

# Interactions Between Biogeochemistry and Hydrologic Systems

Kathleen A. Lohse,<sup>1</sup> Paul D. Brooks,<sup>2</sup>  
Jennifer C. McIntosh,<sup>2</sup> Thomas Meixner,<sup>2</sup>  
and Travis E. Huxman<sup>3</sup>

<sup>1</sup>School of Natural Resources, <sup>2</sup>Department of Hydrology and Water Resources,  
<sup>3</sup>B2 Earthscience and Ecology and Evolutionary Biology, University of Arizona, Tucson,  
Arizona 85721; email: klohse@email.arizona.edu

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## Key Words

carbon, flow paths, nitrogen, reduction-oxidation reactions

## Abstract

Here we review the fundamental interactions between hydrology and the cycling of carbon (C) and nitrogen (N) in terrestrial and stream ecosystems. We organize this review around five commonly studied environments: land-atmosphere interface, soil, groundwater, streams, and headwater catchments. Common among all environments is that hydrological transitions, either episodic changes in water availability or hydrologic transport of reactants, result in disproportionately high rates of C and N cycling. Two major research challenges in coupling hydrological and biogeochemical research are (*a*) effectively scaling reactions at these spatiotemporal transitions and (*b*) combining the progress made within each of the five environments listed above into an integrated understanding of hydrobiogeochemical cycles. Changes in local-to-regional hydrological cycling are likely to result in unexpected surprises at the landscape scale until progress in these research areas is made.

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*“...chemical flux and cycling are intimately linked to the hydrologic cycle. Hence one cannot measure the input and output of nutrients without simultaneously measuring the input and output of water” (1).*

## INTRODUCTION

Water, carbon (C), and nitrogen (N) cycles operate and interact with each other at different spatiotemporal scales; climate change and other environmental changes such as N deposition and land use are dramatically altering these flows and their interactions. Although much research has focused on understanding the cycling of water, C, and N at one scale or another, and human alterations of these cycles (2, 3), knowledge gaps still exist in linking these cycles across scales relevant to ecosystem functioning and human interactions (e.g., 4). Understanding how water, C, and N cycles are coupled at multiple scales and the feedbacks

of human-mediated climate changes on these interacting cycles has thus emerged as one of the eight grand challenges in environmental science (5).

Catchments provide a natural spatial domain within which to study the coupling of water, C, and N cycles because biogeochemical and hydrological processes are tightly coupled at Earth’s surface. Hydrologic fluxes within catchments provide an opportunity to balance material fluxes at defined spatiotemporal scales that capture the diurnal-to-seasonal dynamics of biologically mediated processes. Although both groundwater and atmospheric systems may not correspond to catchment boundaries, close material and energy balance within surface flow paths can be obtained within catchments and thus provide independent constraints for coupling surface-atmosphere and surface-groundwater systems. Catchments thus link the atmosphere, plants, soils, groundwater, and streams through the convergence and interaction of material and energy flows. It is at this scale that water, C, and nutrient flows, altered from the multiple and often interacting effects of climate change and other environmental changes, can also be integrated.

Global climate models project changes in local-to-regional hydrologic cycles that may profoundly impact biogeochemical cycles, interactions, and feedbacks among them. In particular, climate models predict increased interannual variability in rainfall and thus increased risk for floods and droughts in the next several decades (6). Moreover, models predict increased runoff and earlier spring peak discharge in glacier- and snow-fed ecosystems as well as warming of most rivers and lakes. With more than one-sixth of the world’s population living in river basins fed by snow or glacier melt, seasonal shifts in stream flow and possibly reduced low flows caused by decreased glacier extent or snow water storage are likely to adversely affect human and ecosystem functioning, particularly in semiarid regions (6).

Here, we review the fundamental ways in which hydrologic and biogeochemical

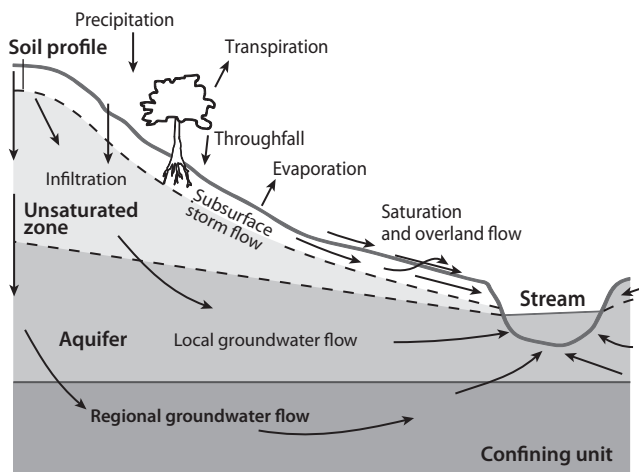
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**Flow path:** the routing of water (and solutes) via surface or subsurface pathways

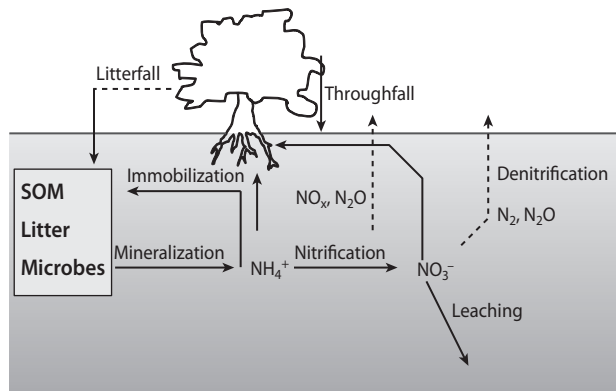
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cycles are coupled, particularly the effect of hydrological variability on C and N cycles, complementing a recent review focused on interactions between C and N cycles (7). Conceptual frameworks in hydrology have traditionally emphasized physical controls on transport, whereas those in biogeochemistry have emphasized substrate/enzymatic constraints on reaction potential (Figure 1). However, an increasing number of empirical and theoretical studies have recognized the tight coupling of water, C, and N cycles (e.g., 8–11). To include contributions from both disciplinary and transdisciplinary research, we organize this review along the concept of flow paths (Figure 2) and examine how hydrological and biogeochemical processes interact at the (a) land-atmosphere interface and at transitions in (b) soils, (c) groundwater, and (d) streams at various spatiotemporal scales. In each research area, we review dominant conceptual models underlying the interactions among hydrological and biogeochemical processes and use empirical studies to identify interactions among water, C and N inputs, processes, loss pathways, and feedbacks. We then examine how the interaction of these processes integrate at the (e) catchment scale [1–10<sup>4</sup> hectares (ha)]. We synthesize our major findings at these various scales and identify research gaps and opportunities to link hydrology and biogeochemistry across research areas. In the last section, we develop predictions of how changes in local-to-regional hydrology could affect biogeochemistry across a select set of ecosystems that are virtually certain to be impacted by climate change. We show that the ecological and biogeochemical community has a framework for predicting biogeochemical reactions that vary among organisms, communities, and ecosystems on the basis of ecophysiology, functional trait evolution, substrate availability, and reduction-oxidation reactions. In addition, we highlight the need for a similar multiscale predictive framework in hydrology that classifies catchment hydrologic residence time, flow-path distribution, and functions (12).

