Hot Spots and Hot Moments in the Critical Zone: Identification of and Incorporation into Reactive Transport Models

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Abstract

Biogeochemical processes are often spatially discrete (hot spots) and temporally isolated (hot moments) due to variability in controlling factors like hydrologic fluxes, lithological characteristics, bio-geomorphic features, and external forcing. Although these hot spots and hot moments (HSHMs) account for a high percentage of carbon, nitrogen and nutrient cycling within the Critical Zone, the ability to identify and incorporate them into reactive transport models remains a significant challenge. This chapter provides an overview of the hot spots hot moments (HSHMs) concepts, where past work has largely focused on carbon and nitrogen dynamics within riverine systems. This work is summarized in the context of process-based and data-driven modeling approaches, including a brief description of recent research that casts a wider net to incorporate Hg, Fe and other Critical Zone elements, and focuses on interdisciplinary approaches and concepts. The broader goal of this chapter is to provide an overview of the gaps in our current understanding of HSHMs, and the opportunities therein, while specifically focusing on the underlying parameters and processes leading to their prognostic and diagnostic representation in reactive transport models.

1. Introduction

The Critical Zone encompasses the biosphere and its heterogeneities, with an extremely high differentiation of properties and processes within each compartment from bedrock to canopy, and across terrestrial and aquatic interfaces. Given this complexity, a comprehensive areal characterization of the critical zone environment at multiple temporal resolutions is needed but not always possible, and failing which the ecosystem fluxes, exchange rates and biogeochemical functioning may be under- or over-predicted. The hot spots hot moments (HSHMs) concept provides an opportunity to identify the dominant controls on carbon, nutrients, water and energy exchanges. Hot spots are regions or sites that show disproportionately high reaction rates relative to surrounding area, while hot moments are defined as times that show disproportionately high reaction rates relative to longer intervening time periods (McClain and others 2003).

By definition, hot spots and hot moments are rare sites and events that are significant for element and nutrient cycling at landscape and ecosystem scales. Some examples of HSHMs include:

- Spring melt and storm events constituted hot moments that were important contributors of mercury loading to Lake Michigan, which had direct consequences for fish spawning and ecosystem health (Hurley et al., 1998);
- Rainfall magnitude and duration controlled hot moments of pesticide leaching within the Wheatbelt region of Western Australia, which has important implications for groundwater quality (McGrath et al., 2010);
- Temperature fluctuations constituted hot moments that resulted in a 170% increase in groundwater carbon exports to the river from a floodplain site in Rifle, Colorado (Arora et al., 2016b);
- Stream stage fluctuations, and specifically high stream stage, are biogeochemical hot moments that promote hyporheic exchange and nutrient cycling (Gu et al., 2012);
- Root tips were identified as hot spots of assimilated carbon in the rhizosphere of rye-grass grown on a long-term pastureland in Germany (Pausch and Kuzyakov, 2011);
- Topographic features such as hollows and depressions are denitrification hot spots and have a significant impact on wetland-scale denitrification (Frei et al., 2012);
- South-facing swales (concave hillslopes) were identified as carbon hot spots because they exhibited significantly higher soil organic carbon storage and more active hydrology as compared to the rest of the catchment (Andrews et al., 2011);

- Agricultural wetlands, particularly shallowly flooded rice fields, constituted hot spots of methylmercury accumulation (Ackerman and Eagles-Smith, 2010);
- Riparian buffer strips are considered hot spots for the purpose of developing mitigation measures aimed at preventing phosphorus and nitrogen transport from agricultural land to surface waters (Vidon et al., 2010).

In general terms, HSHMs may be associated with elevated concentrations of solutes, such as arsenic (Yu et al., 2003), uranium (Liu et al., 2008), pesticides (McGrath et al., 2010) and nitrate (Dwivedi et al., 2017), or processes rates, such as denitrification (Henson et al., 2017; McClain et al., 2003; Palta et al., 2014; Zarnetske et al., 2012), mercury methylation (Ackerman and Eagles-Smith, 2010) and organic carbon degradation (Arora et al., 2016b). Therefore, identifying and quantifying the distribution of HSHMs in the critical zone is important from the perspective of resolving resource management problems such as eutrophication, toxic algal blooms, groundwater contamination, heavy metal transport, and greenhouse gas fluxes to the atmosphere.

1.1. Definition of terms

In their seminal work, McClain et al. (2003) defined HSHMs as associated with rare locations and non-uniform times where biogeochemical rates are maximized. Adding to this definition, Vidon et al. (2010) made a distinction between transport-dominated and biogeochemically-driven HSHMs. In the former category, transport processes control the location, timing and duration of solute contact and transformation resulting in higher solute fluxes or concentrations; while the latter HSHMs correspond to higher reaction rates occurring from a convergence of ideal biogeochemical conditions that includes electron acceptors and donors transported through different flow paths. Several studies have shown the impact of *transport-driven* hot moments such as rainfall events, wetting-drying cycles and water table fluctuations on changes in concentrations of conservative and redox-sensitive chemicals (Arora et al., 2013; Barcellos et al., 2018; Han et al., 2001; McGuire et al., 2005). An example of *biogeochemical* hot moments includes the work of Palta et al. (2014) wherein they linked the presence of anaerobic conditions and nitrate availability to higher nitrate removal rates in brownfield wetlands. Another example includes the association of temporal patterns in contaminant distribution to the presence of chemically-reduced sediments (rich in pyrite, uranium and carbon) within a floodplain environment (Arora et al., 2016a).

Implicit in the definition from Vidon et al. (2010) is the fact that the types of HSHMs are not mutually exclusive, such that they may occur together due to a convergence of ideal biogeochemical conditions with the transport of the limiting reactant, or they may occur separately, with brief overlaps at certain times. In this regard, Harms and Grimm (2008) showed that peak nitrogen retention and removal occurred during the monsoon season (*transport-dominated*) and coincided with seasonal shifts in microbial community carbon use (*biogeochemically-driven*) in the riparian zone of the San Pedro River, Arizona. In contrast, Andrews et al. (2011) reported that *transport-dominated* hot moments of dissolved organic carbon were observed during periods of snowmelt (linked to flushing), while *biogeochemically-driven* hot moments were observed during late summer to early fall wet-up (related to temperature). Together, both types of hot moments contributed to ~55% of the total dissolved organic carbon exported in the Shale Hills Catchment in 2009.

Research on hot spots has also focused on critical zone interfaces, where biogeochemical rates, nutrient cycling and biodiversity is often orders of magnitude higher than the surrounding area. These critical interfaces are defined as the interacting boundaries between zones of distinct ecohydrological, geochemical, microbial and lithological properties (Arora et al., 2019a; Li et al., 2017). In their review, Kuzyakov and Blagodatskaya (2015) described rhizosphere (i.e., the root-soil interface) and detritusphere (i.e., the soil-litter interface) as microbial hot spots. In a recent study, Krause et al. (2017) described the soil-atmosphere interface, capillary fringe zone, the interface between terrestrial upland and lowland aquatic ecosystems, as well as groundwater-surface water interface as ecohydrological hot spots. Their work further highlighted the dynamic nature of these interfaces in contrast to the stationary physical boundaries that separate different ecosystems or ecotones (boundaries that have a defined thickness and share characteristics with each of the systems they separate). This dynamic nature of HSHMs was also stressed in a review by Bernhardt et al. (2017). Bernhardt et al. (2017) made the case for merging hot spots and hot moments into the concept of ecosystem control points, defined as "…areas of the landscape that exert disproportionate influence on the biogeochemical behavior of the ecosystem..." They argued that any spatiotemporal domain within the watershed continuum contains a broad range of biogeochemical rates, and that knowledge of the rate distributions has more relevance than knowledge of maximum rates. This is a revision of the classical HSHM concept and takes a more continuous perspective on ecosystem control points, in contrast to the traditional concept of discrete 'hot or not' conditions. As a framework for understanding HSHM influences, they suggest a focus on the controls and transferability of HSHMs to improve our understanding of critical zone functioning and dynamics. We agree that understanding the mechanisms that govern HSHMs at profile, ecosystem and landscape levels, as well as identifying their origin, spatial and temporal organization, along with critical thresholds of reaction rates necessary for functions at higher scales, can greatly reduce conceptual uncertainties and provide better estimation of the development and occurrences of HSHMs.

1.2. Scope and overall impact

An over-emphasis on C and N processes in riparian systems has dominated the research on HSHMs so far. Vidon et al. (2010) brought attention to this shortcoming by emphasizing the drivers controlling the occurrence and formation of HSHMs of phosphorus, organic matter, pesticides, and mercury across riparian zones. They further emphasized that HSHM for one solute may not necessarily be a HSHM for another, and this diversity of response for different solutes should be recognized when considering riparian zone management decisions. More recently, studies are bridging this gap by focusing on HSHMs of soil moisture, sediments, trace metals, greenhouse gases and coupled biogeochemical cycles within the critical zone. For example, Barcellos et al. (2018) reported that rapid fluctuations in soil moisture and O_2 content created hot moments that impacted coupled Fe and C pools within day-to-week timescales. In another study, hot moments of sulfate in a municipal landfill site were found to be associated with re-oxidation of FeS minerals, groundwater recharge and reduced vegetation uptake in winter months (Arora et al., 2013). Since Vidon et al.'s study, exciting work on HSHMs in unique ecosystems is also challenging our concepts of how certain environments may be more important to capture the integrated and aggregated hydrological and biogeochemical responses at local and global scales. This includes work on peatlands, bogs and arctic ecosystems where fluxes of CO_2, N_2O and other greenhouse gases have motivated several fundamental and applied questions related to the mechanisms that create HSHMs or their stability in different hydrological and climatic contexts (e.g., Loiko et al. 2017; Grant et al. 2017; Arora et al. 2019b).

