010) and is appealing because using the predicted or measured frequency of hot spots and hot moments based on landscape characteristics allows for more accurate scaling compared to extrapolation of average rates (Detty and McGuire, 2010; Duncan et al., 2013). The generalized Damköhler number estimates the reaction potential of a catchment or sub-catchment component and is defined as:

$$Da = \frac{\tau_E}{\tau_R}$$

where τ_E is the exposure time defined as the portion of total transport time when conditions are favorable for a specific process, and τ_R is a characteristic reaction time for the process of interest (Oldham et al., 2013). When $Da > 1$ there can be efficient removal or retention of the chemical reactant of interest, whereas when $Da < 1$, the system is transport dominated in regards to that reactant (Fig. 2). *Da* varies systematically with hydrological flow, approaching infinity in isolated components when transport is near zero, and typically decreasing when the ratio of advective transport rate to diffusive transport rate (the Péclet number) increases (Oldham et al., 2013).

The generalized *Da* represents a scalable metric of biogeochemical transformation and has been shown to explain variation in the capacity for catchments or catchment components to remove or retain carbon and nutrients (Fig. 3; Ocampo et al., 2006; Oldham et al., 2013; Zarnetske et al., 2012). Conceptually the hot spots and hot moments concept is concerned with the "where" and "when" of hydrological connectivity and biogeochemical activity while *Da* estimates the "how much" (Fig. 1). The HotDam framework combines these concepts in an effort to provide a realistic and predictive approach to localize and quantify biogeochemical transformation (Oldham et al., 2013; Pinay et al., 2015). While it is straightforward to understand the relevance of exposure time and connectivity, measuring these parameters in natural systems can be extremely challenging, requiring the careful use of multiple tracers. In the following section we outline how tracers can be used to constrain flowpath, residence and exposure times, and biogeochemical transformation at multiple scales to generate process knowledge across multiple catchments.

3. Crossing proxies for flowpath, residence time, and biogeochemical transformation

Almost any attribute of water (e.g. temperature, isotopic signature, hydrometric measures such as hydrograph analysis) or material transported with water (e.g. solutes, particles, organisms) carries information about water source, residence time, or biogeochemical transformation and can be used as a tracer (Table 1; Fig. 4). Tracers vary in their specificity (level of detail for the traced process or pathway), detectability (limit of detection), and reactivity (stability or durability in a given environment). In practice, there are no truly conservative tracers but instead a gradient or spectrum of reactivity. Tracers can be reactive biologically, chemically, or physically, and all these possible interactions need to be accounted for when interpreting results. Compounds that are not used as nutrients or energy sources by biota or which occur at concentrations in excess of biological demand tend to exhibit less biological reactivity, though they may still be chemically or physically reactive. Reactivity is contextual temporally and spatially, particularly in regards to transport through heterogeneous environments typical of the terrestrial-aquatic gradient. Variations in redox conditions and elemental stoichiometry mean that the same substance may be

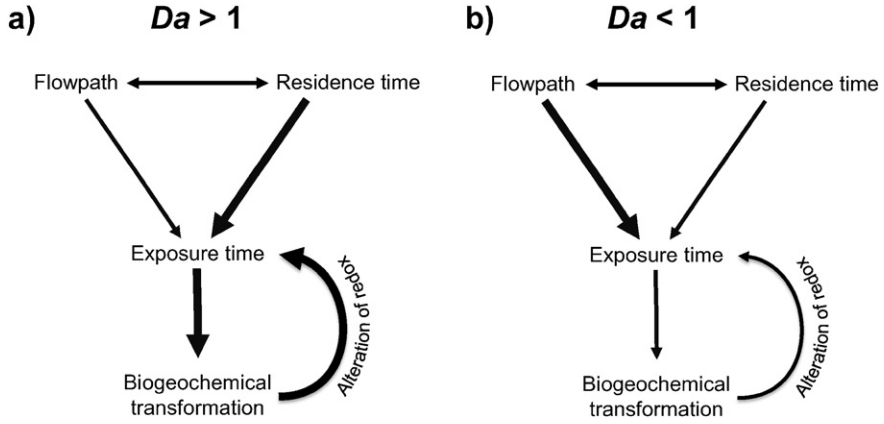


Fig. 2. Schematic relationships between water transport (flowpath and residence time) and biogeochemical processes such as respiration and assimilation when a) $Da > 1$ (diffusion- or reaction-dominated conditions), and b) $Da < 1$ (advection- or transport-dominated conditions). *Da* is the generalized Damköhler number: the ratio of exposure and reaction time scales.

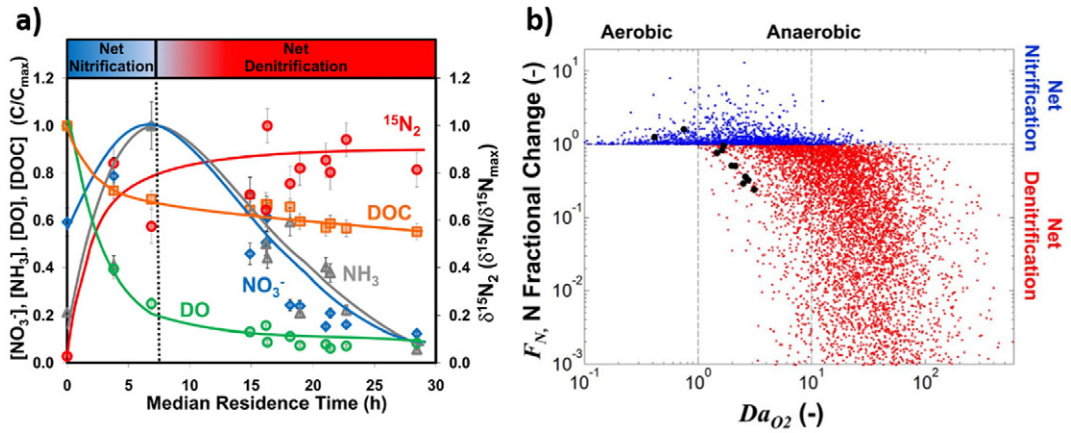


Fig. 3. Examples of the links between residence time, reaction rate, and exposure time. a) Normalized values of dissolved organic carbon (DOC), dissolved oxygen (DO), isotopic signature, and reactant concentration as water passes through a gravel bar. Reproduced from Zarnetske et al. (2011). b) Modeled prevalence of nitrification and denitrification as a function of the ratio of transit to reaction times (i.e. the Damköhler number; *Da*). Reproduced from Zarnetske et al. (2012).

transported conservatively for a portion of its travel time and non-conservatively for another. Often, the very reactivity that renders a tracer unsuitable for conservative duty imparts useful information about interactions and transformations (Haggerty et al., 2008; Lambert et al., 2014). Combining two or more tracers with contrasting properties (crossing proxies) allows partitioning of multiple processes such as dilution and biological uptake (Covino et al., 2010; Bertrand et al., 2014), autotrophic and heterotrophic denitrification (Frey et al., 2014; Hosono et al., 2014; Pu et al., 2014), or aerobic and anaerobic production of dissolved organic matter (DOM; (Lambert et al., 2014). The fact that some tracers are more reactive to certain environmental conditions means that combining a selectively reactive tracer with a generally conservative tracer allows the quantification of exposure time (Haggerty et al., 2008; Oldham et al., 2013; Zarnetske et al., 2012). A final practical distinction in tracer methods is between physicochemical signals that are present within an environment (*environmental tracers*) and substances that are added experimentally (*injected tracers*). Experimentally added tracers have alternatively been referred to as applied or artificial tracers (Leibundgut et al., 2011; Scanlon et al., 2002), but we refer to them as injected tracers since many environmental tracers are anthropogenic (artificial).

3.1. Water source and flowpath: where does water go when it rains?

Besides being one of the existential questions of ecohydrology, asking where water came from and where it has traveled has direct implications for management issues including mitigating human impacts on water quality (Hornberger et al., 2014; Kirkby, 1987) and predicting the movement of nutrients, pollutants, and organisms within and out of the system (Chicharo et al., 2015; Hornberger et al., 2014; Mockler et al., 2015). The course that water takes through a catchment strongly influences residence time and biogeochemical transformation, because where water goes largely determines how long it stays there and what sort of biogeochemical conditions it encounters (Figs. 1, 5; Kirkby, 1987). Flowpaths are influenced by the timing and location of precipitation in combination with catchment characteristics such as vegetation, soil structure, flora and fauna, topography, climate, and geological conditions (Baranov et al., 2016; Beven and Germann, 1982; Blöschl, 2013; Mendoza-Lera and Mutz, 2013). Depending on the purposes of the study, flowpaths can be defined conceptually (e.g. surface, soil, riparian, groundwater) or as spatially-explicitly pathlines describing individual water masses (Fig. 5; Kolbe et al., 2016; Mulholland, 1993). Because flowpaths are temporally dynamic (Blöschl et al., 2007; Hornberger et al., 2014; McDonnell, 1990; Strohmeier et al., 2013), considering seasonal and event-scale variation in whatever tracers are being used is essential (Kirkby, 1987). Evapotranspiration is in some ways a special case, as a dominant flowpath in many environments, and also as a process that influences flowpaths of residual water, influencing soil moisture, groundwater circulation, and water table position (Ellison and Bishop, 2012; Soulsby et al., 2015).

3.1.1. Water isotopes

For a tracer to be an effective proxy of flowpath, it should have high specificity (sufficient degrees of freedom to capture the number of conceptual or explicit flowpaths) and low reactivity over the relevant time period. Perhaps most importantly, it should have similar transport characteristics to water. This is an important consideration because all solute and particulate tracers have different transport dynamics than water, particularly when traveling through complex porous media such as soil, sediment, or bedrock. Even chloride and bromide, the most commonly used "conservative" tracers, can react and be retained by organic and mineral matrices, sometimes resulting in substantial temporal or spatial divergence from the water mass they were meant to trace (Bastviken et al., 2006; Kung, 1990; Mulder et al., 1990; Nyberg et al., 1999; Risacher et al., 2006). Consequently the most effective tracer of water source and flowpath is the isotopic signature of the water itself. Water isotopes have been used to trace storm pulses through catchments (Gat and Gonfiantini, 1981), identify areas of groundwater upwelling (Lewicka-Szczebak and Jędrysek, 2013), and detect environmental change such as thawing permafrost (Abbott et al., 2015; Lacelle et al., 2014). Stable and radioactive isotopes of hydrogen (deuterium and tritium) and oxygen (^{16}O and ^{18}O) are commonly used as environmental tracers but have also been injected (Kendall and McDonnell, 2012; Nyberg et al., 1999; Rodhe et al., 1996). The isotopic signature of water varies based on type and provenance of individual storm systems, climatic context (e.g. distance from ocean, elevation, and latitude), degree of evapotranspiration, and by water source in general (e.g. precipitation or groundwater), allowing the separation of water sources at multiple spatial and temporal scales (Jasechko et al., 2016; Kirchner, 2016a; McDonnell et al., 1990; Rozanski et al., 1993). While water isotopes can behave conservatively at some spatiotemporal scales and in some environments (Abbott et al., 2015; Soulsby et al., 2015), potential alteration of isotopic signature from evaporation, chemical reaction, and plant uptake must be accounted for. If water source and flowpath can be determined with water isotopes, other water chemistry parameters can be used to estimate rates of weathering and biological transformation, or be used as an independent evaluation of model predictions (Barthold et al., 2011; McDonnell and Beven, 2014). Because water isotopes do not have very high specificity (multiple water sources can have the same signature), it is important to characterize site-specific water sources or to cross with another proxy to appropriately solve mixing equations. The recent development of laser

Table 1
List of tracers and their attributes.