### Hydrologic perspective



### Biogeochemical perspective



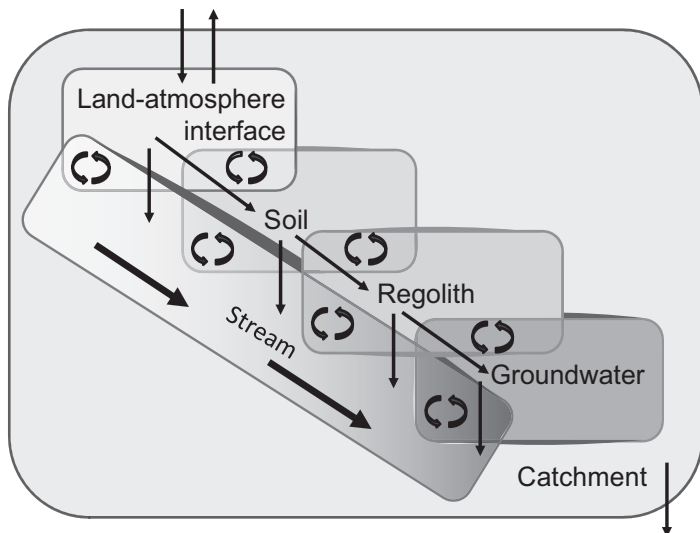
**Figure 1**

Traditional hydrologic and biogeochemical perspectives on transport and reaction. Hydrologists emphasize movement of water as precipitation, evaporation, transpiration, subsurface storm flow, local and regional groundwater flow, and stream flow. Biogeochemists emphasize reaction potential and substrate availability. A simplified N cycle is shown here with N pools and processes (mineralization, nitrification, denitrification). Abbreviations:  $\text{NH}_4^+$ , ammonium;  $\text{NO}_x$ , nitrogen oxide;  $\text{NO}_3^-$ , nitrate;  $\text{N}_2\text{O}$ , nitrous oxide;  $\text{N}_2$ , dinitrogen; SOM, soil organic matter.

## FUNDAMENTAL INTERACTIONS OF HYDROLOGY AND BIOGEOCHEMISTRY

In this section, we review fundamental couplings of water, C, and N at the land-atmosphere interface and in soils, groundwater,

**Reduction-oxidation (redox) reaction:** the transfer of electrons from reduced substances to oxidized substances to capture energy that is available from oxidation



**Figure 2**

Conceptual flow paths, linking hydrology and biogeochemistry at the land-atmosphere interface, in soils, groundwater, and streams, to catchments.

streams, and catchments (**Table 1**). This list of couplings is not exhaustive. We hope that this review promotes interactions and discussions among disciplines and across environments to promote a better understanding of coupled cycles.

### Land-Atmosphere Interface

The interface between the land surface and atmosphere marks a boundary of intense exchange of material, mass, and momentum, which is strongly modulated by vegetation surface properties and processes. We discuss the following interactions at this interface: atmospheric deposition, throughfall and stemflow, and biologically mediated exchanges of material and energy.

**Atmospheric deposition.** Atmospheric deposition is recognized as an important source of N and perhaps C at the land-atmosphere interface, with wet fall typically thought to be the dominant pathway of deposition in mesic and humid regions (e.g., 13) and dry fall dominant in arid-to-semiarid regions (14). Whereas wet deposition can be measured directly in

precipitation, measurement of dry deposits is much more challenging, and therefore the importance of dry fall as an input to many ecosystems remains highly uncertain (15). Dry deposition involves the dynamic exchange of trace gases and aerosol particles and the gravitational settling of particulates, except for large particles, where sedimentation velocities exceed turbulent velocities (16). Surface properties, such as roughness, stickiness, wetness, and atmospheric stability, control deposition rates. Any changes in sources of airborne pollutants, climate, and land-surface properties, owing to land-use change, plant invasions, fire, and vegetation diebacks, are therefore likely to alter rates of deposition. Indeed, human activities have already contributed to a dramatic increase in the sources of airborne pollutants such as N and sulfur (S), resulting in significant deposition of N and S to downwind and downstream ecosystems (17). Less information is available for organic C and organic N deposition rates in dry and wet fall (18). Understanding how changes in climate, land-surface properties, and sources of atmospheric substances alter atmospheric deposition and the consequences for C and N mass balance remain active and challenging areas of research (15).

**Throughfall and stemflow.** The plant canopy can intercept incoming water where vegetation and hydrology interact to influence interception and deposition of solutes, such as dissolved organic C (DOC), organic N (DON), and inorganic N (DIN), as throughfall and stemflow. Many studies have noted that hydrologic properties and vegetation features determine the degree and extent of these interactions (see References 19 and 20 for reviews). However, our understanding of the mechanisms controlling throughfall and its chemistry is inadequate, owing largely to the time requirements for collecting and characterizing event-based throughfall (20). In addition, little is known about the role of canopy structure and morphology on partitioning precipitation into throughfall and stemflow and about its effect on solute inputs (21). Lastly, little is known about

**DOC:** dissolved organic carbon  
**DON:** dissolved organic nitrogen  
**DIN:** dissolved inorganic nitrogen

the effects of intraspecific vegetation variation on throughfall water and solute inputs. Levia & Frost (20) concluded that characterizing patterns of throughfall in relation to meteorological conditions is critical to advancing our understanding of the partitioning of water, C, and N fluxes among the atmosphere, canopy, understory, and soil. Quantifying relationships of throughfall and meteorology may be particularly important in explaining variability in C and N cycling and losses from catchments exposed to high atmospheric deposition as N (22, 23).

**Biologically mediated exchanges of material and energy.** Vegetation structure and function also control other exchanges of material, mass, and momentum between the land surface and the atmosphere (24). Understanding how biological dynamics control land-surface-atmosphere exchanges requires careful consideration of evolutionary and ecological constraints on vegetation dynamics. One of the most fundamental trade-offs facing plants is evaporative water loss from leaves during carbon dioxide (CO<sub>2</sub>) acquisition for photosynthesis (25, 26). This trade-off has influenced the evolution of plant functional strategies (27) and constrained how plants allocate resources to produce biomass in different hydroclimatic conditions (28), affecting the land-surface composition that controls biosphere-atmosphere exchange (**Figure 3**). The biogeochemical consequence of these functional strategies is that plants with slow growth rates are associated with low resource tissue and soil concentrations, along with extended nutrient retention times and longer-lived tissues, whereas plants with rapid growth rates are associated with high resource environments, short tissue turnover times, and high tissue resource concentrations (29, 30). Other ecological and evolutionary constraints have been the distinct separation of different life forms and the covarying trait combinations; longer-lived plants (e.g., perennial evergreens) typically have lower photosynthetic capacities than shorter-lived plants (31) because of the optimization of leaf N investment in photosynthetic enzymes relative to morphological

**Table 1 List of select fundamental interactions of hydrology and carbon and nitrogen cycling at the land-atmosphere interface and in soils, groundwater, and streams**

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**Land-atmosphere interface**

- Atmospheric deposition
- Throughfall and stemflow
- Biologically mediated material and energy exchange