A recent review by Bernhardt et al. (2017) recognizes that while past research may have been limited in scope, the success and appeal of the HSHM concept is such that it transcends disciplinary boundaries and has been applied across a variety of disciplines including but not limited to biogeochemistry, ecology, microbiology, hydrology, environmental science, soil science, and general science. Geostatistics, for example, is an important contributor to the study of HSHMs. Geostatistical analysis is typically used to describe spatial patterns or hot spot locations using variograms and predict the 'hot or not' locations in non-sampled areas using kriging. A wide variety of geostatistical techniques - from kernel density estimates to indicator kriging - have been used to answer important questions about HSHMs, such as (i) which threshold values should be used to classify HSHMs? (ii) what probability distributions should be used to explain the observed HSHM locations or times? and (iii) which factors or variables (topographic indexes, land cover, geology, vegetation indexes, etc.) should be included to define HSHMs at unknown locations or times? These techniques have shown promise for use in environmental monitoring and evaluating risks associated with hazardous materials at non-sampled locations (Komnitsas and Modis, 2009; Lado et al., 2008; Lin et al., 2010). Several other studies suggest that converging ideas and techniques from different disciplines will offer benefits in synthesizing the why of HSHMs, i.e. what factors underlie the creation and distribution of HSHMs (e.g., Abbott et al., 2016; Chen et al., 2020; Pinay and Haycock, 2019). Generating such an understanding will be vital for decision making related to climate change adaptation, mitigation, land use and water management.

The purpose of this chapter is to introduce the concept of hot spots and hot moments and frame them within a numerical modeling context. Although the critical zone extends from impermeable bedrock upward through the porous bedrock, the vadose and saturated zones, rhizosphere to the top of the vegetation canopy, this work is mostly focused on hyporheic zones, floodplains and river corridors. These interfaces and transition zones present essential components of the critical zone, which provide fertile ground for highlighting research on HSHMs. In this chapter, we provide a brief introduction to reactive transport models relevant to HSHM research at hyporheic, floodplain and river reach scales. In section 3, we present some recent developments in current field-based methods and process-based understanding that facilitate HSHM research. In section 4, we provide a few examples of where and how models can be used to tackle challenges related to HSHMs, and summarize opportunities for future work that are applicable to riverine transition zones and beyond. Finally, section 5 provides a summary of the chapter's key points.

2. Capturing scales and complexity using models

HSHMs are known to play an outsized role in the critical zone and act as ecosystem control points. For conceptualizing and quantifying the influence of HSHMs, reactive transport models (RTMs) offer a flexible framework that can incorporate relevant processes at a range of spatial and temporal scales. Likewise, it is essential to conceptualize why, where, and when HSHMs occur and recur to develop a transferrable understanding of HSHMs. Another high-priority objective in HSHMs within the critical zone is to identify drivers that can be manipulated or managed at relevant scales for purposes of resource management. A key challenge is that these drivers or phenomenon are not directly observable due to short timescales or inaccessibility (e.g., fast chemical reactions, deep groundwater circulation). Understanding the mechanisms driving these HSHMs can benefit from numerical modeling that can explore the tight coupling of processes and interactions across critical zone compartments.

During the past decade, most studies have relied on HSHM investigations through data-driven approaches. Only a few studies have investigated why and how HSMHs evolve, and have quantified their aggregated response on biogeochemical processes using a physics-based modeling framework, particularly at the floodplain and riverine scales (Briggs et al., 2014b; Dwivedi et al., 2018a, 2018b; Gu et al., 2012). Although limited data availability and lack of mechanistic models applicable to the Critical Zone due to extreme heterogeneities make the analysis of HSHMs difficult, hot moments are in part more tractable because of the availability of continuous and high-resolution point measurements (e.g., pressure transducers, DO sensors). In contrast, hot spots require extensive data in both space and time (Arora et al., 2020; Groffman et al., 2009). More recently, high-resolution airborne remote-sensing data, such as digital elevation model (DEM) from a LiDAR (light detection and ranging) survey, time-lapse NASA Airborne Snow Observatory (ASO) data, NEON hyperspectral derived leaf chemistry and plant physiology, airborne electromagnetic (AEM), and other developments in sensing techniques are making characterization of critical zone hot spots possible in the spatial domain. However, sufficient temporal resolution of these data is not yet available to develop an understanding of the underlying processes that produce these hot spots.

While several challenges remain unaddressed in developing a generic, scalable template for identifying and characterizing HSHMs, current understanding suggests that interfaces and transition zones function as hot spots, and are responsive to hot moments. For example, HSHMs in riverine systems are most apparent across terrestrial–aquatic interfaces (TAI), such as riparian corridors, wetlands, hyporheic zones, and stream beds, because of distinct hydrological, thermal, biological, and chemical gradients in these zones. These distinct gradients give rise to multi-directional exchanges of water, energy, and nutrients across TAI. For that reason, temperature or water table fluctuations have been found to be drivers of

HSHMs leading to higher biogeochemical reaction rates and variations in dissolved oxygen, U(VI), nitrogen species, and Fe in the pore water of floodplain environments (Arora et al., 2016b; Hubbard et al., 2018; Yabusaki et al., 2017). However, several other factors such as reaction pathways and oxic-anoxic zones potentially play a role in the creation of HSHMs. Herein, we describe the principal models used, the questions generated, and the recent developments in quantifying HSHMs using the example of riverine systems from hyporheic to river reach scales.

2.1. Hot spots within the hyporheic zone – *the redox microzone concept*

The hyporheic zone is the part of the stream system where surface water enters the streambed and is filtered through interstitial pores before returning to the stream (Valett et al., 1996). As a result, reactive processes in these zones are strongly influenced by hydrodynamic exchange. The most broadly used models of stream solute transport (e.g., Runkel 1998) treat retention of water within the hyporheic zone as a single well-mixed zone with homogenous properties. Such parsimonious models do not attempt to capture the inherent physical complexity of hyporheic flow, such as fluid exchange between mobile and adjacent less-mobile porosity, which may be particularly relevant to reactive processes. This simplification may explain why transient-storage model parameters that account for conservative solute transport fail to capture observed stream nitrogen dynamics (Harvey et al., 2013; Lautz and Siegel, 2007). Further, traditional fluid sampling of the saturated subsurface preferentially samples the mobile porosity domain (Harvey and Gorelick, 2000; Singha et al., 2007), so information regarding less-mobile pore space and the reactive processes occurring therein is highly uncertain.

Stream water entering a hyporheic flowpath can contain oxygen, nitrate and organic carbon (Baker et al., 2000; Boulton et al., 1998) (Fig. 1a). As these solutes interact with microbial communities in the sediments, they fuel a bioreactor that is much more efficient per unit time than reactions that may occur in the open stream channel. Numerical modeling of hyporheic fate and transport that include reaction thermodynamics make use of observations that residence time is a strong control on redox state (Gomez et al., 2012; Marzadri et al., 2011; Zarnetske et al., 2012). From a Lagrangian perspective, as a parcel of water containing oxygen and nitrate moves through the hyporheic zone, oxygen is reduced first, leading to a shift to nitrate reduction at later transport timescales. This nitrate reduction occurs primarily via denitrification, which converts nitrate to inert N_2 gas, effectively removing the nutrient from the aquatic ecosystem. Therefore, a reasonable first step in Lagrangian-based reactive nitrate transport modeling is to assume a threshold time transition from aerobic to anaerobic respiration. Net reaction potential along hyporheic flowpaths is tied to a balance of transport velocity (e.g. flowpath residence time) and the reaction rate of the solute of interest. This balance can be expressed as a dimensionless Damköhler number (Da_{O2}) (Zarnetske et al., 2012).

'Anomalous' field data contrasts this type of systematic redox evolution along ideal flowpaths (Briggs et al., 2015), finding strong evidence of denitrification while bulk mobile pore water is still oxygenated (e.g., low small Da_{O2}). Facultative denitrifying microbes only switch to the less thermodynamically favorable nitrate reduction when oxygen is functionally unavailable, which leads to the hypothesis that there are anoxic sites embedded within the less-mobile porosity of bulk oxic sediments. This activity could be further fueled by the aerobic process of nitrification, which often increases the net nitrate concentration in the oxic zone while consuming oxygen. Therefore, the interface between less-mobile pore space and the oxic mobile zone may be hot spots for denitrification. This idea has recently been supported by the work of Harvey et al. (2013), who found that the denitrification rate was greatest just below the streambed interface where bulk water was oxic. Beyond the physical connectivity of mineral soil pores, organic-rich aggregates in streambed sediments are thought to locally increase denitrification rates both by providing fuel for microbial respiration and in supporting greater microbial biomass (Sawyer, 2015).

Dual-domain mass transfer between mobile and less-mobile porosity along subsurface flowpaths has long been recognized by the groundwater community as critical to explaining anomalously long mass retention timescales (Harvey et al., 1994) and its effect on chemical reactions (Haggerty and Gorelick, 1995). Similarly, mass transfer between porosities of varied mobility in hyporheic flow is expected to generate a distribution of local residence times throughout heterogeneous bed sediments (Briggs et al., 2015). Long residence times in less-mobile porosity provides the physical mechanism for the development of anoxic microsites or hot spots for time-dependent reactions, such as denitrification (Fig. 1a). Denitrification within less-mobile pore space in the bulk oxic zone is particularly relevant as there may be a greater chance of the reaction not going to completion at intermediate residence times (Quick et al., 2016), forming at a terminal product of N_2O, which is an extremely potent greenhouse gas (~ 320 times greater than of equivalent concentration of CO_2 (Wrage et al., 2001). Recent watershed research shows that streams may play an important role in the worldwide budget of this potent greenhouse gas, but the production of N_2O varies greatly between watershed systems and within single stream networks (Beaulieu et al., 2011).