Tracer	Type	Specificity	Detectability	Reactivity	Flowpath	Residence time	Biogeochemical transformation	References
Solute								
Dissolved gases								
Propane	I	High	High	volatile	×			Wallin et al. (2011), Soares et al. (2013)
Chlorofluorocarbons (CFCs)	E/I	Intermediate	High	Low (CFC-12, 113) Moderate (CFC-11)		×	×	Lovelock et al. (1973), Thiele and Sarmiento (1990), Thompson et al. (1974)
Sulfur hexafluoride (SF_6)	E/I	Intermediate	High	Very Low		×		Wilson and Mackay (1996)
Radionuclides								
^{3}H, ^{3}He, ^{39}Ar, ^{14}C, ^{234}U, ^{81}Kr, ^{36}Cl	E/I	Intermediate	High	Low		×		Solomon et al. (1998), Lu et al. (2014)
Dissolved organic matter (DOM)	E	High	High	High	×		×	Abbott et al. (2014), Quiers et al. (2013), Baker (2005)
$\delta^{13}C$, $\delta^{14}C$	E/I	Intermediate	High	High	×			Leith et al. (2014), Raymond and Bauer (2001), Schiff et al. (1990)
Chemical properties	E	High	High	High	×		×	Risse-Buhl et al. (2013)
Optical properties	E	High	High	High	×			Fellman et al. (2010)
Fluorescent dyes								
Fluorescein, sodium-fluorescein (uranine)	I	High	High	Low	×	×		Käss et al. (1998), Smart and Laidlaw (1977), Leibundgut et al. (2009)
Rhodamin WT	I	High	High	Low	×	×		Leibundgut et al. (2009), Wilson et al. (1986)
Resazurin	I	High	High	High			×	McNicholl et al. (2007), Haggerty et al. (2008)
Inorganic ions								
Cl^{-}, Br^{-}	I	High	High	Very Low		×		Käss et al. (1998), Bero et al. (2016), Frey et al. (2014)
Other anions and cations								
Rare Earth elements								
e.g. Cerium	E	High	High	Variable	×		×	Davranche et al. (2005), Dia et al. (2000), Gruau et al. (2004), Pourret et al. (2009)
Metabolic products, substrates								
O_2	E		High	High		×	×	Odum (1957), McIntire et al. (1964), Demars et al. (2015)
CO_2, DIC	E/I		High	High			×	Lambert et al. (2014), Wright and Mills (1967)
PO_4^{3-}	E/I		High	High			×	Mulholland et al. (1990), Stream Solute Workshop (1990)
SO_4^{2-}	E/I		High	High			×	Hosono et al. (2014)
DOC (e.g. Acetate)	E/I	Intermediate	Intermediate	High	×		×	Shaw and McIntosh (1990), Baker et al. (1999)
Stable isotopes								
$\delta^{15}N$, $\delta^{18}O$, $\delta^{13}C$, $\delta^{33}P$, $\delta^{34}S$	E/I		High	High		×	×	Newbold et al. (1981), Sigman et al. (2001), Mulholland et al. (2009)
Strontium (^{87}Sr, ^{86}Sr)	E	Intermediate	Intermediate	Very Low	×			Graustein (1989), Wang et al. (1998)
Particulate								
Artificial sweeteners								
Acersulfame-K, sucralose	E	High	High	Very Low	×			Buerge et al. (2009), Lubick (2009), Scheurer et al. (2009)
Pharmaceuticals drugs								
Carbamazepine, sulfamethoxazole, and diclofenac, caffeine, triclosan, and naproxen	E	High	High	High	×			Arvai et al. (2014), Lubick (2009), Riml et al. (2013), Andreozzi et al. (2002), Clara et al. (2004), Kurissery et al. (2012), Durán-Álvarez et al. (2012), Buerge et al. (2003), Liu et al. (2014), Chefetz et al. (2008)
Particles								
Chaff, nano-particles, clay, kaolinite, fluorescent microspheres	I	High	High	variable		×		Davis et al. (1980), Packman et al. (2000a, 2000b), Arnon et al. (2010)
Synthetic DNA (coated or naked)	I	High	High	Low		×		Foppen et al. (2013), Mahler et al. (1998), Sharma et al. (2012)
Particulate organic matter (POM)	E/I	Intermediate	High	variable	×	×	×	Newbold et al. (2005), Trimmer et al. (2012), Drummond et al. (2014)
Macroinvertebrates	E	Intermediate	High		×	×	×	Dole-Olivier and Marmonier (1992), Marmonier et al. (1992), Capderrey et al. (2013), Blinn et al. (2004)
Terrestrial diatoms	E	High	High	Moderate	×			Pfister et al. (2009), Klaus et al. (2015), Tauro et al. (2015), Klaus et al. (2015), Naicheng Wu et al. (2014), Coles et al. (2015)
Bacteria								
Fecal coliforms	E	High	High	Moderate	×			Leclerc et al. (2001), Stapleton et al. (2007), Characklis et al. (2005), Weaver et al. (2013)
Non coliforms	E	High	High	Moderate	×		×	Bakermans et al. (2002), Bakermans and Madsen (2002), Jeon et al. (2003)
Virus								
Pathogens	E	High	High	High	×	×		Harwood et al. (2014), Updyke et al. (2015)
Bacteriophages	E	High	High	High	×	×		Keswick et al. (1982), Rossi et al. (1998), Goldscheider et al. (2007), Shen et al. (2008), Hunt et al. (2014)

Table 1 (*continued*)

Tracer	Type	Specificity	Detectability	Reactivity	Flowpath	Residence time	Biogeochemical transformation	References
Other								
Water temperature	E/I	Intermediate	Low	High	×	×		Carslaw and Jaeger (1986), Stallman (1965), Rau et al. (2014), Hannah and Garner (2015)
Water isotopes (^{3}H, δ^{2}H, δ^{18}O)	E/I	Intermediate	High	Very Low	×	×		Rodhe (1998)

spectrometers has substantially decreased the cost of water isotope analysis, opening up new possibilities for spatially extensive or high frequency measurements (Jasechko et al., 2016; Lis et al., 2008; McDonnell and Beven, 2014).

3.1.2. Solute tracers: pharmaceuticals, ions, dyes, and DOM

While solutes are typically more reactive and have different transport dynamics from the water that carries them, the sheer number of different species that can be measured allows for great specificity in determining water flowpaths. A wide variety of solutes including natural ions, anthropogenic pollutants, fluorescent dyes, and dissolved carbon have been used as environmental tracers to determine water source and flowpath (Hoeg et al., 2000; Kendall and McDonnell, 2012). Solute concentrations and isotopic signatures can convey complementary information, for example strontium (Sr) concentration can distinguish surface and subsurface water, while the $^{87}Sr/^{86}Sr$ ratio which varies between bedrock formations, can reveal regional provenance (Ettayfi et al., 2012; Graustein, 1989; Wang et al., 1998). When many solute concentrations are available, correlated parameters are often combined into principal components before determining water sources via end member mixing analysis (Christophersen and Hooper, 1992). While end member mixing analysis is widely used and provides straightforward estimates of conceptual flowpaths, it is sensitive to the assignment of end members, the selection of tracers, and the assumption of conservancy in solute behavior (Barthold et al., 2011). As always, using multiple tracers of different types (e.g. stable isotopes and solutes) results in more robust and reliable mixing models (Bauer et al., 2001).

Pharmaceuticals and other synthetic compounds have contaminated most aquatic environments and are increasingly being used to trace agricultural and urban wastewater sources and flowpaths (Durán-Álvarez et al., 2012; Liu et al., 2014; Roose-Amsaleg and Laverman, 2015; Stumpf et al., 1999; Ternes, 1998; Tixier et al., 2003). Analyses for many of these compounds have become routine due to emerging concern for human and ecosystem health, bringing down costs and improving detectability (Andreozzi et al., 2002; Clara et al., 2004; Kurissery et al., 2012). Many of these compounds are bioactive or adsorb to