**Soil regolith**

- Decomposition and hydrologic balance
- C and N transformations, water-filled pore space, and gaseous losses
- Soil solution losses, hydraulic properties, and flow paths
- Weathering, CO<sub>2</sub>, and acid rain

**Groundwater**

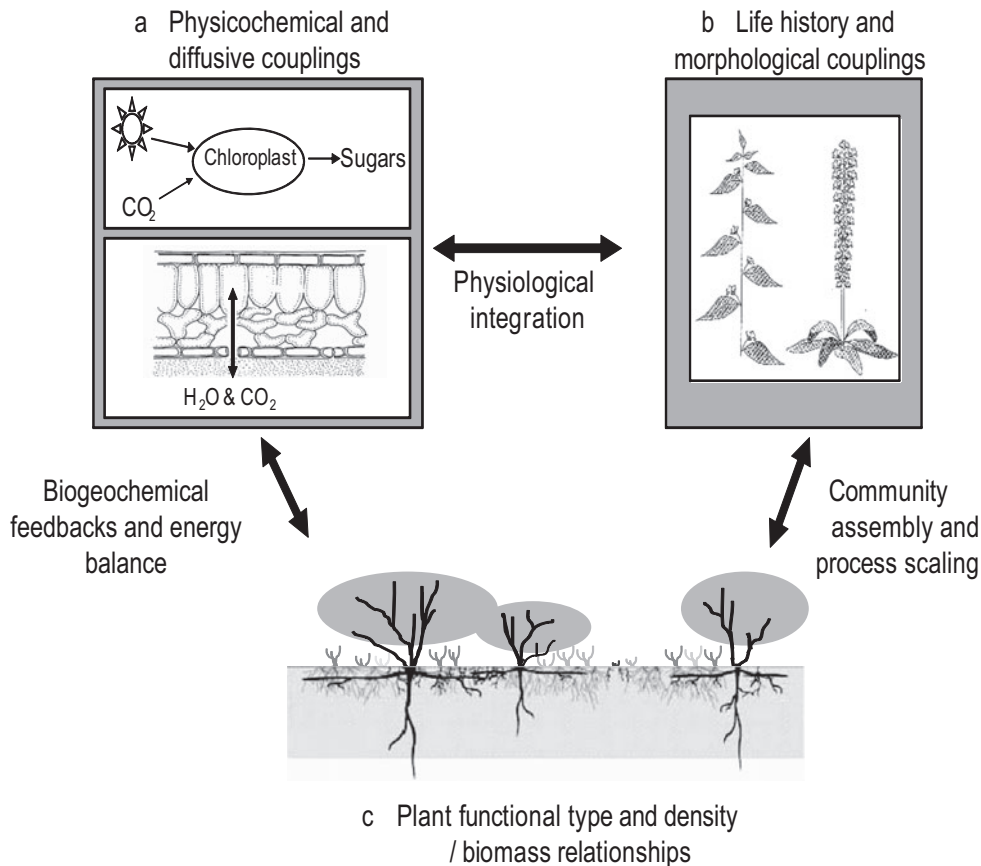
- Recharge rates
- Depth and length of flow paths
- Supply of reactants

**Stream**

- Hydraulics and material spiraling
  - Exchange of subsurface and surface reactive volumes
  - Processes at the interface between streams and the landscape
- 

and stomatal strategies that influence water loss from leaves and constrain CO<sub>2</sub> exchange (31–35). Thus, strategies that plants use to withstand the stress associated with low water availability constrain photosynthetic performance and growth potential within individuals (36) and influence the biological input of N into soils, with feedbacks on N cycling at the ecosystem to catchment scale (37). Key couplings of C, N, and water cycling at the land-surface interface therefore emerge from the integration of process across several spatial and temporal scales; these couplings are associated with basic constraints on physiological processes in plant leaves on short reaction timescales (34, 38), the integration of these processes into whole organisms (39, 40), and patterns of assembly in intact communities (41, 42) that occur on daily to evolutionary timescales (**Figure 3**).

At the ecosystem scale, water availability thus limits aboveground net primary production (ANPP) in many environments (e.g., 45) and strongly structures size-dependent metabolic processes (44). Recent studies have shown that ecosystems differ in their ANPP responses to annual variability in rainfall (41, 46); high-productivity systems, such as grasslands and forests, are less sensitive to changes



**Figure 3**

The feedback structure and couplings that regulate land-surface exchanges with the atmosphere. Three hierarchies are illustrated: (*a*) basic physiological processes that govern photosynthetic energy conversion within leaves and/or physicochemical dynamics of the biochemistry and diffusive constraints associated with leaves and gas exchange; (*b*) whole plant patterns of biomass allocation, life history strategy, and gross morphology; and (*c*) functional-type representation and density/biomass relationships of intact plant communities. Those in (*a*) are coupled by trade-offs associated with investment of scarce resources (primarily N) to different biochemical functions (34, 43) as optimized by the behavior of stomata (25, 38), which regulate the fundamental trade-off in plants, water loss-for-energy gain. Hierarchies in (*a*) and (*b*) are coupled by ecological and evolutionary trade-offs that relate to the partitioning of resources in time associated with the availability and seasonality of resources (e.g., the ecohydrology of annual versus perennial life forms) (39, 40) and scaling constraints associated with the delivery of resources throughout a plant body (metabolic scaling theory) (44). Those in (*b*) and (*c*) are coupled by the constraints of community assembly, which are dominated by the potential for biomass to accumulate given historic patterns of perturbation (such as protracted drought, e.g., the maximum rain use efficiency ( $RUE_{max}$ ) hypothesis (41)). Those in (*a*) and (*c*) are a function of the coupling of life-form and the potential for decomposition of organic matter, typically viewed as a positive feedback loop (e.g., fast-growing species with high nutrient tissue concentrations provide substantial substrate for decomposition and increase the nutrient status of soils).

in rainfall compared to low-precipitation regions, such as deserts, that are more responsive to changes in precipitation (41). At low water availability, sites converge on a com-

mon rain-use efficiency (RUE) (ANPP/annual precipitation). As precipitation increases, biogeochemical feedbacks associated with vegetation structure, nutrient quality of litter, and

climate-driven dynamics of decomposition, rather than water-use attributes of the individual species, appear to constrain ANPP responses to precipitation variability across biomes (47). Consistent with these empirical studies, theoretical studies have shown the tight coupling of net primary production (NPP) through water controls on N inputs, transformations, and outputs (8, 48). In particular, Schimel et al. (8) identify four principle ecosystem features that serve as major controls on these couplings: (a) water controls on N inputs and outputs, (b) NPP controls on N fluxes and accumulation into organic matter, (c) N availability feedbacks on N release and NPP, and (d) water controls on NPP and N cycling with water and nutrient limitation feedbacks on NPP. These controls provide a framework for understanding key couplings among water, C, and N at the land surface and in soil; these are discussed in detail in the next section.