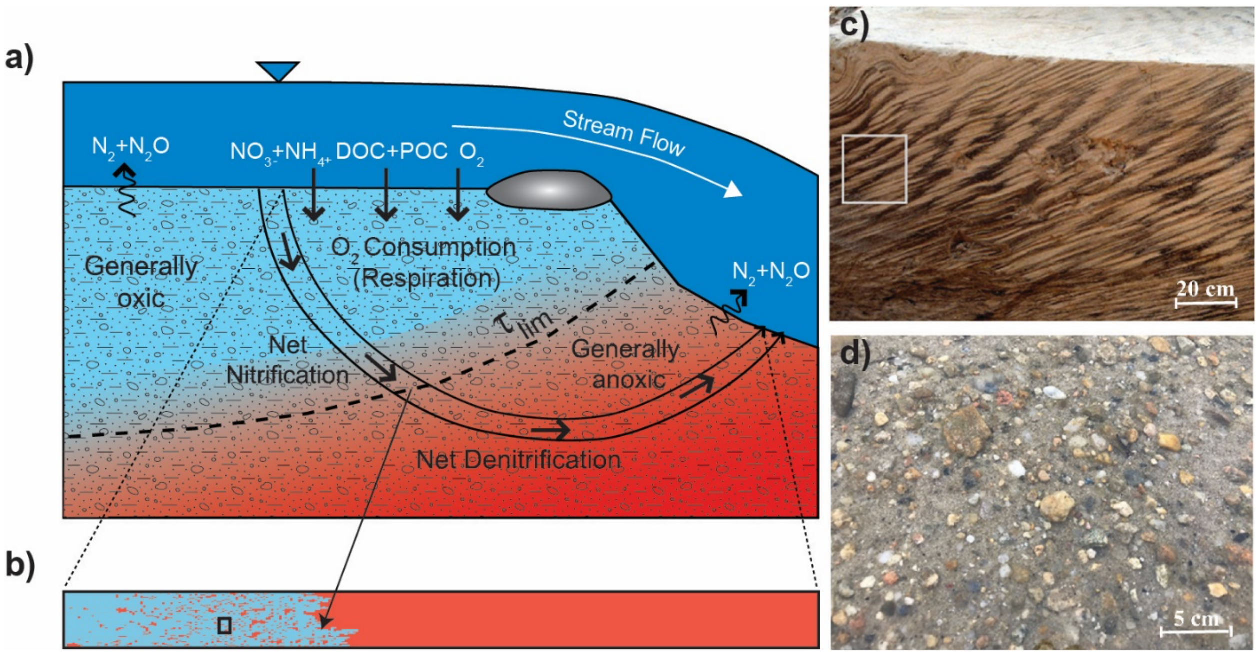

Figure 1. Panel a) The conceptual model of anoxic microzone or hot spot formation in hyporheic sediments shows oxic streamwater being carried into the hyporheic pore network. As dissolved oxygen is taken up via aerobic respiration there is a bulk transition to anoxic conditions that can be predicted with the Da_{O2} (τ_{lim}), but embedded redox microzones may be expected upgradient of this bulk transition due to enhanced local residence time in less-mobile porosity (modified from Briggs et al., 2015). Panel b) shows a hypothetical flowpath simulated with a 2D pore-network model with varied pore throat connectivity, where red zones are anoxic and tend to cluster toward the bulk anoxic transition. Panel c) shows a cross section of a climbing ripple deposit (photo courtesy of Gary Kocurek and Audrey Sawyer) that provided the sediment texture for simulations of Dehkordy et al. (2018) where the white rectangle delineates the model domain. Panel d) displays the sand and cobble sediments of a groundwater flow-through glacial lakebed, where flow around the inclusions may create anoxic microzones or hot spots near the lakebed interface.

2.1.1. Simulating the physical controls on hot spot formation and their dynamics in time

The skew of reach-scale residence time distributions toward 'anomalous' late-time retention has been directly linked to streambed sediment type and heterogeneity (Aubeneau et al., 2014). Although redox microzones are known to form across biofilms and via bioclogging (Holmes et al., 1996), along with spatially-variable organic carbon lability (Jørgensen, 1977; Sawyer, 2015), we focus here on the physical control of varied sediment permeability in enhancing localized residence times that may create embedded anoxic pockets or hot spots. Spatially variable flow through heterogenous hyporheic sediments can be conceptualized from the pore- (Liu and Kitanidis, 2012), to bedform- (Dehkordy et al., 2018), to reach-scale (Dehkordy, 2019), and simulated with various levels of complexity.

As a first direct translation on the concept of mobile/less-mobile porosity from groundwater flowpaths to river corridor sediments, one-dimensional groundwater flow models were developed in MODFLOW-2000 (Harbaugh et al., 2000) to analyze anomalous solute transport at the cm-scale (Briggs et al., 2013), though the rigid dual-domain physics of these models offered little room to explore how hot spots might develop naturally. Therefore, Briggs et al. (2015) developed two-dimensional (2D) 'pore network models' were created to efficiently track water and solute movement through a lattice of voids with variable connectivity. By simulating advective-diffusive transport at the sub-mm scale using a network of pores with a bimodal distribution of pore throat connectivity and inferred pore-scale anoxic transitions based on the Da_{O2} concept (Fig. 1b). As might be intuitively expected, clusters of tight pore throats in the models that could represent inclusions of fine sediment resulted in localized zones of enhanced residence time and potential microzone conditions. These microzones or hot spots showed minimal sensitivity to hyporheic flow rate and direction of flow, but were sensitive to the distance from the streambed (inflow) boundary. However, another general class of microzones or hot spots were also observed in the pore network models: 'flow dependent' pockets of enhanced residence time that formed adjacent to flow-invariant microzones and were highly sensitive to varied hydraulic conditions. This result suggests that predictions of HS functionality in heterogenous hyporheic sediments will need to consider bulk hyporheic water flux rate in addition to varied pore connectivity and dissolved oxygen reaction rate. When all three of these factors were simultaneously varied using the pore network model framework, Briggs et al. (2015) found that there were likely to be hot moments of microzone formation, with the highest fraction of embedded hyporheic pore spaces displaying anoxic conditions at a combination of low water flux and slower oxygen uptake. At higher oxygen reaction rates a greater fraction of the total hyporheic zone trends toward anoxic conditions, collapsing the bulk oxic zone in which HS have functional relevance.

The pore network code is highly efficient and capable of simulating column scale experiments, although its representation of flow and transport are approximate, and it is limited to lattice-type pore/grain architectures. Dehkordy et al. (2018) developed more realistic 2D advection-dispersion models at the 20 cm flowpath scale based on disparate types of observed stream and lakebed sediments using COMSOL Multiphysics 5.2 (Fig. 1c,d). According to these models, interbedded sand and silt layers formed by climbing ripple deposits in lowland rivers are expected to generate zones of less-mobile porosity (enhanced local residence time) associated with the low permeability of the finer sediment deposits (Fig. 1c). However, hot spot formation associated with these layers is likely sensitive to bulk hyporheic flow direction, specifically how aligned flow direction is with the layering. As hyporheic flowpaths are known to show strong temporal variability in orientation and magnitude based on changes in stream and groundwater pressures (e.g., Briggs et al., 2012), hot spot dynamics will also show temporal patterning. When a poorly-sorted glacial sand-and-gravel bed sediment is considered (Fig. 1d), zones of locally-enhanced residence time form in leeward of the larger inclusions, even though all pores in the matrix are fundamentally well connected. The models of Dehkordy et al. (2018) suggest that hot spot formation in heterogeneous but high-permeability bed deposits are likely to be extremely sensitive to changes in flow rate and direction, particularly if the larger clasts are irregular in shape. A primary finding of this work was also that in natural streambed sediments, hot spot formation may be dominated by a spectrum of advective flow rates, rather than zones of diffusive-dominated exchange as was more commonly conceptualized. However, as pore- to cm-scale zones of less-mobile porosity are embedded within a more permeable matrix even pores with diffusion-controlled exchange remain fundamentally well connected to the bulk streambed as diffusion lengths are short.

Dehkordy et al. (2019) extended the COMSOL modeling domains to the reach scale, considering hyporheic exchange through multiple consecutive dune bedforms of varied geometry. These simulations indicated zones of less-mobile porosity form below streambed bedforms based on flow dynamics alone, similar to the stagnation points predicted by Marzadri et al. (2015), at the convergence of hyporheic and groundwater flow cells. This less-mobile stagnation zones will also be impacted by heterogeneous bed sediment layering, driving complex HS dynamics.

2.2. HSHMs at the floodplain scale

Floodplains are areas that are periodically inundated by the lateral overflow of rivers or lakes, that result in the formation of HSHMs and consequentially have an impact on the cycling and transport of nutrients and metals (Junk, 2013; Meitzen, 2018). Past work on floodplains and riparian aquifers has focused primarily on spatial redox gradients and steady state conditions. A challenge in HSHM studies has been the difficulty in collecting groundwater chemistry data at high temporal or spatial resolution in response to extreme events such as storms (Groffman et al., 2009; Sawyer et al., 2014). As a variety of data streams have become increasingly available, data-driven techniques have gained traction in facilitating our understanding of HSHMs at this scale. While statistical and data-driven models allow for a faster execution and have been primarily used for identifying temporal components, they are not as explainable as process-based models. On the other hand, process-based models are computationally demanding and require extensive data for adequate parametrization; however, they hold potential for developing a predictive capability of HSHMs. Below, we summarize the current state of modeling approaches focused on HSHMs at the floodplain scale.