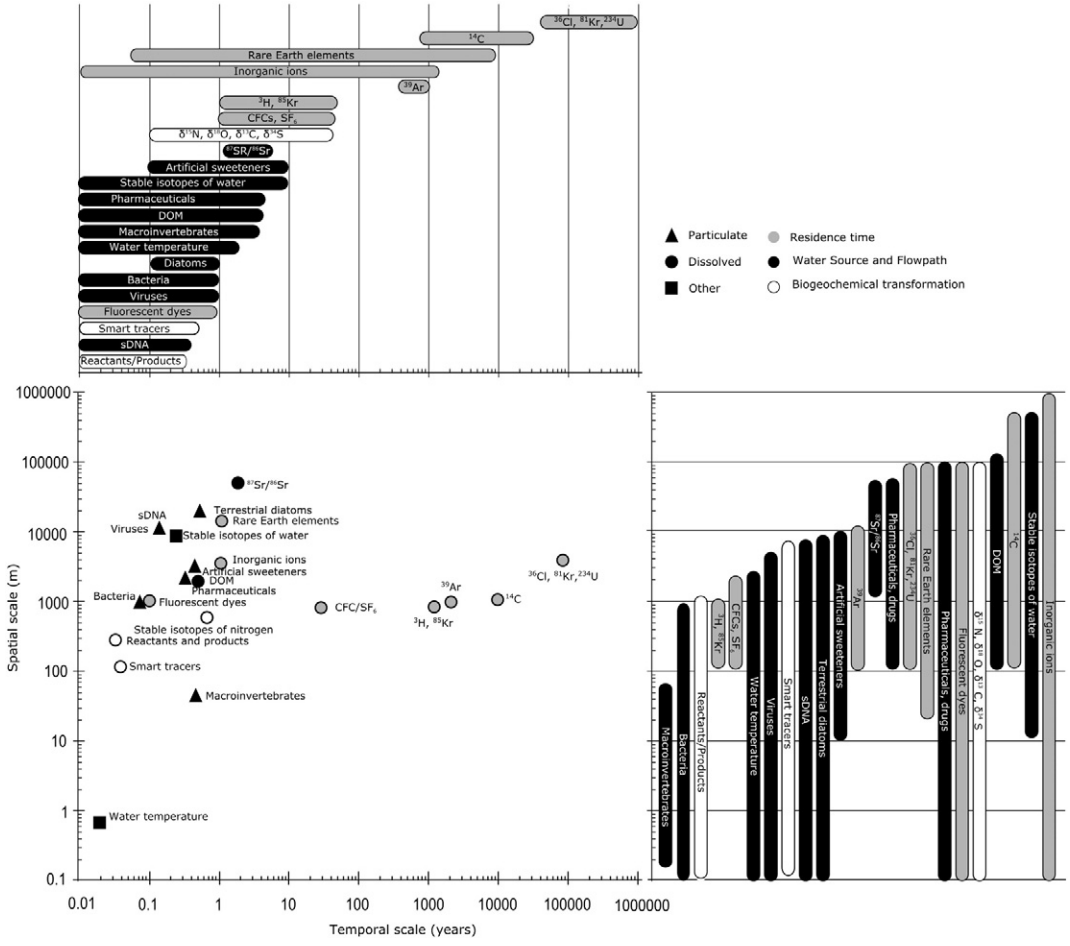


Fig. 4. A variety of ecohydrological tracers organized by temporal and spatial scale. The range of scales reported in the literature for each tracer or group of tracers is indicated by the bars with the points representing the typical or most common scales of use. Shading represents fundamental ecohydrological question (where does water go, how long does it stay, and what happens along the way) and shape represents tracer type.

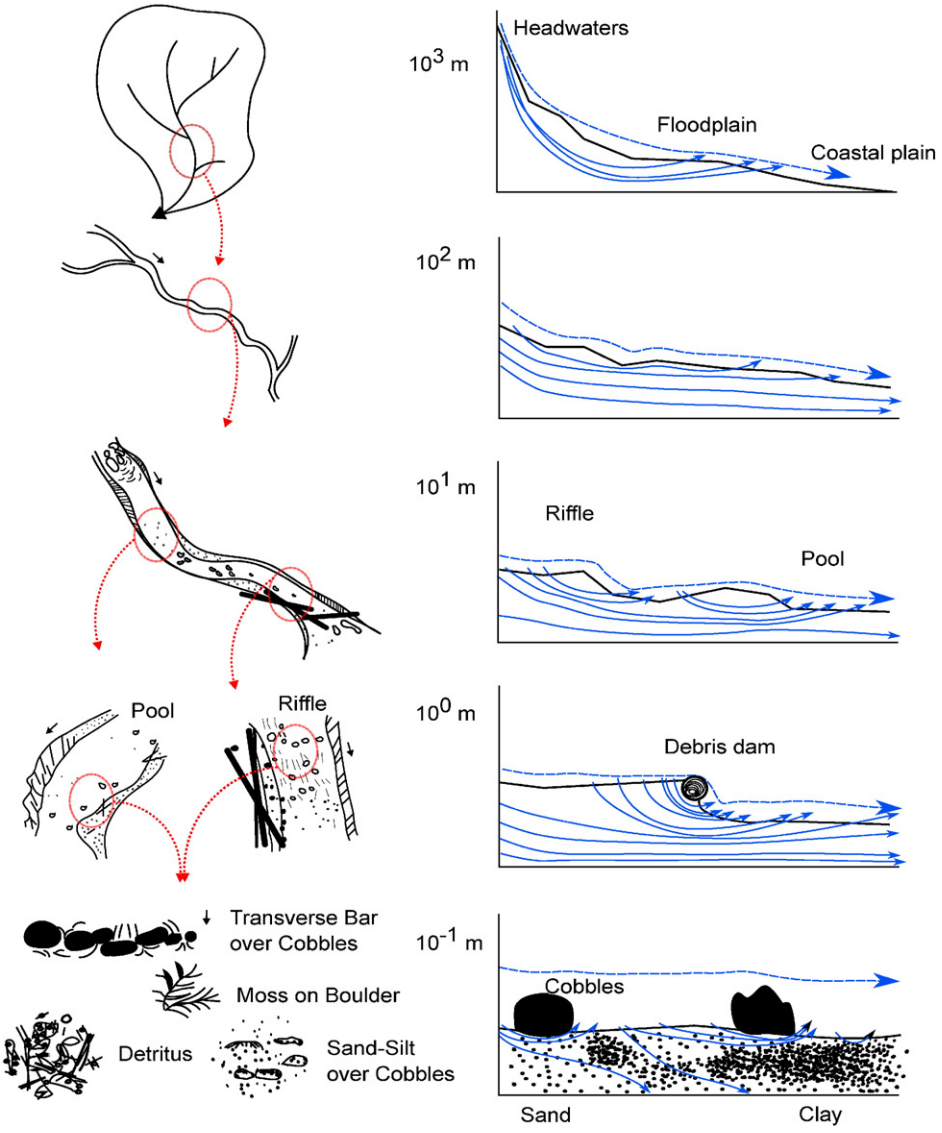


Fig. 5. Hierarchical spatial scales from an ecohydrological perspective for various catchment components. Relevant physical and ecological controls on flowpath, residence time, and biogeochemical reaction often change with scale, requiring the use of tracers with different characteristics. Adapted from Frissell et al. (1986).

sediment (e.g. caffeine, triclosan, and naproxen), limiting most applications to small temporal and spatial scales (Buerge et al., 2003; Chefetz et al., 2008; Durán-Álvarez et al., 2012). However, artificial sweeteners (e.g. acesulfame-K and sucralose) and some drug compounds (e.g. carbamazepine, sulfamethoxazole, and diclofenac) appear to be resistant to degradation for several weeks under a range of conditions and could be used as biomarkers of human activity (Arvai et al., 2014; Buerge et al., 2009; Lubick, 2009; Riml et al., 2013; Scheurer et al., 2009). The biodegradability of some pharmaceuticals (e.g. tetracycline) decreases with redox potential (Cetecioglu et al., 2013), meaning their concentration relative to more resistant compounds could be used to quantify anoxia, though to our knowledge this approach has not yet been used.

In addition to environmental tracers that are already present in a system, experimentally injected solutes have long been used to quantify flowpath and water source. Synthetic fluorescent dyes such as fluorescein have been used since the end of the 19th century and are still widely used today to test connectivity and water transfer (Flury and Wai, 2003; Smart and Laidlaw, 1977). Fluorescent dyes express a range of reactivity and offer outstanding detectability and specificity, with some dyes such as fluorescein and rhodamine WT detectable at concentrations in the parts per trillion range (Turner et al., 1994). Most dyes suitable for duty as flowpath tracers have sulfonic acid groups and are synthesized from sodium salts to increase solubility in water (Cai and Stark, 1997; Leibundgut et al., 2011). Emission wavelengths are characteristic for each dye, making it possible to combine multiple dyes with different properties (Haggerty et al., 2008; Lemke et al., 2014). Drawbacks to fluorescent dyes include a relatively small number of suitable dyes (less than ten families), sensitivity to pH and temperature, adsorption to sediment, and relatively high cost depending on how much dye is needed (Leibundgut et al., 2011).

Dissolved carbon compounds are some of the most versatile solute tracers and also some of the most complex. Unlike the single-compound tracers discussed above, DOM consist of thousands of different compounds with distinct properties (Cole et al., 2007; Zsolnay, 2003) and turnover times that can vary from minutes to millennia (Abbott et al., 2014; Catalá et al., 2015; Hansell and Carlson, 2001). DOM chemical composition, isotopic signature, optical properties, and stoichiometry constitute a highly detailed signature or fingerprint that can be used to determine water source and flowpath (Clark and Fritz, 1997; Schaub and Alewell, 2009). Using multiple DOM characteristics allows DOM to effectively be crossed with itself, e.g. simultaneously determining flowpath, residence time, and biogeochemical transformation (Chasar et al., 2000; Helton et al., 2015; Palmer et al., 2001; Raymond

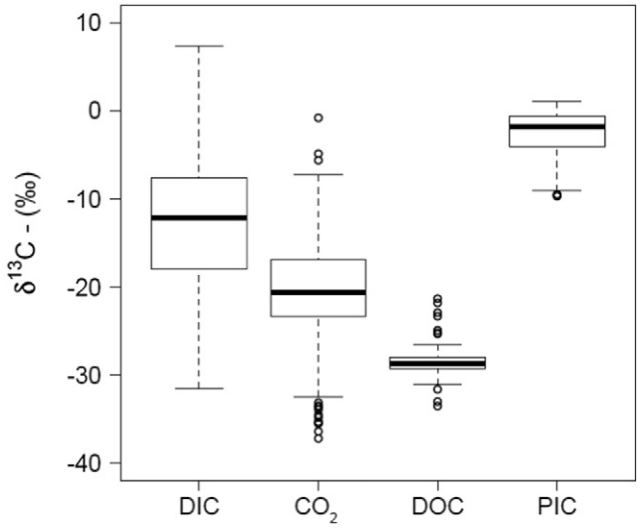


Fig. 6. A meta-analysis including unpublished data of $\delta^{13}C$ values observed in streams and rivers across the globe for dissolved inorganic carbon (DIC), particulate inorganic carbon (PIC), dissolved organic carbon (DOC), and dissolved CO_2. Note that mostly C_3 plant dominated catchments are included.

and Bauer, 2001). While DOM has incredible specificity, it is the primary food and nutrient source for microbial food webs and is therefore highly reactive (Evans and Thomas, 2016; Jansen et al., 2014). Nonetheless, at the catchment scale, DOM concentration is often assumed to be conservative and is regularly included with other solutes to determine water source in end member mixing analysis (Larouche et al., 2015; Morel et al., 2009; Striegl et al., 2005; Voss et al., 2015). Stable and radioactive carbon isotopes of DOM, particulate organic matter (POM), and dissolved inorganic carbon (DIC) have been used to distinguish surface water from groundwater as well as determine connectivity between terrestrial and aquatic environments (Doucett et al., 1996; Farquhar and Richards, 1984; Marwick et al., 2015). Because the $\delta^{13}C$ of dissolved carbon derived from algae and terrestrial plants differs in some environments, $\delta^{13}C$ of dissolved carbon can be used to separate terrestrial and aquatic water and carbon sources (Fig. 6; Mayorga et al., 2005; Myrttinen et al., 2015; Rosenfeld and Roff, 1992; Tamooh et al., 2013; Telmer and Veizer, 1999). The $\Delta^{14}C$ of DOM and POM, an indicator of time since fixation from the atmosphere, has been used to separate depth of flowpaths (e.g. modern surface soil carbon versus deeper, older sources) and also as a general indicator of agricultural and urban disturbance (Adams et al., 2015; Butman et al., 2014; Vonk et al., 2010).