Despite advances made in identifying key hydrologic and biogeochemical couplings at the land-atmosphere interface, challenges remain in linking these cycles across scales. Recent hydrologic modeling studies suggest that short timescale variability in soil moisture, temperature, N content, and plant uptake need further consideration in models because a significant fraction of the soil moisture, N trace gas, and nitrate ( $\text{NO}_3^-$ ) solution loss variance occurs at timescales of a few days to weeks (49). Accurate representation of the hydrological mechanisms that control the N cycle at the daily timescale is therefore needed to capture the effect of changing soil moisture on transport in soils with likely feedbacks to groundwater and streams (49). Understanding partitioning of evaporation and transpiration will also be critical because changes in this partitioning may feed back on soil moisture and transport in soils and to groundwater and streams. Placing these ideas into an integrated theory that considers the evolutionary constraints on organisms, the manner in which they assemble in plant communities, and their temporal dynamics as driven by temperature and water availability remains a challenge (42).

## Soil Regolith

Soil water content plays a fundamental role in land-atmosphere interactions by constraining vegetation dynamics (e.g., 9), and it also plays a pivotal role in soil biogeochemical processes (8, 49–51). In this subsection, we examine hydrologic controls on decomposition, C and N transformations and gaseous losses, and soil solution losses. We highlight fundamental interactions of soil water, substrate availability, and redox state on these processes.

## Decomposition and hydrologic balance.

Decomposition of litter and soil organic matter (SOM) is the conversion of photosynthetic products to inorganic forms and represents a fundamental source of nutrients for plants and nutrients and energy for microbes. At global scales, temperature, water content or a scalar of climate, and initial litter quality conditions have been shown to determine rates of decomposition and nutrient release (52). For example, Aerts (52) showed that climate, as measured by actual evapotranspiration, is the best predictor of litter decomposition rates in the first year of decomposition (52), except for arid ecosystems where photodegradation and litter chemistry may be more important (53). However, over longer timescales (years to decades), initial tissue N concentration is a better predictor of nutrient release (54). Parton et al. (54) suggest that patterns in net N immobilization and mineralization during long-term decomposition are predictable based on fundamental constraints of microbial physiology and substrate availability.

Interactions of precipitation, temperature, and substrate availability are also dominant controls on SOM decomposition and nutrient release, and reviews on this topic can be found elsewhere (e.g., 55, 56). Davidson & Janssens (55) described soil decomposition in terms of temperature-dependent reaction rates and substrate availability. Less understood are the impacts of temperature sensitivities and chemical and physical protection on soil decomposition. Moreover, the effects of

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**Redox state or potential:** tendency of environment to receive or supply electrons

**Mineralization:** conversion of organic N to mineral form, ammonium ( $\text{NH}_4^+$ ), also referred to as ammonification

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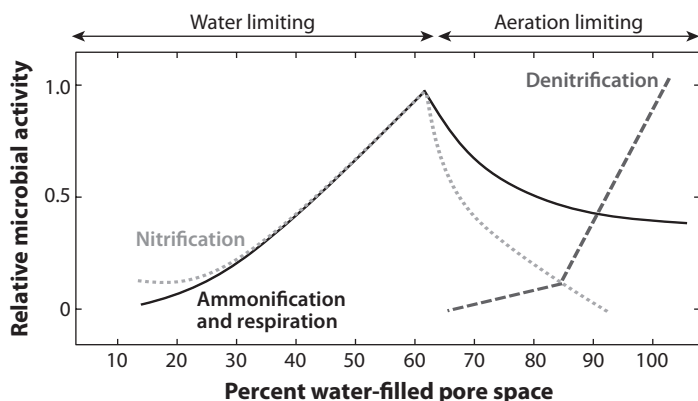
**Hot spots and hot moments in biogeochemical cycling:** areas or periods, respectively, characterized by disproportionately high rates of biogeochemical cycling

changing environmental conditions (drought, freezing/thawing, flooding) on substrate availability at enzyme-reaction sites are unclear. For example, little is known about how climate-driven changes in drainage, precipitation, and evapotranspiration will affect soil water film thickness and the diffusion of soluble substrates and extracellular enzymes. Climate-driven changes in hydrologic balance may be particularly important in ecosystems with high soil moisture contents, such as peatlands and wetlands, but also in upland tropical forests. In these forests, soil water availability has been shown to control soil C and N cycling and storage indirectly through soil aeration on diffusion of oxygen ( $O_2$ ) into the soil and consequently on redox potential (57, 58).

**C and N transformations, water-filled pore space, and gaseous losses.** Thresholds in soil water content also regulate microbially mediated transformations and gaseous loss pathways through controls on soil aeration, substrate availability, and reduction-oxidation reactions (Figure 4). In arid and semiarid ecosystems, water availability can directly limit soil C and N transformations and losses (e.g., 59, 60). In this context, soil water provides essential water required for soil biogeochemical functioning: delivering or carrying away essential materials such as DOC and nutrients

to plant roots and microbial populations, dissolving nutrient salts in soils, and mineralizing C. Indeed, many empirical studies have shown rapid increases or pulses of soil  $CO_2$  fluxes in the field following rewetting after long, dry periods owing to plant and microbial respiration but also probably owing to physical displacement of  $CO_2$  (61–63). These pulses have also been found to cause hot spots and hot moments in biogeochemical cycling (64). Experimental laboratory evidence further supports water limitation on biogeochemical cycling, revealing diffusional limits on ion transport of ammonium ( $NH_4^+$ ) and stress in microorganisms in soil pores at low soil water potential (65).

In more humid environments, soil moisture interacts with soil porosity and temperature to control rates of soil C and N cycling and gas and solution loss pathways through its impact on soil aeration and reduction-oxidation reactions (67). All soil metabolic activities involve reduction-oxidation reactions, the transfer of electrons from reduced substances to oxidized substances to capture energy that is available from oxidation, with organic matter as the preferred electron donor and  $O_2$  and then  $NO_3^- >$  manganese (IV) ions  $>$  iron (III) ( $Fe^{3+}$ ) ions  $>$  sulfate ( $SO_4^{2-}$ )  $>$   $CO_2$  as the preferred electron acceptors (on the basis of free energy) (68). In soils, key N-cycling processes include mineralization, the conversion of organic N to mineral form,  $NH_4^+$ , nitrification, and denitrification. Nitrification is the conversion of  $NH_4^+$  to  $NO_3^-$  and is typically associated with aerobic chemoautotrophic bacteria that derive their C from  $CO_2$  or carbonates, although heterotrophic nitrification can be significant in forest soils. The availability of substrate,  $NH_4^+$ , and high  $O_2$  therefore control nitrification. When  $O_2$  availability decreases because of increases in water-filled pore space, denitrification, an anaerobic heterotrophic process, can take place and reduce  $NO_3^-$  to dinitrogen ( $N_2$ ) (69). In denitrification, the relative availability of electron donors (organic C as substrate) and electron acceptors ( $NO_3^-$ ) affects the relative proportion of nitrous oxide ( $N_2O$ ) and  $N_2$  produced such that any factor



**Figure 4** Influence of percent water-filled pore space on soil microbially mediated C- and N-cycling processes (respiration, ammonification or mineralization, nitrification, and denitrification) (adapted from Reference 66).

that slows the overall rate of denitrification, such as low availability of DOC, will accumulate  $\text{N}_2\text{O}$  as an end product (70). Within this context, relative rates of mineralization, respiration, nitrification, and denitrification can be understood as a function of the percentage of water-filled pore space and substrate availability (**Figure 4**) (66, 71). These findings have been supported extensively and described as the hole-in-the-pipe model (72, 73). Because denitrification takes place under anaerobic conditions, factors decreasing  $\text{O}_2$  diffusion (soil moisture, porosity, drainage) are crucial in controlling fluxes. Perched water tables, fluctuating or rising water tables, wetting and drying events, freezing and thawing, and flow-path boundaries or interfaces are therefore highly redox active because oxidized and reduced species are close to one another and result in the convergence of reactive or limiting solutes along hydrologic flow paths (57, 74).