Data-based studies at the floodplain scale have focused mostly on identifying drivers of HSHMs or evaluating the overall contribution of these HSHMs at a meaningful catchment scale (Duncan et al., 2013; Dwivedi et al., 2018a; Dwivedi and Mohanty, 2016; Pinay et al., 2007; Vidon et al., 2010).To a large extent, data-driven statistical approaches have been used to demonstrate how a variety of landforms and flooding events lead to the formation of HSHMs in riverine floodplains. For example, Bernard-Jannin et al. (2017) used simple statistical analyses (e.g., partial least squares regression, leave-one-out cross validation) to suggest that nitrate HMs were associated with river–groundwater exchange and flood occurrences, while denitrification hot spots were associated with river bank geomorphology particularly at low bank full height. At the same time, these field scale investigations have spurred novel data mining techniques aimed at identifying the distribution and causes of HSHMs. For example, Arora et al. (2016a) developed a novel wavelet-entropy approach to identify geochemical hot moments in a mining impacted floodplain environment. In another study, Saha et al. (2018) employed the use of graphical and quantitative indicators typically used in economics, i.e. the Lorenz curve to assess the inequality and thereby HSHMs of N_2O emissions.

In most cases, numerical "flow" models have been used to analyze the origin, properties and functioning of HSHMs. For example, Singer et al. (2016) used HEC-RAS hydraulic modeling framework to assess how frequently inundated floodplain areas of the Lower Yuba/Feather River system in California contributed to methylmercury production potential. Shrestha and Wang (2018) used the Soil and Water Assessment Tool (SWAT) to estimate current and future N_2O emissions in a cold climate watershed located in western Canada. They reported that hot moments of N_2O emissions in the boreal floodplain were associated with the summer season, as opposed to that spring season that contributes to >50% of N2O emissions in agricultural dominated regions of the watershed.

Despite the recognition that HSHMs are important for riverine functioning and water quality, adequate prognostic models do not exist. However, hot moments have been better represented in modeling studies, both process-based and data-driven, than hot spots (Arora et al., 2019a, 2019b; Groffman et al., 2009; Pinay et al., 2015). When predicting hot spots, high-resolution, fully coupled variably saturated flow and reactive transport models are needed that are computationally demanding. Although limited, these investigations have provided important insights on how HSHMs are shaped in such environments. For example, a study conducted by Arora et al. (2016b) in a riverine floodplain using a 2-D reactive transport model (Fig. 2a,b) showed that different abiotic and biotic reaction pathways, including heterotrophic and chemolithoautotrophic pathways, exert different controls and, as a result, lead to the release of significantly different amounts of dissolved carbon exports to the river. More recently, Dwivedi et al. (2018a) demonstrated that three-dimensional modeling is needed to explicitly simulate the formation of nitrate HSHMs at the floodplain scale. In their study, HSHMs of nitrogen were found to be sustained by microbial respiration, the chemolithoautotrophic oxidation of reduced minerals in the riparian zone, and the mixing of oxic and reduced waters due to flow reversals (Fig. 2c). Collectively, these studies argue that factors such as reactant delivery effectiveness and biogeochemical conditions (e.g., sediment properties, organic matter, microbial community) in addition to hydrological events and cyclic fluctuations determine HSHMs at this scale.

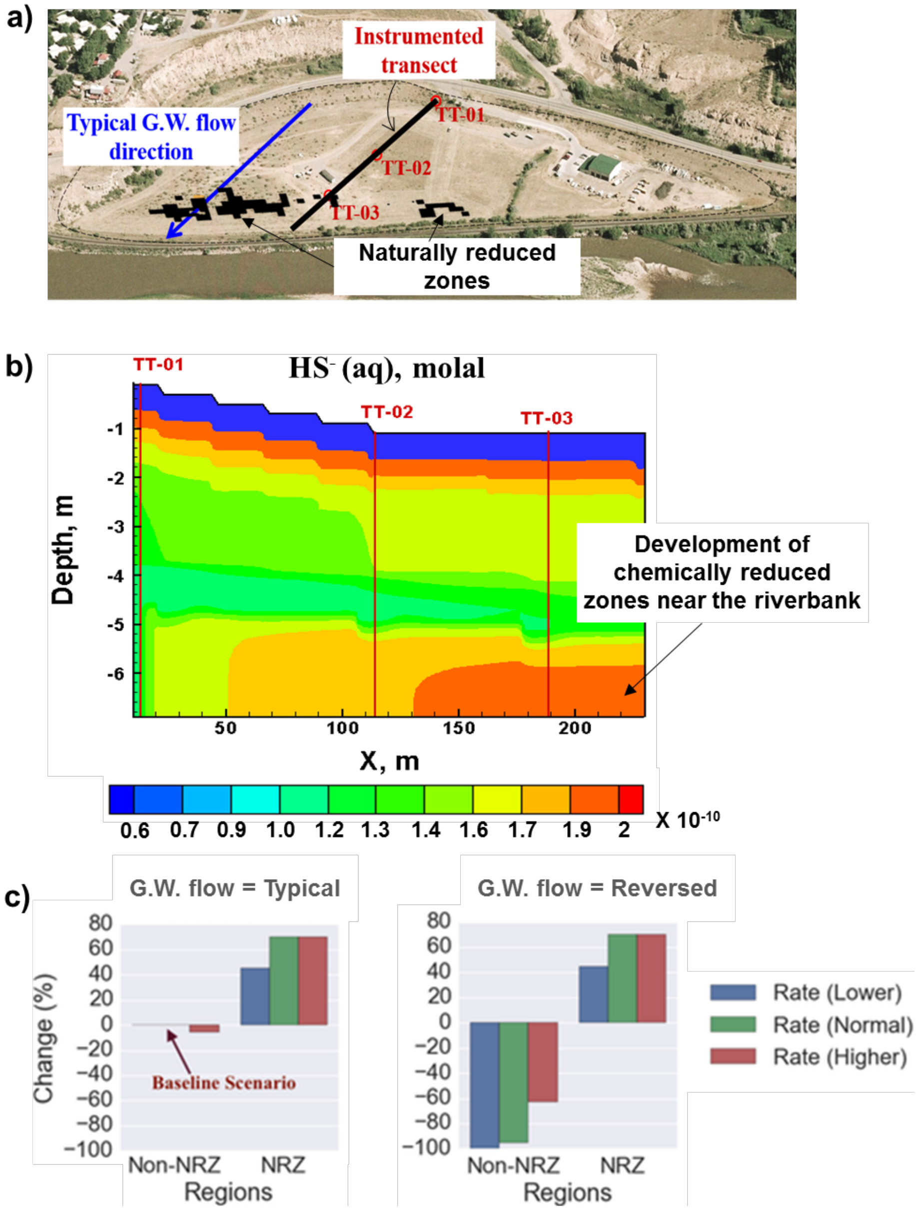

Figure 2 a) Distribution of Naturally reduced zones (NRZs) in the Rifle floodplain and their proximity to the riverbank, b) 2-D modeling of the NRZs demonstrating localized zones rich in sulfide (Arora et al., 2016b), and c) modeling analysis shows enhanced capacity of NRZs for denitrification under typical and reversed groundwater (G.W.) flow (from Dwivedi et al. 2018a).

2.3. HSHMs along river corridors

River corridors are complex conveyor belts that mobilize water, solutes, energy, and microorganisms from the landscape along channels and their surrounding environments (Covino, 2017; Harvey and Gooseff, 2015; Harvey, 2016; McClain et al., 2003; Pinay et al., 2002; Wohl et al., 2019; Wollheim et al., 2018). River channels, the central axis of these conveyors, are characterized by a continuous exchange with hyporheic zones, floodplains, ponded waters (i.e., lakes, reservoirs, and wetlands), and transient storage zones that results in prolonged contact with reactive environments where mixing drives important chemical and biogeochemical reactions with significant implications for local and regional water quality (Covino, 2017; Harvey et al., 2019). Furthermore, this exchange process plays a central role as a boundary condition that determines the export dynamics from hillslopes and floodplains and ultimately impacts the spatial and temporal evolution of the critical zone.

Our understanding of the mechanisms and importance of river corridor connectivity has significantly improved during the last half-a-century (Wohl et al., 2019). Even though the focus has been on studying local to reach scales, the need for predictions at the regional scale has driven a revolution in bottom-up approaches that can capture the granularity of local processes and their spatiotemporal variability and cumulative effects over large spatial domains (Gomez-Velez and Harvey, 2014; Harvey et al., 2019; Pinay et al., 2015; Ward and Packman, 2019). Central to this effort is the explicit representation of river corridor exchange processes by using parsimonious parameterizations that improve the physics and prediction of the next generation of regional water quality models (Gomez-Velez et al., 2015; Gomez-Velez and Harvey, 2014; Kiel and Cardenas, 2014).