There are many methods to characterize DOM molecular composition (e.g. exclusion chromatography, nuclear magnetic resonance, thermally assisted hydrolysis and methylation-gas chromatography-mass spectrometry, and Fourier transform infrared spectroscopy-mass spectrometry) and optical properties (e.g. ultraviolet-visible absorption spectra and fluorescence spectroscopy; Jaffé et al., 2012; Jeanneau et al., 2014; Spencer et al., 2015). Often the post-processing of these measurements is as technically involved as the measurements themselves (Chen et al., 2003; Jaffé et al., 2008; Stedmon and Bro, 2008), and interpreting the ecological relevance of the outputs of these analyses remains a major challenge and area of active research (Fellman et al., 2009; Huguet et al., 2009; Spencer et al., 2015; Zsolnay, 2003). Consequently, analyses of DOM composition and optical properties are often most useful when paired with field or laboratory assays of DOM reactivity or biodegradability (McDowell et al., 2006; Vonk et al., 2015). The recent development of field-deployable fluorometers and spectrometers has allowed real-time monitoring of DOM characteristics to determine changes in water source and flowpath (Baldwin and Valo, 2015; Downing et al., 2009; Fellman et al., 2010; Khamis et al., 2015; Sandford et al., 2010; Saraceno et al., 2009). For example total fluorescence has been used to trace infiltration of surface water into karst systems and protein-like fluorescence has been used as an indicator of fecal bacteria and DOM biodegradability (Balcarczyk et al., 2009; Baldwin and Valo, 2015; Quiers et al., 2013). Excitation-emission matrices of DOM (Chen et al., 2003) have been used to trace landfill leaching into rivers, with signals detectable at dilutions of 100–1000 fold, suggesting this detection method is fast and cost-effective for river managers and water quality regulators (Baker, 2005; Harun et al., 2015, 2016).

3.1.3. Particulate tracers: synthetic particles, bacteria, viruses, and invertebrates

Particulate tracers such as chaff and sediment have been used for thousands of years to make invisible flowpaths visible (Davis et al., 1980). Bacteria were first used to trace water source before the advent of germ theory when John Snow traced the London Broad Street cholera outbreak to sewage-contaminated water from the Thames and local cesspits (Snow, 1855). More recently, a wide range of particles including biomolecules, viral particles, bacteria, biofilms, diatoms, colloids, and macroinvertebrates have been implemented to trace flow and water source (Capderrey et al., 2013; Foppen et al., 2013; Mendoza-Lera et al., 2016; Rossi et al., 1998). Particles can have extremely high specificity and detectability and have been used in a variety of environments including flowing surface waters, lakes, groundwater, and marine environments (Ben Maamar et al., 2015; Garneau et al., 2009; Harvey and Ryan, 2004; Vega et al., 2003). While particles travel through complex media differently than the water that moves them, this is an advantage when the goal is to trace particulate transport such as sediment or POM. Because POM is an important carbon and nutrient source in aquatic ecosystems (Pace et al., 2004; Vannote et al., 1980), tracing its transport and accumulation provides insight into the development of hot spots and moments (Drummond et al., 2014; Vidon et al., 2010); see Section 3.3).

Bacteria are the most common particulate tracer, with fecal coliforms routinely used to identify human contamination of water sources (Leclerc et al., 2001). The purposeful use of bacteria as tracers began with an antibiotic-resistant strain of the bacterium *Serratia indica* which was readily assayed by its bright red colonies on nutrient agar media (Ormerod, 1964). Subsequent applications combined actively reproducing *Serratia indica* with dormant *Bacillus subtilis* spores that behaved as conservative tracers, to model dispersion and transit times of a field of sewage discharge to a coastal zone (Pike et al., 1969). Starting in the 1970s, improved imaging techniques allowed viruses, particularly bacteriophages, to be used as tracers of groundwater and ocean circulation (Hunt et al., 2014). Because of their small size, high host-specificity, low cost of detection, and resistant physical structure, bacteriophages tend to perform better than bacteria or yeasts, particularly in groundwater applications (Rossi et al., 1998; Wimpenny et al., 1972), suggesting that bacteriophages could fill an important gap in the current hydrogeology toolbox. Improvements in quantitative polymerase chain reaction techniques and biosynthesis technologies have lowered costs of bacterial and viral analyses and opened the way for a new generation of high specificity, high detectability tracers.

Still smaller than bacteriophages, environmental and synthetic DNA (eDNA and sDNA, respectively) have extremely high specificity and detectability and relatively low reactivity (Deiner and Altermatt, 2014; Foppen et al., 2013). While extracellular eDNA has primarily been used for species detection in freshwater environments (Ficetola et al., 2008; Vorkapic et al., 2016), it also has potential as a hydrologic tracer, with eDNA from lacustrine invertebrates used to trace lake water up to 10 km from its source (Deiner and Altermatt, 2014). Tracer sDNA is produced by automatic oligonucleotide synthesis and is normally short (less than 100 nucleotides), which allows approximately limitless unique sequences ($4\ \text{nucleotides}^{100} = 1.61 \times 10^{60}$). Stop codons distinguish the sDNA from eDNA, and injected sDNA is analyzed by quantitative polymerase chain reaction with custom primers. sDNA has been used to trace sediment transport when bound with montmorillonite

clay (Mahler et al., 1998) and in combination with magnetic nano-particles (e.g. polylactic acid microspheres and paramagnetic iron particles) to enhance recoverability and durability in the environment (Sharma et al., 2012). Though high tracer losses (50 to 90%) can occur immediately after injection, the remaining sDNA shows transport dynamics similar to chloride or bromide and is stable for weeks to months (Foppen et al., 2011, 2013; Sharma et al., 2012).

Diatoms (eukaryotic microalgae; 2–500 μm) have long been used as indicators of water quality (Rushforth and Merkley, 1988) and more recently as tracers of flowpath (Pfister et al., 2009). The timing and abundance of the arrival of terrestrial diatoms to the stream channel can indicate the source of stormflow and the extent and duration of hydrologic connectivity across the hillslope-riparian-stream continuum (Pfister et al., 2009). Because some terrestrial diatoms are associated with certain landscape positions or land-use types, this tracer has high specificity, though sample analysis requires substantial expertise (Martínez-Carreras et al., 2015; Naicheng Wu et al., 2014). The possibility of using quantitative polymerase chain reaction techniques to automate diatom identification and quantification could increase the availability and applications of this approach.

Finally, macroinvertebrates (aquatic insects, crustaceans, mollusks, and worms) have been used as indicators of ecosystem health and to delineate surface and groundwater flowpaths (Boulton et al., 1998; Marmonier et al., 1993). The presence or absence of individual macroinvertebrate species can be used to identify zones of hyporheic exchange as well as to distinguish upwelling from down welling zones both at the bedform and reach scales (Blinn et al., 2004; Capderrey et al., 2013; Dole-Olivier and Marmonier, 1992). For example, the presence of stygobiont species (i.e. species living exclusively in groundwater) in the hyporheic zone is indicative of strong upwelling patterns (Boulton and Stanley, 1996).

3.1.4. Heat tracer techniques

Water temperature is an extremely reactive tracer with low specificity and detectability that has nevertheless been widely used to identify water source and flowpath by exploiting thermal differences in groundwater, surface water, and precipitation (Anderson, 2005; Constantz, 2008; Hannah et al., 2008; Krause et al., 2014). Similar to water isotopes, heat is a property of the water itself, rather than a solute or particle. However, unlike isotopes, thermal signature is very rarely conservative over long distances or times. Heat is an effective tracer at ecohydrological interfaces where it has been used to predict the behavior of aquatic organisms in streams (Ebersole et al., 2001, 2003; Torgersen et al., 1999) and to understand the impact of groundwater-surface water exchange flows on catchment-scale biogeochemical budgets (Brunke and Gonser, 1997; Krause et al., 2011; Woessner, 2000). Until recently, the thermal resolution of most temperature sensors has been quite low and temperature data has been limited to point measurements. The development of distributed temperature sensing (DTS) was a watershed moment for heat tracers since DTS allows large-scale, fine resolution temperature measurements. DTS takes advantage of temperature-sensitive properties of standard or specialized fiber optic cable to quantify temperature along the length of the cable (Selker et al., 2006a; Tyler et al., 2009; Westhoff et al., 2007). Because cable can be deployed in any configuration, DTS allows quantification of vertical, lateral, and longitudinal flowpaths and fluxes. Cables in riverbeds have been used to detect spatial variability of groundwater discharge and recharge (Lowry et al., 2007; Mamer and Lowry, 2013; Mwakanyamale et al., 2012; Selker et al., 2006b), identify and model lateral inflows (Boughton et al., 2012; Westhoff et al., 2007), and assess the role of solar radiation and riparian vegetation shading on stream heat exchange (Boughton et al., 2012; Petrides et al., 2011). Cable can be wrapped around poles to increase spatial resolution and installed in streambeds to monitor vertical hyporheic and groundwater flowpaths (Briggs et al., 2012; Lautz, 2012; Vogt et al., 2010). With "active" DTS, heat pulses can be sent along the length of the cable to determine thermal conductivity of the soil and water matrix (Ciocca et al., 2012). In combination with solute or particulate proxies, heat could be a sensitive tracer of changes in water source during storm events and of how much and how fast water moves between different compartments of the catchment.

Another technological breakthrough in heat tracing was the development of thermal imagery techniques that can remotely measure surface and shallow subsurface water temperatures from satellites, airborne platforms, or on the ground (e.g. Cherkauer et al., 2005; Deitchman and Loheide, 2009; Durán-Alarcón et al., 2015; Jensen et al., 2012; Lalot et al., 2015; Lewandowski et al., 2013; Pfister et al., 2010; Schuetz and Weiler, 2011; Stefan Kern et al., 2009; Wawrzyniak et al., 2013). Though quantification of thermal images remains challenging, thermal imaging is a valuable complement to other tracers of flowpath and water source because it makes intersecting water masses visible at ecohydrological interfaces. It has proven effective in characterizing in-stream flowpaths, lateral water exchanges, groundwater inputs, and distribution of thermal refugia (Dugdale et al., 2015; Jensen et al., 2012; Johnson et al., 2008; Lewandowski et al., 2013; Pfister et al., 2010).