**Soil solution losses, hydraulic properties, and flow paths.** Thresholds in soil water content and gradients in water potential are also primary controls on hydrologic and biogeochemical losses of inorganic and organic forms of C and N to streams and groundwater. At the plot scale, first-order hydrologic controls on runoff generation include rain intensity, the amount and depth of decline in hydraulic conductivity, and drainable porosity as these properties affect soil water depth storage functions. However, routing of water and solutes via preferential flow paths, such as cracks and macropores, are common in many soils (75). Indeed, preferential flow has been shown to influence the source, age, and timing of water, C, and N loss in many systems, with important implications for biogeochemical reactions, residence time, and routing to downstream ecosystems (76–80). At the hillslope scale, hydrologic connectivity, the connection and disconnection of disparate landscape units via subsurface flow (81), and depth to bedrock have emerged as two important controls on hillslope runoff generation mechanisms and C and N losses (12, 82–84). For instance, McGlynn & McDonnell

(85) have shown that DOC fluxes from catchments depend on the relative timing of source contributions from riparian and hillslope zones and the connection and disconnection between these zones. Numerous other field studies have shown that subsurface features, such as the bedrock topographic surface, control lateral water flow; delivery of this water to streams depends on precipitation thresholds (86, 87).

Much of our understanding of biogeochemical controls on soil solution comes from studies examining controls on N transport and retention in forests receiving chronic additions of anions such as S and N from acid rain (88). Reviews of variation in N soil solution losses and sensitivity to N additions can be found elsewhere (89–91). In brief, climate, disturbance, previous land-use history, inorganic N inputs, and their interactions (92) are thought to explain broad-scale sensitivity of soils to  $\text{NO}_3^-$  solution losses. More proximal biogeochemical controls on soil solution losses include through-fall inputs (89), nutrient status (93–95), stand vigor and succession (96), and species composition/forest type (97). In particular, differences in C:N ratios in the forest soil floor and thresholds in mineralization and nitrification appear to explain the onset of N soil solution losses (**Figure 5**) (89). This observation again supports the concept that initial N content in detritus places a fundamental physiological constraint on N immobilization and N release (44), with feedbacks to transport in soils, groundwater, and streams.

Controls on DOC dynamics and solution losses are more complex; reviews on these topics can be found elsewhere (e.g., 98–100). In soils, the interactions of the decomposer community, amount and quality of litterfall, and SOM are thought to be the primary biological controls on the availability of DOC (99). Desorption, adsorption, and exchange reactions and interactions with pH and ionic strength then control soil solution chemistry on DOC. Controls on DON solution fluxes remain poorly understood.

In spite of these advances in coupling cycles in soils, many research gaps loom in coupling

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**Denitrification:**

microbial reduction of nitrate ( $\text{NO}_3^-$ ) to dinitrogen ( $\text{N}_2$ ), an anaerobic heterotrophic process

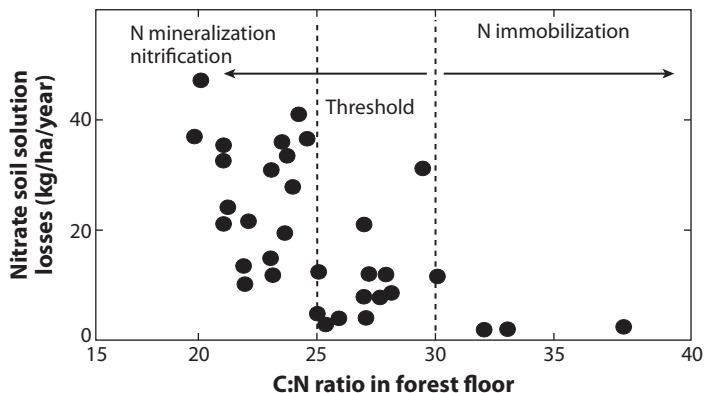
**Nitrification:**

an aerobic chemoautotrophic process that converts ammonium ( $\text{NH}_4^+$ ) to nitrate ( $\text{NO}_3^-$ )

**Drainable porosity:**

the difference in water content between saturated conditions and field capacity

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**Figure 5**

Relationships of annual soil solution  $\text{NO}_3^-$  losses ( $\text{kg ha}^{-1} \text{ year}^{-1}$ ) and soil C:N ratio of forest floor from 35 sites in North America and Europe, suggesting thresholds in immobilization and mineralization of N and subsequent nitrification [adapted from Gunderson et al. (89)].

water, C, and N across scales. In particular, understanding the influence of soil moisture and soil solution fluxes on the residence time of C and water in catchments and their feedbacks to groundwater, streams, and also atmosphere remain challenging owing to the unsolved issues of linking the spatiotemporal variability of water, C, and N cycles in heterogeneous soils. More research is needed to understand how soil hysteretic properties interact with biogeochemical processes to regulate catchment functions, such as water, N, and C storage and losses (79). In addition, more research is needed to understand how hillslope properties, including topography and other lower boundary conditions such as fracture bedrock, influence biologically mediated reduction-oxidation reactions and weathering processes. Finally, scaling runoff mechanisms across hillslope length scales and catchment sizes remains problematic.

**Weathering,  $\text{CO}_2$ , and acid rain.** Over long timescales ( $10^2$ – $10^6$  years), the formation of carbonic acid ( $\text{H}_2\text{CO}_3$ ), derived from  $\text{CO}_2$  reaction with soil water, as well as organic acids, derived from plants and microbes, drive chemical weathering in most ecosystems and consequently soil development, although acid rain from N and S emissions has enhanced rates of

weathering in recent years (101). Many studies have documented that soil and ecosystem properties and processes, such as SOM, mineralogy, and nutrient availability, change systematically over soil development with time (102). Recent studies have also shown that soil hydrologic properties and flow paths shift over soil development with time, from dominantly vertical flow to the frequent occurrence of subsurface lateral flow (103), and these changes in hydrologic controls strongly influence water and biogeochemical reaction and residence times (84, 104). As coupled soil development and transport models begin to include biogeochemical transfer processes, it will be important to develop quantitative linkages between soil properties, hydrology, and biogeochemistry as they evolve over time. Increases in temperature, atmospheric  $\text{CO}_2$ , and precipitation variability and extremes caused by climate change will likely accelerate weathering rates, with feedbacks to groundwater and streams. Changes in precipitation extremes will also likely alter the occurrence of runoff mechanisms as overland flow, saturated overland flow, and subsurface storm flow (Figure 1) and hence the trajectory of soil development and landscape evolution at local-to-regional scales.