To this end, the scientific community has focused on the use of reduced-order models for individual exchange processes. Reduced-order models (ROMs) are simplifications of computationally-expensive, high-fidelity models (Pau et al., 2014; Razavi et al., 2012). These ROMs serve as tools to gain mechanistic understanding about the exchange itself, but also to propose parsimonious parameterizations that can be used within a more general and multi-scale modeling framework. Reduced-order models for river corridor exchange have significantly evolved over the past decade (Harvey et al., 2019), with a particular interest on upscaling hyporheic and transient storage connectivity and its biogeochemical implications (Boano et al., 2014; Grant et al., 2018; Harvey et al., 2019). In general, these models use numerical or analytical solutions for flow and transport in both the water column and surrounding sediments to estimate exchange, residence times, and biogeochemical transformations driven by different river morphologies such as bedforms (Cardenas and Wilson, 2007a; Gomez-Velez et al., 2014; Marzadri et al., 2012, 2011, 2010; Stonedahl et al., 2010), meanders (Boano et al., 2010; Cardenas, 2009; Gomez et al., 2012), and transient storage zones (Jackson et al., 2012; T. R. Jackson et al., 2013; Tracie R. Jackson et al., 2013). Because these models are intended for a large scale contextualization, where the multi-scale nature of regional groundwater flow (Cardenas, 2008, 2007; Frisbee et al., 2013; Gomez and Wilson, 2013; Winter et al., 1998) plays a critical role, the ambient groundwater fluxes modulating the exchange are typically included as a prescribed flux boundary condition (Boano et al., 2009, 2008; Cardenas and Wilson, 2007b; Gomez-Velez and Harvey, 2014; Mojarrad et al., 2019). Early efforts focused on steady flow conditions; however, the inherently transient nature of rivers has driven significant interest on the development of new approaches that capture the dynamics of the exchange (Boano et al., 2007; Gomez-Velez et al., 2017; Singh et al., 2019; Song et al., 2018, n.d.; Ward et al., 2017; Wu et al., 2018).

Stonedahl et al. (2010) proposed a multi-scale model to represent the role of multiple morphological features along river reaches. This model allows them to quantify the relative role of bedforms and meanders within a single reach, highlighting the dominant role of bedform-driven hyporheic exchange (Stonedahl et al., 2013, 2012, 2010). With a similar spirit, Gomez-Velez and Harvey (2014) proposed the modular modeling framework Networks with Exchange and Subsurface Storage (NEXSS) to estimate the magnitude, residence times and relative importance of multiple river corridor exchange processes for predictions at the watershed to continental scales (Fig. 3a). Initial applications of the NEXSS model within Mississippi River Basin accounted for lateral exchange driven by partially-submerged alternating bars and meanders and vertical exchange driven by bedforms (ripples, dunes, and riffle-pool sequences) (Fig. 3b). These simulations illustrate NEXSS's potential as a tool to gain understanding about the emergence of hot-spots resulting from hydrogeomorphic variability across the basin (Gomez-Velez et al., 2015). In addition, by using the Reaction Significance Factor (RSF) (Harvey et al., 2013), a simple yet informative metric for the potential for biogeochemical reactions, Gomez-Velez et al. (2015) highlighted the dominant role of bedform-driven hyporheic exchange along the Mississippi River Basin, which is expected to control denitrification along the river network and be a critical target for efficient restoration efforts.

More recently, Schmadel et al. (2018, 2019) explored the regional importance of lakes, reservoirs, and other ponded waters along the river corridors and their role as modulators of water quality. They used the model SPARROW (Schwarz et al., 2006) to evaluate the importance of location and density of ponded waters in the removal of nitrogen along river networks of the Northeastern United States. These simulations highlight the critical role that these features play on the removal of nitrogen, and in particular, how their spatial distribution and physical metrics (size, shape, and connectivity to the network) determine the emergence of thresholds where their role becomes a major control of water quality downstream (Schmadel et al., 2018). In a related paper, Schmadel et al. (2019) evaluated the role of small ponds, a ubiquitous exchange zone throughout river networks, and found that depending on their spatial location these small reactors can dominate the retention of nutrients and sediments and therefore impact water quality at the regional scale. Similar efforts have focused on capturing the importance of floodplains and their inundation dynamics at the regional scale. Numerical analysis by Czuba and Foufoula-Georgiou (2015) and Czuba et al. (2018) have provided a clearer picture of the importance of location and size of floodplain inundation along river networks and how these factors determine their potential to affect water quality at the regional scale. In a recent empirical analysis, Scott et al. (2019) showed the richness of behavior in flood-plain inundation, another ubiquitous exchange process that represents a significant fraction of the total water mass moving though river network. These efforts will ultimately inform reduced-order models that can be incorporated into river-corridor modeling frameworks such as NEXSS.

The empirical and modeling efforts mentioned above emphasize the importance of a coherent river-corridor modeling framework that can be either parsimonious and capture the main physical and biogeochemical characteristics of their connectivity with channels and the landscape, or high-fidelity and provide an adequate spatial representation and predictions of hydrologic states and fluxes. Both parsimonious and detail-oriented models are essential to support the evaluation of water resources and quality at the scale of the nation, where the convolution of processes within the critical zone and the river corridor determine water quantity and quality. Ultimately, these approaches can provide a predictive understanding of river corridor processes that is critical for consistent water resources management, restoration, and planning under present and future weather, climate, and human demand.

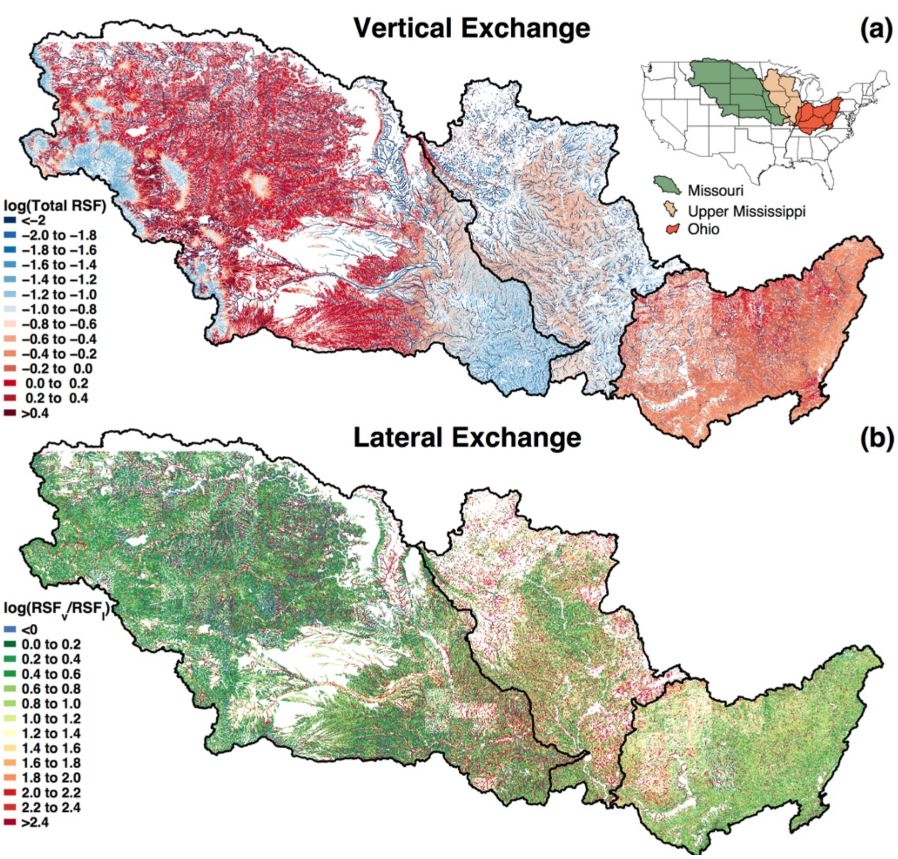

Figure 3 Total reaction significance factor (RSF) (a) and ratio of vertical and lateral RSF for denitrification in the headwaters of the Mississippi River Basin. Figure taken from Gomez-Velez et al. (2015).

3. Current understanding and the path forward

Robustly predicting impacts of disturbances on critical zone structure, function, and evolution is essential to addressing energy and environmental challenges such as clean water availability (DOE, 2018). Altering carbon and nutrient fluxes as well as critical zone services, these disturbances also create a need for new theoretical approaches and models that apply across sites to predict shifts in integrated Earth system function. The idea of biogeochemical HSHMs proposed by McClain et al. (2003) is a core paradigm in studies linking disturbances to integrated hydrology and biogeochemistry (i.e., hydro-biogeochemistry). Developing rules and concepts that enable prediction of biogeochemical HSHM influences is particularly important because of their outsized influences on aggregate system function. However, developing a predictive understanding of HSHMs across a large landscape, such as river reach or regional, includes multiple challenges. First, there is no agreed-upon approach to transfer small-scale process understanding at the large scale. Second, it is essential to characterize the multi-scale heterogeneity at the large scale; frequently, scale-relevant data are not available. Third, the presence of surface water bodies such as lakes, wetlands, reservoirs and beaver dams adds another level of complexity for resolving the dynamics of HSHMs. Finally, climatic perturbations such as low-frequency considerable precipitation or early snow melt can lead to the formation of HSHMs. To tackle this extreme-scale HSHMs problem, we envision the development of approaches for the rapid identification of precursors of HSHMs through the assimilation of diverse, multi-scale data into models at the larger catchment or regional scales. A few developments are highlighted below.

3.1. A conceptual take on HSHMs using a trait-based framework

Here, the notion of ecosystem control points proposed by Bernhardt et al. (2017) is further extended to a new quantitative approach that estimates 'control point influence' (CPI). A CPI compares the contribution of elevated biogeochemical rates in space (hot spots) or time (hot moments) to the net aggregated rate within a defined system. Therefore, CPIs are elevated when HSHMs are common enough and have high enough rates to drive aggregated rates. While not called out explicitly in Bernhardt et al. (2017), the control point concept is based on the distribution of biogeochemical rates through space and/or time. Focusing on what governs the shape of biogeochemical rate distributions, instead of maximum rates as proposed by McClain et al. (2003), provides an opportunity to move towards a transferable and mechanistic HSHM framework that aligns with the needs of critical zone science.

CPIs can be estimated by quantifying the fraction of the cumulative rate (e.g., total respiration) that is contributed by rates above the distribution's median (Fig. 4). This is a new and robust metric that can be estimated for distributions of any shape. It provides a single quantitative value—conceptualized as a biogeochemical trait—that can be directly compared across systems and across scales, thereby providing an opportunity to understand mechanisms governing cross-system/scale variation in the influence of biogeochemical HSHMs. It is also distinct relative to previous approaches focused on (i) identifying contributions of a given ecosystem compartment to overall function (Tall et al., 2011; Troxler and Childers, 2010; Zhu et al., 2013), (ii) identifying outlier rates (Harms and Grimm, 2012), and (iii) comparing mean rates to historical conditions (Jenerette et al., 2008).