3.2. Residence time: how long does it stay there?

Where water goes is closely connected to how long it stays there. Water residence time is a key parameter that influences hydrology, biogeochemistry, and ecology at the catchment scale and within different catchment components (Fig. 5; Kirchner, 2016b). Because residence time is directly proportional to the volume of water, it is also important for management of water resources (Collon et al., 2000; Scanlon et al., 2002). Compared with the infinite variety of potential water sources and flowpaths, residence time is satisfyingly straightforward. It is defined as the amount of time a mass of water stays in a domain of interest (e.g. catchment, reach, bedform; Fig. 4) and can mathematically be described as pool size (amount of water) divided by the rate of inflow (input residence time) or outflow (output residence time), or as the distribution of water ages in the domain of interest (storage residence time; Davies and Beven, 2015). The similarity or divergence of these three parameters of residence time depends on spatiotemporal scale and changes in storage, which can alter interpretation of modeling and tracer estimates of residence time (Botter et al., 2010; Rinaldo et al., 2011). The simplest and most common metric of residence time is the mean residence time, but for many practical problems (e.g. prediction of contaminant propagation or removal) it is desirable to know the residence time distribution or transit time distribution, which can be modelled based on environmental or injected tracer data (Eriksson, 1971; Gilmore et al., 2016; McGuire and McDonnell, 2006; Stream Solute Workshop, 1990). Because residence time is defined by the chosen spatial realm, it is inherently scalable across point, hillslope, catchment, and landscape scales (Fig. 5; Asano et al., 2002; Maloszewski and Zuber, 1993; Michel, 2004; Poulsen et al., 2015; Vaché and McDonnell, 2006), though the relative influence of antecedent storage, celerity, and the ratio of new to old water on residence time varies with scale (Davies and Beven, 2015).

Residence time is central to the HotDam framework because it is necessary to calculate rates of biogeochemical transformation and because the amount of time water, solutes, and particulates spend in different catchment components can determine the location and duration of hot spots (McClain et al., 2003; Oldham et al., 2013; Pinay et al., 2015). Residence time at event and seasonal scales is commonly modeled based on hydrograph analysis. While this method has been very effective at predicting water discharge, it cannot separate young and old outflow due to the celerity problem (see Section 2) and therefore cannot reliably determine residence time on its own (Clark et al., 2011; McDonnell and Beven, 2014). Tracer methods in conjunction with hydrometric analysis can overcome this problem by determining flowpath (Martinec, 1975; Poulsen et al., 2015; Tetzlaff et al., 2015) or

water age directly (Gilmore et al., 2016; Rodhe et al., 1996). Techniques for determining residence time have been reviewed in great detail elsewhere (Darling et al., 2012; Fontes, 1992; Foster, 2007; Hauer and Lamberti, 2011; Kendall and McDonnell, 2012; Kirchner, 2016b; Payn et al., 2008; Plummer and Friedman, 1999; Scanlon et al., 2002), so in this section we will focus on how crossed-proxy methods could be brought to bear to quantify and reduce uncertainty, organized by spatial and temporal scale.

3.2.1. Determining residence time in fast systems

For rapid-transit systems with residence times on the order of minutes to months (e.g. bedforms, river networks, shallow soils, and small lakes), most methods of measuring residence time use injected tracers (Bencala and Walters, 1983; Stream Solute Workshop, 1990). All methods for determining residence time by tracer injection work on the same basic principle. Assuming that a tracer has the same transport dynamics as water, its rate of dilution after injection is proportional to the renewal time of a system. Mean residence time and the distribution of residence times can be calculated from the overall rate of disappearance and the change in removal rate over time, respectively (Payn et al., 2008; Schmadel et al., 2016; Wlostowski et al., 2013). Conservative behavior of the selected proxy is therefore paramount, since removal by any processes other than dilution and advection (e.g. biological, chemical, or physical reactivity) will directly bias the estimate of residence time (Nyberg et al., 1999; Ward et al., 2013). Tracers can be added instantaneously or at a known, constant rate depending on the size of the system and the desired level of detail for the distribution of residence times (Payn et al., 2008; Rodhe et al., 1996; Wlostowski et al., 2013). For surface water systems (e.g. streams), tracer concentration is measured at a downstream sampling point, and for subsurface systems, tracer propagation can be monitored via wells (Zarnetske et al., 2011) or electric resistance tomography for electrically conductive tracers such as salts (González-Pinzón et al., 2015; Kemna et al., 2002; Pinay et al., 1998, 2009). The shape of the breakthrough curve (the change in tracer concentration over time at the sampling point) represents the distribution of residence times. Adequate sampling of the tail of the break through curve is important to capture slower flowpaths and because flowpaths with residence times longer than the arbitrary duration of the monitoring will be missed (González-Pinzón et al., 2015; Schmadel et al., 2016; Ward et al., 2013). Tracers with high detectability that can be monitored continuously (e.g. fluorescent dyes or sodium) are particularly well suited to determine residence time. There is a huge diversity of more or less conservative tracers that have been used to determine short-term residence time including isotopically labelled water (Nyberg et al., 1999; Rodhe et al., 1996), solutes such as chloride, bromide, and fluorescent dyes (González-Pinzón et al., 2013; Payn et al., 2008), dissolved gases such as propane, sulfur hexafluoride (SF6), and chlorofluorocarbons (CFCs; Molénat et al., 2013; Soares et al., 2013; Thompson et al., 1974; Wallin et al., 2011), particulates like sDNA, viral particles, and nanoparticles (Foppen et al., 2011, 2013; Hunt et al., 2014; Ptak et al., 2004; Sharma et al., 2012), and even hot water (Rau et al., 2014).

For systems with residence time greater than a few days but less than a year (e.g. hillslopes, headwater catchments, and the non-saturated zone), hydrometric methods such as mass balance or hydrograph decomposition are often used to estimate residence time (Kirchner, 2016b; McDonnell and Beven, 2014; Poulsen et al., 2015). For systems with available background chemistry data, it is possible to directly trace residence time using variation in system inputs (i.e. precipitation or upstream inflow). Typically the isotopic or chemical signature of precipitation or inflow over time is compared with the signature of system outflow (McGuire et al., 2002; Peralta-Tapia et al., 2015; Rodhe et al., 1996; Stewart and McDonnell, 1991; Stute et al., 1997). The integrated discharge and timing of the arrival of the distinct water mass in different system components allows the calculation of reservoir size and residence time.

3.2.2. Residence time in slow systems

For systems with residence times longer than a year, injected tracer methods are obviously not practical due to time constraints, not to mention the inordinate mass of tracer that would need to be injected into the system. For slow systems, a variety of environmental tracer methods have been used including historical or current anthropogenic pollution, naturally occurring geochemical tracers, and known paleo conditions (Aquilina et al., 2012, 2015; Böhlke and Denver, 1995; Kendall and McDonnell, 2012; Plummer and Friedman, 1999; Schlosser et al., 1988).

For "young" groundwater less than 50 years old, radioactive tritium (^{3}H) from aboveground nuclear testing in the 60s and 70s, radioactive krypton (^{85}Kr) produced during reprocessing of nuclear rods, and CFCs and SF6 from manufacturing have been used to determine the time since a water parcel was last in contact with the atmosphere (Fig. 7; (Ayraud et al., 2008; Leibundgut et al., 2011; Lu et al., 2014). Dating with these tracers relies on comparing the concentration in the groundwater sample with known historical atmospheric concentrations after applying a solubility constant based on recharge temperature and atmospheric partial pressure. ^{3}H and ^{85}Kr have half-lives ($t_{1/2}$) of 12.3 and 10.8 years, respectively, meaning an additional correction must be applied to back calculate initial concentration. The ratio of ^{3}H to ^{3}He (the radioactive decay product of ^{3}H) is often used to achieve greater certainty and precision in this correction (Schlosser et al., 1988). ^{3}H is attractive as a tracer because it recombines with water and therefore has the same transport dynamics, though drawbacks include its short window of production and uneven global distribution (Fig. 7b). As noble gases, ^{85}Kr and ^{3}He are biochemically highly conservative, but dispersion and degassing can complicate interpretation. Until recently, large sampling volumes (>1000 L) were needed for ^{85}Kr and other radionuclide analyses. The development of atom trap trace analysis (ATTA) and advanced gas extraction techniques are bringing these volumes down, though sampling procedures are still non-negligible (Lu et al., 2014). CFCs are synthetic organic compounds that were used in

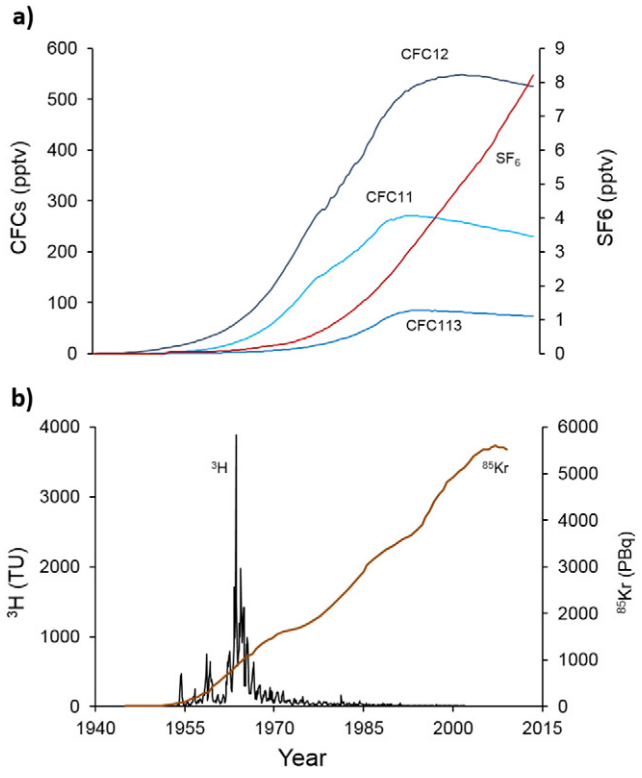


Fig. 7. Atmospheric concentrations of a) chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6) produced for refrigeration and insolation, and b) tritium (^{3}H) and ^{85}Kr produced from nuclear testing and rod reprocessing. Data from Ahlswede et al. (2013) and water.usgs.gov/lab/software/air_curve

refrigerants from the 1930s to the 1990s. Trace concentrations of many CFCs, some of which are detectable at extremely low levels, were incorporated into the hydrological cycle, allowing groundwater dating with small sample volumes (<1 L). CFCs have been widely used to date groundwater and ocean residence times (Ayraud et al., 2008; Bullister and Weiss, 1983; Gammon et al., 1982; Hahne et al., 1978; Hammer et al., 1978; Kolbe et al., 2016; Lovelock et al., 1973; Thiele and Sarmiento, 1990). The fact that most CFC concentrations have peaked and are now decreasing means a single concentration can correspond to multiple eligible dates (Fig. 7a). Crossing multiple CFCs with different atmospheric curves is therefore necessary for definitive dating. The success of the Montreal Protocol of 1987 which banned CFC manufacturing means CFC concentrations will soon be too low for effective dating. Fortunately for ecohydrologists, another anthropogenic gas, sulfur hexafluoride (SF_6), is monotonically increasing (Fig. 7a). SF_6 is used primarily as an insulator in electronic components and is very conservative, though it has the limitations of other gas tracers, namely rapid equilibration with the atmosphere in open systems (Glover and Kim, 1993). Current techniques allow SF_6 dating of waters that lost contact with the atmosphere after 1990. Another approach to dating young groundwater is to use the concentration of weathering products as a proxy of residence time (Tesoriero et al., 2005). While dissolution rates are non-linear at very low and very high concentrations, some elements such as silica appear to be suitable for dating groundwater between 2 and 60 years old (Becker, 2013), approximately the same time period previously covered by CFCs.