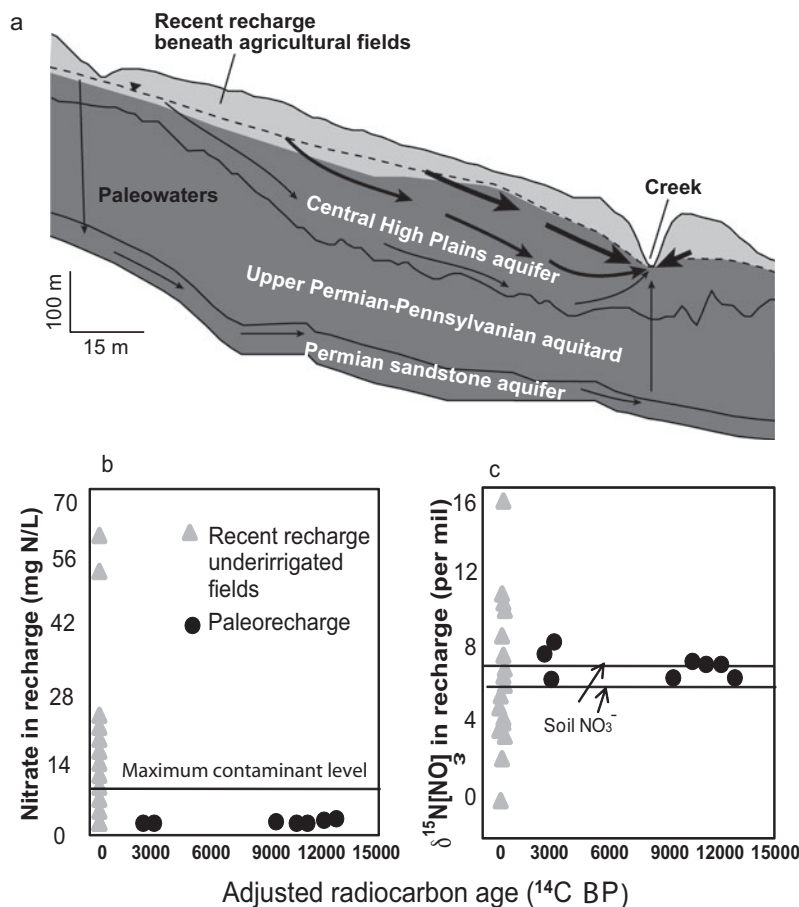
## Groundwater

The interface between the unsaturated and saturated subsurface marks the upper boundary of groundwater systems. The lower limit of groundwaters at Earth's surface varies with location, often extending in depth for thousands of meters, and typically with increasing salinity. In this subsection, we discuss the effects of water recharge rates, depth and length of flow paths, and supply of reactants on key biogeochemical interactions in this environment.

**Recharge rate.** Water recharge transports C, N, solutes, and microorganisms from shallow soils and surface environments to groundwater systems. Advection in high-velocity regimes, such as fracture flow, and diffusion in low-velocity systems, such as clay confining beds,

dominate transport processes. Multiple studies have shown that  $\text{NO}_3^-$  and DOC concentrations increase in groundwater in periods of rapid recharge because of climate change, urbanization, and irrigation practices (105–107). The timing of recharge and land use critically influences C and N transport to groundwater. Groundwater in catchments typically has a residence time on the order of tens to thousands of years. Waters recharged before fertilizer use

can contain intrinsically low  $\text{NO}_3^-$  concentrations derived from soil organic N (**Figure 6**). Researchers have observed decreasing  $\text{NO}_3^-$  concentrations with depth and groundwater age in multiple aquifer systems in the United States, including the Atlantic Coastal Plain, Snake River Plain, and Midwestern Plains, owing to the mixing of “young” high- $\text{NO}_3^-$  anthropogenic waters with “old” low- $\text{NO}_3^-$  pristine waters (105, 108, 109). Without



**Figure 6**

Influence of recharge history and flow paths on groundwater and surface water  $\text{NO}_3^-$  concentrations beneath an agricultural region in the Midwest United States (adapted from Reference 105). Recent recharge waters ( $>0.5$  tritium units, shown in *light gray*) contain high nitrate concentrations from fertilizers. The majority of regional groundwater was recharged before fertilizer use (paleowaters shown in *dark gray*) and have low  $\text{NO}_3^-$  concentrations, sourced from soil N. Discharge of low- $\text{NO}_3^-$  paleowaters and/or denitrification of agricultural  $\text{NO}_3^-$  sources along regional flow paths that intersect organic substrates may dilute surface water N pools.

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**DIC:** dissolved inorganic carbon

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accounting for the timing of recharge, loss of  $\text{NO}_3^-$  in groundwater may be mistakenly attributed to denitrification. In addition, where these low- $\text{NO}_3^-$  old groundwaters discharge to surface waters, they can significantly dilute stream and riparian N pools (110).

Groundwater systems are often below the rooting zone, making microbial processes the primary driver of biogeochemical cycling of C and N. DOC is converted to dissolved inorganic carbon (DIC) as microbes metabolize DOC and generate  $\text{CO}_2$  and alkalinity. At the same time, DON is converted to DIN, in the absence of  $\text{O}_2$ , by microbial metabolism. Organic acids generated by respiration of organic matter are also consumed through mineral weathering along groundwater flow paths, producing DIC. Groundwater is usually high in DIC and DIN and low in DOC and DON, in contrast to soil and surface waters.

**Depth and length of flow paths.** The depth and length of groundwater flow paths strongly control the conversion of DOC to DIC and N cycling as well as the coupling back to surface systems. In local flow systems, groundwater is in close communication with soil waters and streams, with relatively short flow paths and residence times ( $<1$  year). DOC and particulate organic C transported to the water table are the primary sources of C for N cycling.  $\text{CO}_2$  generated in situ can be exchanged with the atmosphere, soil gas, and/or discharged to surface waters. C and N cycles in local groundwater flow systems are similar to cycles in soils.

In regional flow systems, low recharge rates and long flow paths limit DOC transport into deep aquifers, making the total organic carbon (TOC) of the aquifer matrix the most important C source for N cycling. Examples of subsurface sources of TOC include organic-rich clay confining units, peat/coal, black shales, and hydrocarbons. As groundwater containing high  $\text{NO}_3^-$  concentrations comes in contact with organic-rich horizons along discrete flow paths (as shown in **Figure 6**), these localities can become zones of intense denitrification (e.g., 111, 112). In addition, interface zones between

confining units and adjacent aquifers are hot spots for microbial activity, as nutrients, electron donors/acceptors, and organic acids generated in aquitards are transported into more permeable layers (or vice versa) via diffusion (113).  $\text{CO}_2$  produced via redox reactions can accumulate at depth in confined flow systems and precipitate carbonate cements, effectively storing C on geologic timescales (114). These  $\text{CO}_2$ -charged waters may also eventually discharge to the surface along faults or fractures.

**Supply of reactants.** Both the quantity and quality of organic matter can control cycling of N in groundwater systems. McMahon & Chapelle (115) recently evaluated regional patterns in redox conditions and in the persistence of  $\text{NO}_3^-$  in major U.S. aquifer systems. They concluded that the potential for denitrification in groundwater directly correlates to the amount of organic matter in the aquifer system, which is related to the regional geology. For example, groundwater in the glaciated Great Lakes region is dominantly anoxic, contains low  $\text{NO}_3^-$  concentrations, and is affected by  $\text{SO}_4^{2-}$  reduction because of the presence of organic-rich tills mantling the surface. In contrast, groundwater in the Basin and Range province in the Southwest and the Pacific Northwest is dominantly oxic and may contain high  $\text{NO}_3^-$  concentrations with long residence times because of low TOC content.