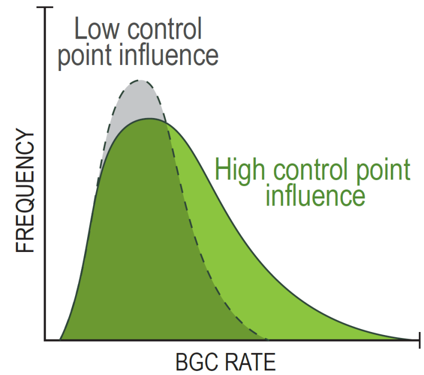

Figure 4. Quantifying influences of hot spots/moments over total system function as control point influence (CPI) provides opportunities to reveal governing processes through cross-site and multi-scale comparisons.

Previous studies have implicitly looked at the shape of rate distributions by identifying statistical features such as outliers (Harms and Grimm, 2012); however, systematic evaluations of mechanisms underlying cross-site variation in the shape of biogeochemical rate distributions are lacking. Quantitative estimates of CPI can be considered a "trait" of the system that reflects the degree to which whole system biogeochemical function is influenced by hot spots/moments. Summarizing system behavior into traits has been useful across numerous disciplines because it abstracts complex systems into quantifiable concepts that are straightforward and computationally tractable to use across systems (Cadotte et al., 2011; McGill et al., 2006; Violle et al., 2007; Weiher and Keddy, 2009). Trait frameworks allow transferability for cross-system prediction and integration (Allison, 2012; Allison and Martiny, 2009; Arora et al., 2017; Cheng et al., 2018; Enquist et al., 2003; Green et al., 2008; Lau et al., 2018; Martiny et al., 2015; Stegen et al., 2012; Wang et al., 2019; Wright et al., 2004).

As an example application of the CPI approach placed within a trait framework, we consider the hyporheic zone, which is itself often considered a biogeochemical hot spot as described above. To help understand biogeochemical behavior in dynamic transition zones such as hyporheic zones, McClain et al.'s (2003) concept of biogeochemical HSHMs focused on the mixing of complementary electron donors and acceptors. In the hyporheic zone, this can occur when DOM-rich water mixes with water rich in terminal electron acceptors (e.g., O_2). This mixing simultaneously overcomes electron acceptor limitation and electron donor limitation, thereby stimulating biogeochemical activity (Craig et al., 2010). Reactive transport models (Steefel, 2019; Steefel et al., 2015) are ideal for studying this phenomenon because they link the hydrology of groundwater–surface water mixing with redox biogeochemistry (Gu et al., 2012; Song et al., n.d.; Yabusaki et al., 2017). These models often represent a biogeochemical reaction network that includes dissolved organic matter (DOM), terminal electron acceptors, and intermediate products. This modeling construct aligns with the perspective from McClain et al. (2003) that bringing DOM together with electron acceptors increases biogeochemical rates. Lacking, however, are models linking the detailed properties of DOM chemistry to HSHMs and CPIs.

In soil science, there is an increasing focus on physical protection of organic matter and a move away from the perspective that organic C chemistry influences microbial oxidation of organic C (Schmidt et al., 2011). In subsurface sediments, however, there is greater hydrologic connectivity and potentially less influence of aggregate formation, which may enhance the influence of DOM chemistry. Consistent with this hypothesis, there is mounting evidence that DOM chemistry has strong influences over biogeochemical function in hyporheic zone sediments (Boye et al., 2017; Graham et al., 2018, 2017; Stegen et al., 2018). For example, DOM chemistry can explain ~70% of the variation in hyporheic zone respiration rates, while microbial community functional potential (i.e., metagenomes) and expressed function (i.e., metaproteomes) explained virtually none (Graham et al., 2018). Hyporheic zone microbes preferentially target organic molecules based on thermodynamic properties, pointing to a key role of C chemistry. Graham et al. (2017) and Stegen et al. (2018) further showed that stimulated biogeochemical activity during groundwater–surface water mixing is the result of changes in DOM thermodynamic properties. Boye et al. (2017) also found that organic C thermodynamics provide strong constraints on subsurface biogeochemistry. Given these studies, using a trait-based approach centered around CPIs has potential to generate the knowledge and data needed to bring DOM chemistry into hydro-biogeochemical models aimed at predicting the influences of disturbance on hyporheic zone function. As an initial demonstration, two simulation models were used to (1) link environmental disturbances to variation in DOM chemistry and (2) link variation in DOM chemistry to CPIs. These are simple simulation models that provide preliminary (i.e., hypothesis-generating) outcomes indicating that (1) increasingly frequent disturbances (i.e., greater temporal environmental variation) can cause DOM chemistry to become less variable (Fig. 5a), and (2) that CPI can be a unimodal function of DOM variability (Fig. 5b).

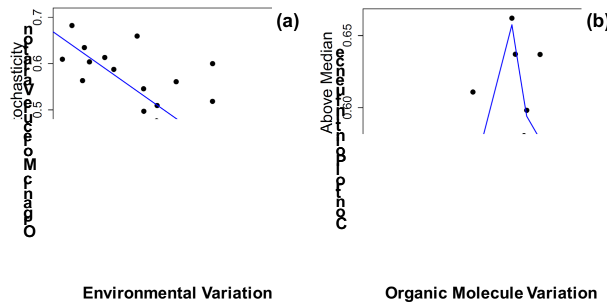

Figure 5. Simulations provide hypotheses connecting environmental variation to variation in the composition of organic molecules that underlie biogeochemical function and CPI. (a) Variation in organic molecule composition decreased with environmental variance. (b) CPI varied as a unimodal function of organic molecule variation. Black symbols are outcomes of individual simulations. The level of environmental variation was manipulated across simulations. The level of variation in organic molecules was estimated via null models derived from meta-community ecology. The application of the null modeling framework to ecological communities is described in Stegen et al. (Stegen et al. 2012) and its application to organic molecules is described in Danczak et al. (forthcoming).

Much more modeling and experimental work is needed to evaluate these initial simulation-based outcomes. The underlying models are extensions of those used in Stegen et al. (2015) and Graham and Stegen (2017). The models make simplifying assumptions, whereby prevailing environmental conditions select for particular kinds of organic molecules. The models are not truly mechanistic whereby the specific environmental variables are not defined; the environment is generic in the sense that it is anything that leads to changes in relative abundance of different organic molecules. This is conceptually analogous to an ecological system in which the environment selects for particular biological taxa (as in the models from Stegen et al. (2015) and Graham and Stegen (2017)). In turn, increasing environmental variation leads to strong selective pressures for a defined set of organic molecules, just as has been observed in ecological communities (Chase, 2007). The pattern that emerges is a decrease in the variation of organic molecules as environmental variation increases (Fig. 5a). Further work is needed to refine the model and explore the consequences of changing the underlying assumptions.

The second simulation model allows us to connect the degree of variation in organic molecules to CPIs. This model follows the conceptual approach of Graham and Stegen (2017) such that when organic molecules are deterministically organized by the environment, it leads to maximum biogeochemical function. A high CPI is the result of large outliers driving the cumulative biogeochemical function of a defined system. In context of the simulation model, large outliers occur when a small number of locations contain organic molecules that lead to high rates, while most locations contain organic molecules that are a poor match to the needs of associated microbial communities. As such, when there are high levels of variation in organic molecules, there is a low probability of achieving high biogeochemical rates and a high probably of achieving low to moderate rates. This leads to a skewed rate distribution characterized by a small number of large outliers, and thus high CPI. The effect is non-monotonic, however. With very low variation in organic molecule composition, all biogeochemical rates are similar to each other. Consistency in rates leads to low CPI because there are no large positive outliers. As variation in organic molecule composition increases there is increasing chance that a small number of locations will have high rates. This leads to an increase in CPI with increasing levels of variation in organic molecule composition (Fig. 5b). As molecular variation increases even more, the system becomes unstructured such that organic molecules are always a poor match to the needs of microbial metabolism. This results in all rates being low and thus low CPI. The result is a unimodal function between CPI and the degree of variation in organic molecular composition (Fig. 5b).

Here, we presented an example of how CPIs can be used to examine the influence of DOM composition on the overall functioning of the hyporheic zone. In a similar manner, other scenarios can be developed by linking CPIs to other data types (e.g., vegetation, bedrock properties, soil characteristics). We believe that quantifying the influence of HSHMs as CPIs provides opportunities to reveal the underlying mechanisms and functioning of the critical zone. Given the transferable and quantifiable nature of this approach, CPIs can be beneficial to evaluating hypotheses about HSHMs across sites and scales, and providing guidance to improving model architecture.

3.2. Improvements in field-scale characterization of hyporheic zones

Over the past decade, fine-scale geophysical methods have been developed to evaluate the exchange of electrically conductive solute through all porosity domains simultaneously. Again, using the example of the hyporheic zone, these methods can sample the less-mobile porosity domains where “micro” hot spots or anoxic microzones are more likely to form (Day-Lewis and Singha, 2008). Specifically, the delayed loading and unloading of solute tracer in the less-mobile domain during tracer injection and flush phases, respectively, creates predictable hysteresis curves when bulk-streambed electrical conductivity is plotted against mobile-water fluid conductivity. Using a range of simple models of 1D dual-domain transport Briggs et al. (2014) suggested that analysis of the these hysteresis curves for paired mobile/less-mobile porosity characteristics could be performed in semi-analytical fashion, without the need for numerical model parameterization. Electrical conduction dynamics added to the numerical models of Day-Lewis et al. (2017) and Dehkordy et al. (2018) provided mechanistic explanation for the development of the hysteresis curves, and supported the use of cm-scale geophysical field techniques to measure enhanced local residence times within discrete packets of natural hyporheic sediments.