For "old" groundwater with a residence times longer than 50 years, most dating methods depend on atomic decay of cosmogenic radionuclides such as ^{14}C and ^{39}Ar (Leibundgut et al., 2011; Lu et al., 2014). For example, ^{14}C is created naturally in the upper atmosphere due to the recombination of a nitrogen atom with a free neutron (Geyh et al., 2000). ^{14}C makes its way directly to the water table as dissolved CO_2 in precipitation or indirectly as respired CO_2 in the soil. When groundwater loses contact with the atmosphere its ^{14}C content starts to decrease, acting as an atomic clock (Fontes, 1992). Datable ages and precision depend on sensitivity of the analytical techniques and the half-life of the radionuclide. The most common radionuclides in order of increasing half-life are ^{39}Ar ($t_{1/2}$ = 269 a), ^{14}C ($t_{1/2}$ = 5730 years), ^{234}U ($t_{1/2}$ = 25 ka), 81Kr ($t_{1/2}$ = 230 ka), and ^{36}Cl ($t_{1/2}$ = 300 ka; (Bauer et al., 2001; Collon et al., 2000; Lu et al., 2014). There are several important confounding factors to account for when using any radioactive nuclide, including variation in the background rate of production of the radionuclide, anthropogenic sources, degree of mixing in the atmosphere, geologic sources, and sometimes complex equilibrium dynamics in the non-saturated zone above the water table (Ahlswede et al., 2013; Han and Plummer, 2013; Lu et al., 2014).

One of the major limitations of both young and old groundwater tracers is that none have a unique source and almost none are completely conservative (with the possible exception of ^{3}H). Radionuclides such as ^{39}Ar and gases such as SF_6 can be produced geologically at rates sufficient to obscure the atmospheric signal on decadal timescales (Lehmann et al., 1993) and anthropogenic tracers such as CFCs can be degraded, particularly in anoxic zones typical of soils and wetlands (Oremland et al., 1996), the very environments where determining residence time is the most important for anaerobic metabolisms such as denitrification.

3.2.3. Modeling residence time distributions from tracer data

Each of the measures described above provides a single apparent age (equivalent to the mean residence time) which does not reflect the diversity of flowpaths and residence times characteristic of natural systems (McCallum et al., 2014a). With crossed-proxy estimates of residence time and flowpath, it is possible to model the continuous distribution of residence times (Aquilina et al., 2012; Kolbe et al., 2016; Massoudieh et al., 2014) and consequently the distribution of *Da* (Oldham et al., 2013). The two major approaches for modeling residence time distributions from tracer estimates depend on either multiple independent residence time proxies (the shape-free method) or prior information about the shape of the residence time distribution (lumped-parameter approach; Turnadge and Smerdon, 2014, Marçais et al., 2015).

The shape-free interpretation method represents the residence time distribution as a histogram with a limited number of bins based on multiple environmental tracers of residence time (e.g. ^{85}Kr, SF_6, and CFCs; Fienen et al., 2006; Massoudieh et al., 2014; McCallum et al., 2014b; Visser et al., 2013). Because the atmospheric chronicles for many current tracers are similar (Fig. 7), some of this information is redundant and quantitative Bayesian methods or qualitative screening should be used to extract the salient information and avoid introducing epistemic error (Beven and Smith, 2015; Sambridge et al., 2013).

The second and more common method is the lumped-parameter approach (Jurgens et al., 2012; Maloszewski and Zuber, 1996; Marçais et al., 2015). It can be carried out with fewer tracer estimates of residence time but requires selection of a distribution model a priori. The simplest models are the Dirac and exponential distributions, representing piston-flow advective transport (Begemann and Libby, 1957), and well-mixed advective-diffusive-dispersive transport (Gelhar and Wilson, 1974), respectively. Both have a single degree of freedom and can be calibrated by a single tracer concentration, but they represent widely differing groundwater flow and transport conditions. The Dirac model is appropriate for estimating residence time in areas where flow lines are diverging and where dispersion can be neglected compared to advection (high Péclet numbers; (Koh et al., 2006; Solomon et al., 2010), whereas the exponential model is more relevant for well mixed areas such as deep sampling wells or areas of flow convergence (Haitjema, 1995; Lerner, 1992). Other distributions have been proposed, a comprehensive list of which can be found in Leray et al. (2016), including inverse Gaussian, gamma, and hybrid distributions to bridge the gap between recharge and discharge areas (Engdahl and Maxwell, 2014; Ozyurt and Bayari, 2003; Zheng and Bennett, 2002).

Successfully calibrated models provide a continuous residence time distribution as well as descriptive parameters of the underlying flow structure, allowing prediction of the development of hot spots and hot moments and shedding light on the overall biogeochemical capacity of the catchment (Eberts et al., 2012; Green et al., 2014; Kolbe et al., 2016; Larocque et al., 2009), the key parameters in the HotDam framework (Pinay et al., 2015). The most critical limitation of both shape-free and lumped-parameter approaches is currently the limited variety and temporal coverage of tracers. While repeated measures can partially compensate for this limitation (Cornaton, 2012; Massoudieh et al., 2014), more abundant and diverse residence time tracers are needed to better constrain model assumptions and allow meaningful comparison between catchments (Thomas et al., in press). Identifying or developing more tracers with distinct properties is a priority for hydrologists and ecologist alike, since the systematic bias (epistemic uncertainty) of models is inversely related to the number and quality of independent estimates used in parameterization and testing (Beven and Smith, 2015).

3.3. Biogeochemical transformation: what happens along the way?

Understanding when, where, and how much biogeochemical alteration occurs as materials pass through a catchment is central to many management issues including assessing ecosystem resilience to human disturbance, evaluating effectiveness of restoration and mitigation efforts, and detecting environmental change (Baker and Lamont-Black, 2001; Gaglioti et al., 2014; Kasahara et al., 2009). The huge diversity of biogeochemical reactions can be simplified in terms of respiration and assimilation (Borch et al., 2010; Nicholls and Ferguson, 2013). Respiration is the catabolic transfer of electrons to fuel synthesis of adenosine triphosphate (ATP), the universal energy currency of life. Assimilation is the anabolic uptake of material to build

proteins, enzymes, organelles, and cells. Respiration reactions are typically not easily reversible (e.g. the reduction of NO_3^- to N_2 during denitrification or O_2 to CO_2 and H_2O during heterotrophic respiration) and therefore represent removal pathways. Assimilation uses energy from respiration to incorporate inorganic elements into organic compounds which can be remineralized, representing temporary retention. Assimilation can therefore only "remove" material under non-steady state conditions (i.e. when biomass is increasing), however, because respiration depends in part on community size or biomass, these parameters are functionally linked. The sum of respiration and assimilation determines the rate of removal and retention of biologically reactive material passing through a system. While abiotic reactions do not technically fall within this biological classification, redox and acid-base reactions are analogous to respiration (removal) and sorption reactions are similar to assimilation (retention). The potential types and rates of respiration and assimilation that can occur depend largely on redox potential (Borch et al., 2010). Redox potential is determined by the presence of different electron donors (reducers such as DOM) and electron acceptors (oxidizers including O_2, Fe^{3+}, NO_3^-, SO_4^{2-}, and CO_2 arranged from greatest to least energy yield; (Schlesinger and Bernhardt, 2012). Determining redox conditions in space and time is key to quantifying exposure time and is of particular importance because redox is a major control on and consequence or the removal of contaminants (e.g. NO_3^-; Zarnetske et al., 2011), the mobility of many nutrients and trace elements including heavy metals (Borch et al., 2010), and the likelihood of mercury methylation (Gilmour and Henry, 1991).

Along with characterizing redox conditions, determining connectivity is one of the biggest challenges in predicting biogeochemical transformation (Pringle, 2003; Soulsby et al., 2015). Connectivity (the transfer of material or energy between subsystems) can be defined in regards to any stock or flux of interest (e.g. water, carbon, heat, organisms, sediment) and is a major control on the development and duration of hot spots and hot moments (McClain et al., 2003; Oldham et al., 2013; Pringle, 2003). Connectivity is a concern at all spatial and temporal scales though it generally is less problematic at shorter temporal scales, where connectivity is relatively stable, and larger spatial scales, where small-scale heterogeneities average out (Pringle, 2003; Rastetter et al., 1992).

Tracers of biogeochemical transformation can be classified as *direct tracers*, which are consumed or transformed by the biogeochemical reaction itself, and *indirect tracers*, which are consumed or transformed when exposed to conditions favorable for the reaction of interest. Indirect tracers are effective at quantifying exposure time (the proportion of residence time when physicochemical conditions are favorable for the reaction of interest) and direct tracers can determine reaction rate, the central parameters in the HotDam framework (Oldham et al., 2013; Pinay et al., 2015). The most common direct tracer techniques include monitoring changes in reactants and products (e.g. O_2 consumption or CO_2 production), fractionation of isotopic signature, and application of "smart" tracers that are modified by the reaction in a measurable way (Fontvieille et al., 1992; Frey et al., 2014; Haggerty et al., 2008; Zarnetske et al., 2012). Indirect tracer methods are more numerous and diverse, but typically rely on the divergence of two or more contextually-reactive tracers such as anomalies in rare earth element concentration (Gruau et al., 2004; Hissler et al., 2014), or overall differences in substrate signature, such as enriched $\delta^{13}C$ for DOC produced in oxic versus anoxic environments (Lambert et al., 2014). In the following sections we summarize current techniques used to directly and indirectly trace biogeochemical reactions, and discuss the role of dissolved carbon as both a tracer and control of assimilation and respiration.