In organic-rich groundwater systems, the quality of the TOC appears to be the primary control on microbial processes. Complex molecules in TOC are not easily degradable by N-reducing bacteria without the aid of fermenting microorganisms, which break down the long chain hydrocarbons to produce simple substrates that serve as electron donors for N reduction, such as acetate, formate, and hydrogen gas. The quality of TOC and rates of fermentation can change over time and space within groundwater systems. For example, in the Middendorf aquifer in the U.S. Atlantic Coastal Plain, shallow nonmarine sediments contain TOC significantly degraded by microbial activity (less bioavailable), whereas deeper

marine sediments contain abundant labile C (116).

Ancient organic materials, such as Paleozoic organic-rich shales, are often assumed recalcitrant because of millions of years of biodegradation. Recent studies, however, show that these Paleozoic shales sustain large communities of fermenting bacteria and methane-producing Archaea at great depths (up to  $\sim 1$  km) in sedimentary basins (117). In addition, a significant component of DOC transported in surface waters from northeastern U.S. catchments derives from near-surface weathering of Paleozoic black shales (118). Other redox reactions, besides organic matter respiration, can also play a key role in  $\text{NO}_3^-$  reduction in groundwater. For example, diffusion of hydrosulfide anions ( $\text{HS}^-$ ) and iron II ions ( $\text{Fe}^{2+}$ ) into aquifers from oxidation of sulfides in confining units can be coupled to N reduction.

In spite of major advances in the understanding of biogeochemical cycling of C and N in groundwater systems, major knowledge gaps exist. Important research opportunities include (a) developing new techniques to make use of isotopic tracers, both natural and introduced; (b) in situ study of microbial, geochemical, and hydrologic reactions as well as scaling issues; and (c) predicting the response of groundwater systems to changing boundary conditions (e.g., recharge rates caused by climate change and changes in inputs of C and N).

N isotopes of  $\text{NO}_3^-$  have been shown to be relatively ineffective tracers of N sources in groundwater systems, except on local scales where groundwater can be directly tied to specific land-use types. The major issues appear to be the overlapping N isotope values of N sources (e.g., soil N and fertilizers) and biologic fractionation of N, which can modify  $^{15}\text{N}/^{14}\text{N}$  ratios. **Figure 6** shows the large range of  $\delta^{15}\text{N}$  values of recent recharge from an agriculturally dominated catchment versus preanthropogenic  $\text{NO}_3^-$  sourced from SOM. Although coupling oxygen isotopes of  $\text{NO}_3^-$  with  $\delta^{15}\text{N}$  values helps to constrain better sources of N and the effects of denitrification, wide variations in the isotopic composition of N sources, mixing,

and biologic cycling can greatly obscure these values. Measuring  $\text{N}_2$  to argon ratios of dissolved gases in groundwater is an additional tool that has been used to detect denitrification, as microorganisms convert  $\text{NO}_3^-$  to  $\text{N}_{2(\text{g})}$  (119). Oxygen-17 is also being developed as a tracer of atmospheric  $\text{NO}_3^-$  inputs to groundwater systems (120).

In situ studies are essential in resolving the physical, chemical, and biologic processes that control C and N cycling in groundwater systems and reaction rates. Field measurements of C and N species and chemical parameters (e.g., pH, dissolved  $\text{O}_2$ , and  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ,  $\text{SO}_4^{2-}$ ) are widely used to delineate redox zones in aquifers on the basis of available energy from electron donors/acceptors. However, Park et al. (116) showed that microbial redox reactions are much more complex and that redox zonation is less well defined than previously thought. In the U.S. Atlantic Coastal Plain, microbes of different functional groups (i.e.,  $\text{SO}_4^{2-}$  reducers and Fe reducers) can coexist throughout the aquifer system, and the availability of thermodynamic energy and/or the presence of organic substrates does not limit them. Initial rates of fermentation of organic matter and the presence of localized sulfide minerals in aquifer materials seem to be the more likely control on redox reactions. The mixing of waters from various depths with different chemistries—a particular problem for wells with large screened intervals—can also affect samples collected from groundwater wells. In addition, scalability to catchment-scale systems still limits laboratory micro- and mesocosm experiments.

Finally, observational and modeling studies are needed to ascertain transient changes in groundwater systems and C and N cycling in response to changing climatic conditions. Previous studies, such as those discussed above, provide important baseline conditions and show how catchment systems have responded to dramatic changes in water and chemical fluxes over the past several decades owing to agriculture. In addition, we need to further investigate surface water storage in alluvial aquifers and the

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**Autotroph:** an organism that produces complex organic compounds from simple inorganic molecules, using energy from light or inorganic chemical reactions

**Heterotroph:** an organism that requires organic substrates to get its C for growth and development

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impacts of these alluvial aquifers on hydrologic connectivity in streams.

## Streams

Streams are critical habitats in landscapes and key locations of hydrologic and biogeochemical interactions (121–123). The concept of hydrologic and biogeochemical coupling in streams builds from the River Continuum Concept (RCC) (123, 124). Simplistically, the RCC views the longitudinal movement of water in streams and rivers as shaping lotic structure and function; stream communities shift from reliance on predominantly allochthonous terrestrial organic matter in headwater reaches to autochthonous C sources in middle reaches, and eventually to allochthonous sources as receiving drainage area and flow volume increase. Although useful in explaining broad patterns in energy and food web dynamics, the RCC fails to explain stream biogeochemical processes. Moreover, it is limited in its concept of horizontal and vertical exchange (125), temporal changes associated with flood pulses (126), and spatial variation in processes associated with drainage networks (127).

**Material spiraling.** One particularly useful concept that emerged from the RCC was material spiraling (121). As streams propagate water and chemicals downstream, the dissolved and particulate chemicals are continuously reworked, first consumed by one set of autotrophs or heterotrophs, then reworked into secondary consumers, and finally rereleased to the water column by another round of heterotrophy. Implicit in the concept of nutrient spiraling is the physical interaction between streams and the hyporheic environments as well as the groundwater environments that underlie and parallel the stream. The hyporheic zone is the subsurface sediment and porous space volume next to the stream that readily exchanges with the stream water (128). It is in this interaction with the hyporheic zone and groundwater that the spatiotemporal complexity of the near-stream zone increases dramatically, particularly following disturbance.

Hydrologic studies quantifying the physical interaction between streams and the hyporheic and groundwater environments have typically used solute tracer experiments to characterize timescales and lengths of exchange with storage zones (e.g., 129). Although this method is limited to specific scales of space and time (processes operating length scales from meters to a kilometer and at hours to weeks), it has been successful at quantifying stream-groundwater interactions (e.g., 130). The technique also has been applied to a large variety of ecosystems with different flow volumes, under dramatically different geomorphic and land-use conditions (131–134), and it has also been used to model two-dimensional groundwater flow and particle-tracking to simulate vertical and longitudinal hyporheic exchange (135). Several fundamental interactions between stream-groundwater systems and biogeochemistry have emerged from this research discussed below (136–138).