A field tool for performing controlled solute injections within isolated zones of stream and lakebed sediments was developed for the experiments of Briggs et al. (2018) and described in detail by Scruggs et al. (2018). The ‘dual-domain porosity apparatus’ makes use of precisely controlled surface-water head levels within an isolated chamber similar to an infiltrometer though a system of float switches and pumps. Head within the flux chamber is adjusted based on prior measurement of bulk hydraulic conductivity to achieve specific bulk-downward fluid-flux rates. This allows in-situ testing of the flow-dependent anoxic microzone dynamics, predicted by various numerical models, when the injections are paired with electrical resistivity and fluid conductivity measurements made at discrete distances from the surface water interface. Experiments performed by Briggs et al. (2018) in a groundwater flow-through kettle pond with a sand and cobble bed indicated the inclusions could enhance local residence times on the order of 1 hr, creating the template for potential anoxic microzone formation. Residence time within this less-mobile porosity was found to vary qualitatively with bulk downward flowrate (1, 3, and 5 m/d tested).

Dehkordy et al. (2019) performed the first geophysical less-mobile porosity experiments within a stream hyporheic zone that specifically targeted less-mobile porosity model parameters such as the exchange coefficient or *α*. The experiments were performed in an urban stream outside Boston, MA, USA where previous work had identified strong NO_3^- transformations and N_2O production occurring in the stream (Beaulieu et al., 2011). Due to extensive road-sand application in this watershed with approximate 25% impervious area, this urban streambed is dominated in places by introduced silica sand, intermixed with native till soils and organic material. Using the dual-domain porosity apparatus Dehkordy et al. (2019) targeted two adjacent streambed sites of varied apparent road sand abundance that resulted in a factor 2x difference in bulk hydraulic conductivity. They conducted a range of downward flux experiments that demonstrated that both streambed locations had appreciable less-mobile porosity fractions (approximately 30% total porosity) that varied by depth and location. Further, the size of the less-mobile domain at both locations was found to increase slightly with higher downward bulk water flux rate, but local less-mobile residence time was found to systematically *decrease* with flow rate. These emerging empirical approaches and the data they are generating indicate that flow-dependent anoxic microzone dynamics may be predictable for certain hyporheic sediment types.

3.3. Recent developments in observation and modeling of hot spots featuring the sediment water interface

Extending our review of promising developments, here we summarize novel field experiments (Hampton et al. 2019 and in review) and models (Roy Chowdhury et al., in revision) that are starting to directly reveal some of the biogeochemical implications of hot spots in the sediment-water interface (SWI). The field experiments in the SWI provide some of the first direct evidence of anaerobic biogeochemical bi-products occurring in bulk-oxic sediments. Hampton et al. (2019), using 15N-NO_3 as a tracer, monitored the transformation of lake-water NO_3 as it passed through the SWI under different head conditions. Their study was paired with the geophysical tracer methods of Briggs et al. (2018) and explored how variable head (bulk residence time) conditions controlled the fate of NO_3, including denitrification bi-product of N_2O. The study was able to link the presence of less-mobile porosity to the fate of NO_3, thereby, identifying the potential biogeochemical importance of less-mobile porosity and anoxic microzones in heterogeneous SWI sediments. Concurrent with the predictions of Briggs et al. (2015), anoxic microzone formation appeared to be enhanced in bulk-oxic near-surface sand and gravel sediments as the deeper bulk anoxic transition was shallowed through a combination of increased residence time and organic carbon availability.

When similar experimental methods were applied to the urban headwater stream mentioned in Section 3.2 (i.e., in Dehkordy et al. 2019), Hampton et al. (in review) documented large fluxes of both denitrified N_2 and N_2O from their studied sediments while porewater O_2 concentrations were still bulk oxic (>6.25 μmol O2/L). This finding is the most direct evidence of microzones or hot spots in a field experiment, but there are many previous studies documenting anaerobic microbial metabolism occurring in bulk-oxic conditions, and further implicating anoxic microzones as important denitrification sites in SWI sediments (Briggs et al., 2018; Harvey et al., 2013; Kravchenko et al., 2017; Triska et al., 1993; Zarnetske et al., 2011). Together, this growing set of field studies suggest that models of the SWI that rely on bulk intrinsic properties and formulations that use threshold controls on anaerobic processes, such as oxygen inhibition of anaerobic reactions, are not accounting for, and therefore missing, some of the anaerobic regions of the SWI that might be contributing to biogeochemical budgets. For example, in SWI processing of nitrate and its reduction to N_2O and N_2 via denitrification pathways, Quick et al. (2016) identified a "Goldilocks' Zone" where there is a region along SWI flowpaths where there is a balance between transport and reaction timescales that produces an N_2O generation hotspot. Relatedly, Zarnetske et al. (2012) and Marzadri et al. (2011) suggested that there is a predictable threshold when transport timescales and oxygen update timescales are at unity that predict if an SWI is a net source or sink of nitrate (i.e., net nitrification vs net denitrification). These threshold perspectives assume bulk-fluid properties and clear transitions from one biogeochemical outcome to another along flowpaths. Perhaps, these threshold perspectives need to be revisited in light of the evidence that N_2O production was clearly observed outside of the Goldilocks' zone of the SWI in the Hampton et al. (in review) study. Making progress on identifying where N_2O production occurs in stream networks would address a key knowledge gap in current stream research as where and when N_2O is being generated is largely unknown (e.g., Beaulieu et al. 2011). The implications of the recent microzone field studies suggest that future models and experiments that incorporate microzone or hot spot processes may better account for the missing N_2O sources documented in streams. Further, there are many future opportunities in extending the efforts of documenting and accounting for hot spots by exploring for other redox sensitive processes in the SWI, such as metal, carbon, and contaminant transport.

Process-based modeling of the SWI has been critical to extending field observations and experiments by enabling the exploration of a range of biogeochemical and hydraulic conditions. Collectively, these modeling efforts have provided insights to the spatial distribution and temporal stability of stream biogeochemical processes and the role of SWIs on biogeochemical budgets from reach to basin scales (Gomez-Velez et al., 2015; Zarnetske et al., 2015). Recently, progress has been made on how to start to incorporate microzone formation and function into SWI process-based models that also incorporate the potential key role of microbial biomass. Roy Chowdhury et al. (in revision) provided one of the first assessments of what processes occurring in SWIs lead to the formation of microzones. As discussed above, representing simple hydraulics and biogeochemical reaction rate models can lead to HS formation, but the microbes driving much of these reactions have additional consequences for SWI conditions. In fact, microbes, and their associated biomass growth, are also capable of altering hydraulic flux, leading to bioclogging (e.g., Caruso et al. 2017). Consequently, Roy Chowdhury et al. (in revision) simulate a synthetic 2D hyporheic zone with different hydraulic fluxes (0.1-1.0 md^{-1}), nutrient concentrations (O_2 = 8 mgl^{-1}, organic C = 20 mgl^{-1}, NO_3^- = 1.5-3 mgl^{-1}, NH_3 = 0.5-1 mgl^{-1}), and biomass scenarios (with/without growth). Their model domain was a pore network with heterogeneous pore-throat radii creating localized zones of extended residence time where pore connectivity was reduced, similar to the models of pore network models of Briggs et al. (2015), but with variable biogeochemical conditions and a dynamic biomass formation. Roy Chowdhury et al. (in revision) found that over the course of 30 day-long simulations anoxic microzones formed in all scenarios, and biogeochemical function of these microzone populations was dynamic over time (Fig. 6). This study illustrates that when biological factors are considered, microzone spatial distributions are not simply controlled by variable sediment connectivity alone, but rather by the complex interactions of hydraulic flux, nutrient concentrations and biomass, with bioclogging having strong feedbacks on both the hydraulics of the hyporheic zone and nutrient transport through the media. Also, under conditions with biomass growth, anoxic microzones were ultimately unstable, and were enveloped in the bulk anoxic zone only days after the microzones formed, primarily due to extensive bioclogging occurring just at the inlet of the SWI. Consequently, unchecked bioclogging shifts hyporheic transport conditions from advection-dominated to diffusion-dominated, essentially removing all oxic regions in the hyporheic zone and rendering anoxic microzones functionally irrelevant. Overall, the Roy Chowdhury et al. (in revision) model results show that anoxic microzones as biogeochemical HS are likely to form under many combinations of hyporheic zone conditions, but their distribution and biogeochemical function will be dynamic and microbial biomass should be considered as an important control in addition to substrate availability and sediment heterogeneity.

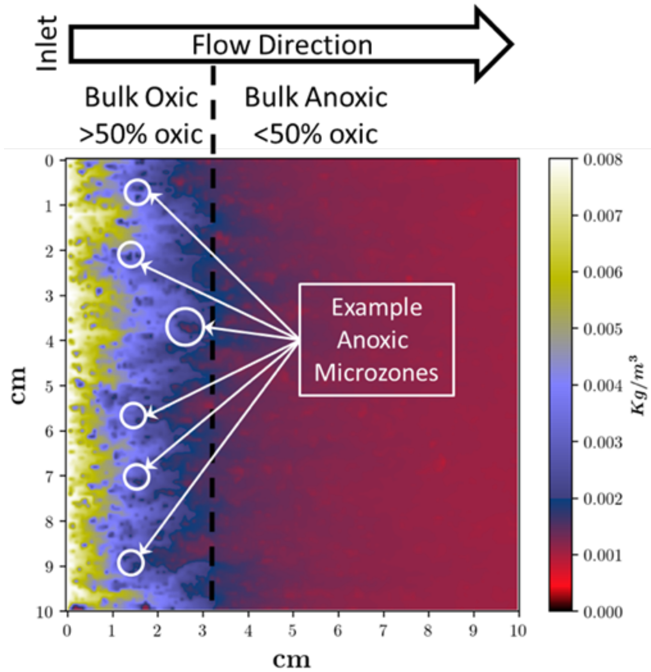

Figure 6. Spatial map of O_2 concentrations that evolved after 400 h in a simulated sandy hyporheic zone with 0.5 md^{-1} flux with abundant nutrients and carbon. Note where the visual demarcation of oxic and anoxic pore water conditions is in this example as shown with the dashed line, plus six examples of anoxic (< 2 mgl^{-1}) microzones are circled in white to highlight their location.