3.3.1. Direct tracers of biogeochemical transformation

Measuring the change in concentration of biogeochemical reactants and products is the most fundamental method of directly tracing biogeochemical transformation. Both environmental and injected tracers can be used to determine transformation, though residence time must be constrained if the rate of transformation is of interest. For injected applications a conservative tracer is added with the reactive tracer to correct for hydrologic losses before calculating the rate of respiration or assimilation (Schmadel et al., 2016; Stream Solute Workshop, 1990). Injected reactants may be labeled with radioactive or stable isotopes to allow quantification of turnover as they pass through different system components or trophic levels (Gribsholt et al., 2009; Mulholland et al., 1985; Pace et al., 2004). Recently, a new method has been developed for flowing systems called *tracer additions for spiraling curve characterization* (TASCC), which quantifies nutrient and carbon transformation at multiple concentrations with a single slug injection (Covino et al., 2010). While this method has so far only been used with injected tracers in streams, it could be adapted to take advantage of natural pulses such as storm events.

In addition to or in conjunction with concentration measurements, the isotopic signatures of solutes have been widely used as direct tracers of biogeochemical transformation (Böttcher et al., 1990; Brenot et al., 2015; Hosono et al., 2014; Zarnetske et al., 2012). Assimilation and respiration can cause isotopic fractionation, enriching residual reactants with the heavy isotope and depleting products. When multiple

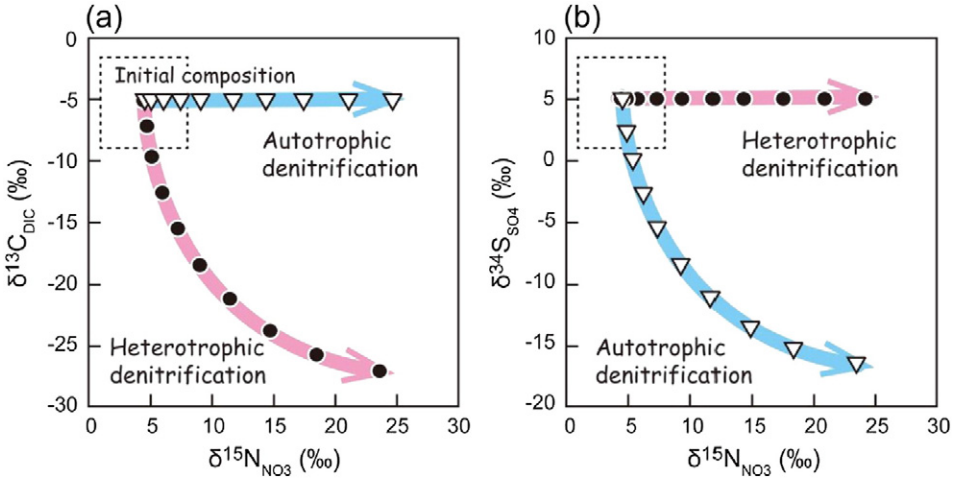


Fig. 8. Theoretical trajectories of carbon, nitrogen, and sulfur stable isotopes for autotrophic and heterotrophic denitrification, demonstrating how crossing isotopic tracers from reactants (NO_3^- and DIC) and products (SO_4^{2-}) allows the partitioning of concurrent biogeochemical reactions. Black circles and pink arrows represent enrichment trajectories of heterotrophic denitrification and white triangles and blue arrows represent autotrophic denitrification. Figure reproduced from Hosono et al. (2014).

concentrations and isotopic ratios are available for reactants and products, simultaneous metabolic pathways can be quantitatively estimated, such as the partitioning of autotrophic and heterotrophic denitrification with stable isotopes of NO_3^-, DIC, and SO_4^{2-} (Fig. 8; Frey et al., 2014; Hosono et al., 2014; Urresti-Estala et al., 2015).

Recent analytical advances have vastly decreased necessary sample volumes and cost for major stable isotope analyses including the development of a bacterial denitrifier method for measuring $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- after bacterial reduction to N_2O (Sigman et al., 2001). Other stable isotope analyses remain somewhat more involved, but straightforward precipitation techniques and availability of elemental analyzers and mass spectrometers have made analysis of $\delta^{13}C$ of DOC and DIC and $\delta^{34}S$ of SO_4^{3-} less costly and time consuming (Hosono et al., 2014; Post, 2002; Zarnetske et al., 2012). The interpretation of isotopic shifts requires a sound understanding of all possible fractionating reactions and usually requires site-specific determination of the initial isotopic signature of reactants. Furthermore, fractionation does not occur all the time for all biogeochemical reactions, notably when reactant concentrations are very low or completely depleted, or when reactants are supplied at or below the biochemical demand (e.g. during diffusive transport; Kritee et al., 2012; Lehmann et al., 2003; Pokrovsky et al., 2006; Sebilo et al., 2003).

Two "smart" dyes have also been used as direct tracers of microbial metabolism. Fluorescein diacetate (FDA) is a non-fluorescent dye which can be metabolized by many microbial enzymes (e.g. proteases, lipases, and esterases; Schnürer and Rosswall, 1982). FDA hydrolysis produces fluorescein, allowing quantification of microbial activity via fluorometry (see Section 3.1.2). Originally developed for soils (Casida et al., 1964), this method has been adapted for aquatic environments including the hyporheic zone and sediment (Battin, 1997; Fontvieille et al., 1992). More recently, resazurin, a mildly fluorescent dye developed for use in medical blood tests (Ahmed et al., 1994), has been used to quantify microbial metabolism (Haggerty et al., 2008; McNicholl et al., 2007). Resazurin irreversibly reduces to resorufin, a highly fluorescent dye, under mildly reducing conditions especially in the presence of microbial activity. The simultaneous quantification of resazurin and resorufin allows the determination of transport dynamics (i.e. transient storage and hydrologic loss) and biogeochemical transformation (Haggerty et al., 2014). Resazurin has been used to quantify microbial capacity in hyporheic sediments, biofilms in flume experiments, and most recently to quantify the effects of bioturbation by chironomids on microbial metabolism in lake sediments (Baranov et al., 2016; Haggerty et al., 2008, 2014).

3.3.2. Indirect tracers of biogeochemical transformation

Tracing biogeochemical transformation with indirect tracers provides information about the physical and biological conditions encountered by a parcel of water and the material it carries. Often the reactivity that is bothersome when using a tracer to quantify flowpath or residence time allows determination of exposure time to certain conditions. Many atoms or compounds are strongly sensitive to changes in redox (e.g. Fe, Mn, Th, and U). However, because many ecohydrological systems are somewhat or mostly inaccessible, to be an effective tracer of redox conditions along a flowpath, the element or combination of elements must somehow record the past conditions until they can be quantified at the sampling point (e.g. catchment outflow, groundwater well, spring). Consequently, irreversible reactions and the combination of tracers with different reactivity portfolios are the most useful tools in determining exposure time.

The abundance of environmental nucleic acids (i.e. eDNA and RNA) from microbial communities capable of different metabolic reactions (e.g. nitrate, iron, or sulfur reduction) can be an effective indirect proxy of substrate and redox conditions (Ben Maamar et al., 2015; Hemme et al., 2010). Analysis of rare earth elements (REEs) has also been used to determine redox conditions and exposure to DOM during transport through near-surface groundwater and riparian zones (Davranche et al., 2005; Gruau et al., 2004). Cerium (Ce; a rare earth in the lanthanide series) readily oxidizes to Ce^{4+} and precipitates as cerianite in the presence of oxygen. Because different bedrocks have characteristic REE ratios, the strength of the departure of Ce from its expected abundance is an indicator of integrated redox conditions along the flowpath. Interpreting a Ce anomaly without other tracers is complicated by the fact that high DOM concentrations can inhibit Ce precipitation, but in combination with other tracers of redox conditions, the Ce anomaly could potentially indicate both redox and exposure to DOM (Davranche et al., 2005; Dia et al., 2000; Gruau et al., 2004; Pourret et al., 2010). Likewise, differences in the anoxic decay rates of various pharmaceuticals (Cetecioglu et al., 2013; Durán-Álvarez et al., 2012) or CFCs could be used to determine exposure time (Horneman et al., 2008; Oremland et al., 1996). Laboratory and field tests indicate that CFC11 decays at least an order of magnitude faster than CFC12 in highly reducing conditions. While this is clearly problematic for the use of CFC11 to date groundwater, the difference in apparent ages of CFC11 and CFC12 could provide a continuous variable of the exposure time to reducing conditions, a major predictor of NO_3^- removal capacity across multiple scales (Ocampo et al., 2006; Pinay et al., 2015; Zarnetske et al., 2012). To our knowledge this proxy has never been used, though it could be widely applied to shallow groundwater systems to characterize exposure times as global CFC concentrations are very well constrained and have been measured in many shallow groundwater systems.

3.3.3. DIC and DOM as tracers and drivers of biogeochemical transformation

In this section we explore applications and limitations of carbon isotopes, both stable ($\delta^{13}C$) and radioactive (^{14}C), as tracers of respiration, assimilation, and abiotic geochemical reactions. Dissolved carbon not only carries information about biogeochemical reactions, it is a major determinant of many of the environmental conditions that modulate biogeochemical reactions including pH, redox, microbial abundance, nutrient supply, and priming (Coleman and Fry, 1991; Guenet et al., 2010; Manzoni et al., 2012; Pinay et al., 2015; Zarnetske et al., 2012). Especially in diffusion dominated systems (Péclet number < 1), where O_2 is not replenished via advective mixing, DOM concentration and biodegradability are the predominant predictors of redox (Fig. 2; Oldham et al., 2013). Despite the fact that carbon is the basis of all organic chemistry, the assumption of conservancy at some time scales can be appropriate such as using the $\delta^{13}C$ or ^{14}C of DOM to link short-term interactions between soil and stream (Leith et al., 2014; Raymond and Bauer, 2001; Schiff et al., 1990). However, in most situations, conservancy should not be assumed, for instance when determining sources of DIC in streams or lakes using $\delta^{13}C$ (Aravena et al., 1992; Finlay, 2003; Waldron et al., 2007). Furthermore, because organic matter originating from different vegetation or soil layers may have systematically different biodegradability, it cannot be assumed that the ratio of ^{12}C, ^{13}C, and ^{14}C in DOM or POM will be preserved once exposed to active mineralization (Marwick et al., 2015). The $\delta^{13}C$ of DIC in a stream, lake, or parcel of groundwater is a composite signal of $\delta^{13}C$ from the products of chemical weathering (HCO_3^- and CO_3^{2-}; carbonate alkalinity) and dissolved CO_2 from soil respiration. DIC $\delta^{13}C$ is therefore a composite tracer of two very different reactions in the carbon cycle, both of which need to be considered for accurate interpretation (Amiotte Suchet et al., 2003). The CO_2 fraction is generally the isotopically lightest component as a result of equilibrium fractionation favoring the accumulation of ^{12}C in CO_2 and ^{13}C in alkalinity (Fig. 6; (Clark and Fritz, 1997; Zhang et al., 1995). Freshwater alkalinity is generated from carbonate and silicate parent material and the $\delta^{13}C$ of alkalinity is a relatively conservative tracer of chemical weathering (Amiotte Suchet et al., 2003). Unlike alkalinity, a series of other fractionation processes govern the $\delta^{13}C$ of dissolved CO_2, including photosynthesis and respiration (Ehleringer et al., 2000; Finlay, 2004), physical fractionation during degassing and dissolution (Doctor et al., 2008), and fermentation and oxidation processes in

anoxic environments (Barker and Fritz, 1981; Whiticar, 1999). The physical fractionation of the $\delta^{13}C$ of CO_2 has been used as a tracer of total CO_2 evasion from streams (Polsenaere and Abril, 2012; Venkiteswaran et al., 2014), though these calculations are sensitive to assumptions about vegetation, geology, and in-stream metabolism, limiting the generality of this approach thus far.