4. How can models contribute?

As documented above, a major challenge in representing hot spots in models is the ephemeral and dynamic nature of hot spots and the fact that they are activated at certain times only. Hot spots are defined as locations with higher reaction rates relative to the surrounding area; however, this functioning can change with time both in terms of their spatial extent and level of activity (Bernhardt et al., 2017; Boano et al., 2010; Krause et al., 2017). Consequently, our incorporation of hot spots in models is dependent on how tightly an intermediate, observable parameter is associated with higher reaction rates, or what proxies or metrics can be used to transfer this understanding across scales and sites. The best path forward is to identify when and under what conditions HSHMs form, or what makes them behave as such (Krause et al., 2017; Pinay and Haycock, 2019). Identifying these controls can help improve model architecture (i.e., mathematical representation of HSHM processes) and parameterization (e.g., Leon et al. 2014). Some promising developments from the modeling side are noted below.

4.1. Scale aware modeling/parameterization

HSHMs in the critical zone can occur across several scales in space and time. An obvious example is the hyporheic exchange flux which results in complex and nested patterns of microbial, ecological and nutrient gradients and dynamics. An important question on HSHMs is to identify how these interfaces scale in space and time, and whether these small-scale interfaces are manifested at larger scales across complex landscapes.

To this end, high-resolution forward models offer considerable opportunity to predict and track the transient and scale-dependent nature of HSHMs. However, high-resolution models are computationally expensive and pose a serious impediment to scientific progress, particularly due to the need for appropriate initialization of high-resolution models requiring several million CPU hours before actual simulations of HSHM processes. On the contrary, coarse-resolution catchment or reach-scale models do not adequately represent sub-grid heterogeneity and may completely overlook hot spots at smaller scales. In addition, these models also require forcing (e.g., precipitation, temperature) or hot moments information at sufficient model resolution to better capture the non-additive and nonlinear behavior of HSHM functioning in critical zone systems. Variable resolution models present an adequate tradeoff between HSHM representation and computational tractability. In this manner, highly localized phenomena such as anoxic microzones can be captured at the scale of the hyporheic zone, while being able to realize these local scale processes at the river reach or regional scales.

Another possibility is the use of reduced order models for capturing small-scale heterogeneities such as varied soil moisture fields to large-scale morphologic features such as bedforms (e.g., Pau et al. 2014; Harvey et al. 2019). These reduced order models are often approached bottom-up and require transfer of parameters from one scale to the next. Even in simplified systems, such as experimental soil columns, parameterization of spatial heterogeneity and scaling of localized reaction rates (e.g., mixing-induced mineral precipitation) can be difficult (Arora et al., 2015, 2011; Battiato et al., 2009). A superior alternative is to use a probability distribution function or higher order moments of parameters that provide adequate bounds on HSHMs or identify CPI.

More recently, machine learning based approaches are offering promising alternatives to identify and characterize important information at scales. For example, work is now being done to downscale precipitation using machine learning assisted techniques and capture the impact of these hydrological fluctuations at relevant model resolutions (e.g., Mital et al., 2020). Although we have not described these techniques in detail here, critical zone research on HSHMs can benefit from the versatility of machine learning approaches.

4.2. A preemptive prioritization of HSHMs

At present, predictive simulations of critical zone systems are mostly undertaken in a deterministic framework under the assumptions of stationarity (Milly et al., 2008). In light of steadily increasing computational capability and greater aspirations for simulation in domains of scientific prediction and engineering design, high-resolution models offer a unique advantage in the sense that they can be used to identify "critical" uncertainties or problem areas in advance of large-scale data collection efforts. Frei et al. (2012), for example, conducted a numerical experiment to suggest that topographic depressions are hot spots of denitrification. More recently, Dwivedi et al. (2017) conducted 3-D numerical simulations considering the impact of high-resolution geomorphic features such as meanders, and their work suggested that inclusion of meanders resulted in significantly different denitrification profiles, than without. Likewise, other numerical investigations can be designed that can help in isolating topographic features that are conducive to high biogeochemical reaction rates.

In a recent review article, (Li et al., 2017) made the case that "models test our understanding of processes and can reach beyond the spatial and temporal scales of measurements." They argued that once a reasonable numerical model exists based on available data, these models can be used to perform virtual experiments that can elucidate the influence of specific features such as HSHMs within the critical zone. Work from Li Li's group has demonstrated the use of virtual experiments in "discovering" general principles about concentration discharge relationships at the catchment scale, and developing and testing hypothesis about properties that impact critical zone functioning (Xiao et al., 2019; Zhi et al., 2019). With a similar spirit, modeling investigations can provide crucial insights on key drivers of HSHMs and mechanisms that govern their variability temporally and spatially. Data-worth analysis is one such metric that can determine the "influential" critical zone properties, whether existing or potential, which can reduce uncertainties of target predictions. Data-worth analysis works by ranking the contribution that each data point makes to the solution of a subsequent predictive simulation, which may eventually be used for resource management or policy relevant decisions (Arora et al., 2019a; Finsterle, 2015). By identifying data or drivers that are crucial to target predictions, we can identify controls as well as circumstances under which these HSHMs form.

Process-based models also offer the advantage to evaluate how hot spots form or change under future stress events such as flooding, fire, drought, permafrost thaw and early snowmelt. These tools can be used preemptively to determine the effectiveness of different management options under different climate and land-use change scenarios (e.g., Butterbach-Bahl et al. 2013). Recent work has also focused on developing decision support systems wherein competing demands and resources are analyzed as a multi-objective optimization problem (e.g., Müller et al., 2020).

5. Concluding remarks

The substantial body of research we review reveals that identifying and incorporating hot spots/moments provides a strong foundation for quantifying nutrient dynamics, greenhouse gas emissions, as well as water and energy exchange in the critical zone. Recent advances in sensing and tracing technologies have further shown that improved resolution and frequency in monitoring HSHMs is now possible (e.g., Briggs et al. 2014a). At the same time, high resolution physics-based models are at crossroads today (Steefel, 2019). 15 years ago, modeling challenges were related to dealing with expensive simulations at larger scales or scaling of local scale observations to entire catchments. Additionally, including fine scale spatial patterns (e.g., size, shape of meander bends) or hot spots (e.g., distribution of riparian wetlands) to larger catchments was problematic. While some of these questions are still relevant today, the increase in computational power and real time monitoring has resulted in much finer flow of information from one scale to the next. With variable resolution models, modelers now have the ability to explicitly characterize HSHMs at relevant scales. In fact, numerical models have become exciting tools that can preemptively predict the location of hot spots, or the time of occurrence of a hot moment, and may ultimately expand our understanding of the spatial and temporal HSHM templates that underlie larger landscapes.

In this regard, systematic and integrated approaches that combine spatial analysis, field observations as well as process-based modeling investigations have led to new insights regarding what constitutes hot spots and how they evolve in time. For example, anoxic microzones in the hyporheic zone, frequently inundated floodplains, and topographic depressions typically constitute biogeochemical hot spots (Andrews et al., 2011; Briggs et al., 2015; Singer et al., 2016). At the catchment sale, Pinay and Haycock (2019) argue that small headwaters are hotspots of nitrogen and nutrient loadings due to the dendritic nature of catchments and the spatial arrangement resulting in higher wet/dry interfaces in these catchments. Dwivedi et al. (2018a) demonstrate that chemically reduced floodplain sediments become denitrification hotspots especially with flow reversal and high oxygen inputs. However, it is necessary to further develop these concepts wherein there is clear information about when hot spots are stable in time (e.g., small headwaters) or when they respond to disturbance events (e.g., flow reversal), which may alter process intensities and even process directions. The recognition that hot spots may be ephemeral in nature is likely to lead to the development of a new generation of models and/or conceptual frameworks.

This ephemeral nature of hot spots begs interdisciplinary knowledge exchange and advances, and adaptations of concepts beyond discipline-specific theories. For example, Krause et al. (2017) identified steep redox gradients across the groundwater-surface water interface as one of the critical ecohydrological interfaces, which is also known to be a biogeochemical hot spot for riparian ecosystems. This exchange of theories across disciplines therefore has the potential to define organizational principles of HSHMs and may be used to quantify their functioning at larger scales. Investigations of hot moments have benefitted from this cross-disciplinary exchange to a much larger extent. Statistical, economic, computational, and geophysical techniques, among others, have been adopted to identify times where intense reaction rates occur. For example, precipitation events, water table fluctuations and wetting drying cycles have been identified as hot moments (Arora et al., 2019b, 2016a, 2013). This delineation in time will be further relevant to evaluate if disturbance and perturbations, such as warming, earlier snowmelt, increased floods and fires, and freeze-thaw cycles, constitute hot moments of critical zone functioning. Such understanding will provide a basis for planning, management, and improved protection of critical zone resources (Abbott et al., 2019; Hubbard et al., 2018; Shrestha and Wang, 2018).

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