4. Using crossed proxies to move beyond case studies

Agriculture, urbanization, and resource extraction have dramatically increased nutrient loading and altered DOM delivery and production in aquatic inland and estuarine ecosystems. In the past 60 years, human activity has more than doubled global nitrogen fixation (Gruber and Galloway, 2008) and quadrupled phosphorus loading (Elser and Bennett, 2011). At the same time, human land-use has directly disturbed half of global land surface (Vitousek et al., 1997), fundamentally altering the capacity of ecosystems to buffer or process these nutrient inputs (Brooks et al., 2016; Earl et al., 2006; Seitzinger et al., 2006), and climate change is altering multiple dimensions of the water cycle (Haddeland et al., 2014; Taylor et al., 2013). Protecting or restoring aquatic ecosystems in the face of these anthropogenic pressures requires an understanding of hydrological and biogeochemical functioning across multiple spatial and temporal scales.

Experimental watershed studies have generated a huge body of catchment-specific literature that is the foundation of current ecohydrological theory as outlined in Section 2. However, a conceptual chasm still separates descriptions of individual catchment behavior and general understanding of the forces controlling water circulation and biogeochemistry across scales (Dooge, 1986; Hrachowitz et al., 2016; McDonnell et al., 2007), seriously limiting our ability to make meaningful predictions of the response of aquatic ecosystems to human disturbance (Abbott et al., 2016; Taylor et al., 2013). In the final section of this review, we present how crossed proxy methods may contribute to bridging that chasm by reducing epistemic uncertainty and generating process understanding across catchments. Specifically we present a rubric for selecting tracers (Fig. 9), revisit the concept of connectivity, and reiterate the value of multi-tracer tools in moving beyond single-catchment ecohydrology.

The field of ecohydrology is limited on the one hand by technical challenges estimating variables in the water balance equation (Beven and Smith, 2015) and on the other hand by difficulties measuring and conceptualizing carbon and nutrient budgets in intermittent and heterogeneous ecosystems (Pinay et al., 2015). In practice, ecologists tend to use overly simplistic hydrological concepts and hydrologists use overly simplistic ecological concepts, attributing unexplained patterns to unknown phenomena in whichever field is secondary (e.g. "hydrological losses" or "biological uptake"; Hunt and Wilcox, 2003). Because the HotDam framework is relatively process-poor, instead relying on the integration of hotspots into exposure timescales, it may be unsatisfying to mechanistic modelers and process-based experimentalists. However, the dual lens of connectivity and exposure time scales has the advantage of being rooted in parameters that are testable at the spatial and temporal scales of interest (Oldham et al., 2013; Pinay et al., 2015). Using crossed-proxy methods to parameterize the HotDam framework allows determination of decay coefficients at the hillslope and catchment scales directly, integrating spatial heterogeneity and temporal nonstationarity (Fig. 5). These estimates of exposure timescales based on crossed proxies can improve our understanding of coupled ecohydrological functioning in two concrete ways.

First, a major source of epistemic uncertainty in hydrology and ecology is the problem of incomplete tracer recovery during tracer injection experiments (Beven and Smith, 2015; Schmadel et al., 2016). In practice, tracer recovery is usually incomplete, and for some systems and tracers it is common for only a fraction of the "conservative" tracer to be accounted for (Bastviken et al., 2006; Kung, 1990; Mulder et al., 1990; Nyberg et al., 1999; Risacher et al., 2006). Without information on where the tracer went, this can lead to systematic overestimation of hydrological losses or biogeochemical uptake. Using multiple proxies with different transport and reaction portfolios can allow the identification and quantification of unknown loss pathways. As discussed in Section 3.1.1, water isotopes are the ideal tracer for constraining water source and flowpath because they are a part of the water mass itself. Quantifying hydrological losses with water isotopes allows accurate calculation of biogeochemical uptake or respiration. Improvement of laser spectrometers and other water isotope analyzers should continue to be prioritized (Jasechko et al., 2016; Lis et al., 2008; McDonnell and Beven, 2014). Second, testing models with multiple, distinct proxies can quantify uncertainty and evaluate whether models are getting the right answer for the right reasons (Kirchner, 2006). Using proxies with different underlying principles (e.g. hydrometric measures, solute tracers, heat, and dissolved gases) can reduce aleatory and epistemic uncertainty during model parameterization and provide the basis for meaningful model evaluation during model testing (Beven and Smith, 2015; Tetzlaff et al., 2015). The challenge is therefore to increase the number and diversity of usable proxies. Many of the tracers presented in this review were discovered by accident (bacteria as tracers) or were unintended consequences of human activity (CFCs and pharmaceuticals). While the proliferation of proxies will doubtless continue whether or not informed by a conceptual framework, intentional cross pollination between research, commerce, and industry, including medicine, telecommunications, resource extraction, forensics, and robotics, could accelerate this process.

While we mentioned the importance of connectivity in Section 2 and identified several tracers of flowpath that are useful for quantifying

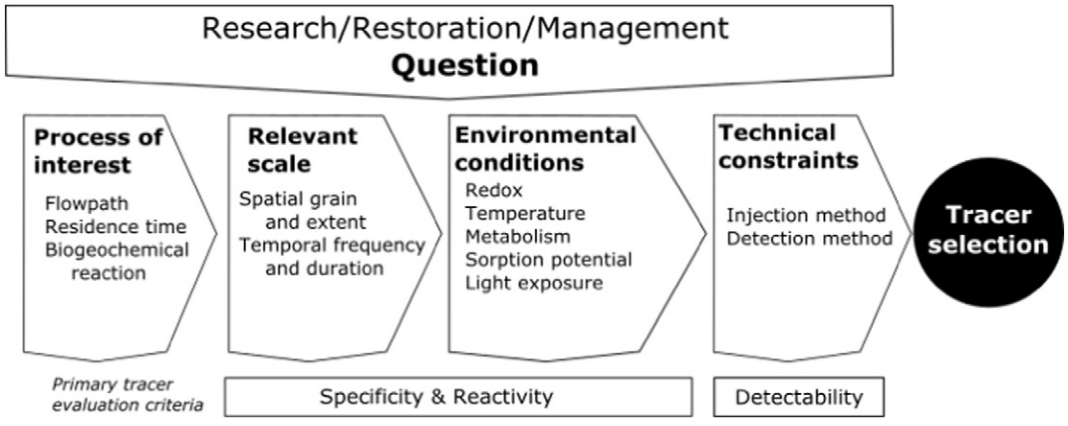


Fig. 9. Rubric for tracer selection based on research question or problem, environmental scale and conditions, and logistical considerations. Using multiple tracers with contrasting characteristics provides greater accuracy and allows quantification of exposure time (Fig. 1).

connectivity in Section 3.1, we wanted to address this key concept in the context of biogeochemical transformation. Identifying the timing and extent of hydrological and material isolation and connectivity between catchment components is key to predicting the frequency and location of hot spots and hot moments and is necessary to calculate the generalized Damköhler number (McClain et al., 2003; Oldham et al., 2013). Combining tracer methods for quantifying flowpath and residence time can allow assessment of connectivity by determining from where and when water or material is coming from (Detty and McGuire, 2010; Martínez-Carreras et al., 2015; Pfister et al., 2010). Detecting connectivity, therefore depends on temporal frequency as much as spatial extent. High frequency measurements of hydrometric parameters, reactant concentrations, optical properties, and isotopic signature can reveal moments of reconnection (Ferrant et al., 2013; Lambert et al., 2014; Saraceno et al., 2009), which if combined with knowledge of flowpath, can be used to localize connectivity. Variability in tracer concentration and characteristics during reconnection events such as storms and isolation events such as low-flow periods can provide an index of connectivity at multiple scales (Kirchner et al., 2004; Krause et al., 2015), allowing quantitative assessment of the ecological relevance of connectivity in regards to the measured parameters (Oldham et al., 2013).

Though the three questions we posed at the outset of this paper are fundamental to ecohydrology, the ultimate goal is not just to understand where, how long, and what happens to water and the materials transported with it. In fact, as important as they are, without comparative measures from multiple catchments, these questions only get us incrementally closer to a conceptual understanding of watershed ecohydrology. The goal is ultimately to explain the "why" of spatial and temporal heterogeneity, that is to say, what factors underlie the co-evolution of hydrological, biogeochemical, and societal behavior (Clark et al., 2011; McDonnell et al., 2007; Thomas et al., 2016a). Generating this type of general understanding of watershed dynamics requires moving between disciplines and across spatial and temporal scales, including ungauged catchments (McDonnell et al., 2007). One of the major advantages of a crossed-proxy approach is the ability to generate process knowledge of flowpath, residence time, and biogeochemical transformation across multiple catchments. Quantifying exposure time with a combination of redox and residence time tracers for a multitude of catchments would improve our ability to predict nutrient retention and pollutant transport and to evaluate between equifinal models (Thomas et al., in press). The application of crossed-proxy methodology across temporal and spatial scales could test the HotDam framework and other general mechanistic theories of watershed function (Dodds et al., 2015; Fisher et al., 2004; McDonnell, 2003; Pinay et al., 2015).

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