**Stream hydraulics: depth, slope, and rate of flow of stream.** Depth, slope, and rate of flow in a stream strongly influence the physical interactions between streams and the surrounding subsurface and, hence, the biogeochemical reactions. Assuming similar substrate, slower-flowing shallower streams with a high ratio of subsurface to surface reactive volume have a greater degree of exchange than streams that flow faster with a higher volume of water and a relatively smaller volume of subsurface with which to interact (130). Decreases in physical interaction of the stream with the subsurface environment (hyporheic to groundwater) over space or time are critical biogeochemically because of the strong contrast in biogeochemical environment between the stream and the subsurface. Streams often have high O<sub>2</sub> and light availability and can thus foster high rates of organic matter metabolism and photosynthesis. In contrast, the subsurface is dark and may or may not be low in O<sub>2</sub> and nutrients depending on the sediment. The contrast in oxidation-reduction conditions produces a situation where continued movement of

water from the surface to the subsurface and back and out of the subsurface and into the surface water system creates opportunities for biogeochemical processing between the surface and subsurface environments. Moving water out of the surface and into the subsurface allows for the thin film microbial heterotrophy common in the hyporheic zone to rework nutrients bound in organic matter and rerelease the nutrients into solution. These shifts in redox state cause shifts in nutrient availability, from nutrient sources to sinks, in streams with upwelling and downwelling stream reaches (139–142) and thus have profound influence on stream ecosystems. Large diel shifts in redox state have also been observed in more eutrophic streams (143).

The combination of these physical and biogeochemical exchanges between streams and the subsurface have led to several large-scale studies that have demonstrated the critical importance of headwater and low-flow streams on nutrient availability and organic matter metabolism in a variety of settings. Studies have empirically identified that smaller slower-flowing streams have shorter nutrient spiraling lengths and thus greater nutrient assimilative capacity than larger streams (131). Similarly, a broad study of the Mississippi River basin has indicated that small first-order streams have greater capability to remove nutrients than larger-order streams (144). Although total biotic uptake and denitrification of  $\text{NO}_3^-$  are high in low-order streams and increase with stream  $\text{NO}_3^-$  concentration, a recent study across 72 streams and 8 regions has shown that the efficiency of biotic uptake and denitrification declines as concentration increases, thereby reducing the proportion of in-stream  $\text{NO}_3^-$  removed from transport (145).

Although these studies seem to indicate a monotonic decrease of nutrient-removal capacity with stream flow and/or stream order, recent studies have indicated a more complex relationship in larger semiarid streams and alpine catchments. For example, work in the arid and semiarid Southwest has shown that lower-order stream systems, whether in irrigated systems or more natural near-stream conditions,

export water, C, and N to higher-order settings where nutrients and C then await removal or metabolic processes (146, 147). Similarly, studies indicate that headwater alpine catchment areas act as sources of DIN and DOC to downstream high-order streams and that retention of N is high at the alpine/subalpine transition as the areal extent of soil and vegetation cover increases (148, 149). Predictive frameworks using conservative versus nonconservative solute comparisons to separate transport from biologically mediated controls provide promise for elucidating hydrobiogeochemical coupling across scales (e.g., 150).

### **Processes at the interface between streams and the landscape.**

Research has also demonstrated that physical connections to the uplands and the sources of waters from uplands to streams change over time, particularly in arid and semiarid ecosystems. In humid climates, the connections are more continuous, and upland waters are typically in constant communication with riparian areas. In semiarid regions, the connection is more episodic over space and time. River-riparian ecosystems in semiarid environments respond to episodic storms that deliver water, C, and N in rainfall but also from upland systems as floodwaters that stimulate pulsed biogeochemical processes in riparian ecosystems. Floodwaters may also bypass the riparian area before entering the stream (121). Although this bypass means little processing occurs before the entry of floodwaters into streams, it does not mean that the water and material are not subject to later storage and release. In fact, several recent papers have demonstrated that floodwaters can be stored in the near-stream zone for periods of weeks to years and continue to influence surface water quality and nutrient status long after the flood wave has passed (147, 151, 152). This longer-term storage of floodwater and material requires further investigation so that we may better understand the spatiotemporal scale and magnitude of continuing floodwater influence in stream and river systems, as well as the response to decadal-scale climate changes.

The connection of streams to local and regional aquifers is more easily defined; streams and rivers are perennial only when supported by a connection to a groundwater system. As such, the materials in groundwater are critical for determining the water quality of streams. The inputs of materials from the subsurface can be mediated by interactions with streambed sediments that may either increase dissolved organic matter (DOM), DOC, and other elements that make up DOM, as well as DIN concentrations through respiration and mineralization or may decrease both of these constituents through respiration and denitrification. The net change is dependent on groundwater redox conditions as compared to the availability of substrate and the redox conditions in the groundwater-stream interface.

Stream biogeochemists and hydrologists have focused on the continual interaction between flowing water and gradients of biogeochemical processes with microbial processes treated as “black boxes” (122). The concept of continual interaction between flowing water and life may, in fact, offer a grand vision for the linked study of hydrology and biogeochemistry (122). In essence, flowing water carries reactants and products either into a reactive setting, or out of one, and the degree of this interaction depends upon volume, residence time of water, and the volume and reactivity of the substrate with which water interacts. These axioms are as true in upland, catchment, and groundwater environments as they are in the stream and near-stream zone areas.

## Catchments

Hydrological and biogeochemical coupling within catchments is based on the supposition that the chemical composition of water leaving a defined catchment represents an integrated signal of the biotic and abiotic processes occurring along flow paths that generate stream flow (**Figure 2**). Bormann & Likens (153) spurred the study of watershed ecosystems, postulating that the “vegetation of a watershed and the stream draining it are an

inseparable unit functionally, and it would be of great interest to obtain information on the biological interaction between them”. Prominent examples of catchment-based research that coupled hydrology and biogeochemistry include studies at Hubbard Brook, NH (154); Panola, GA (155); Walker Branch, TN (156); HJ Andrews, OR (10); Coweeta, NC (157); Sleepers River, VT (158); Emerald Lake, CA (159); both Green Lakes Valley (160) and Loch Vale, CO (161); Svartberget, Sweden (162); the Lake District, United Kingdom (163); and many other experimental catchments, including those operated by the U.S. Department of Agriculture, U.S. Forest Service, and U.S. Geological Survey. Although varying in climate and vegetation, most of these studies have been performed at the scale of headwater catchments because their size characteristics are widely perceived to facilitate the identification and quantification of process-level linkages between biotic and abiotic processes.

Many initial watershed studies treated the catchment ecosystem as a black box where differences between inputs and outputs were used to evaluate the effect of changes in land cover, specifically the effects of forest vegetation on water and nutrient yield (e.g., 164). In these studies, the removal of vegetation typically increased both the magnitude and flashiness of stream discharge and elevated inorganic N concentrations. Although N concentrations remained elevated while vegetation was actively excluded, these concentrations rapidly decreased if vegetation was allowed to regrow. The focus on water and N gradually expanded to encompass dissolved solutes including DOC, nutrients, and acid-generating solutes (e.g., 165). Notably absent from most early studies were specific isotopic or geochemical tracers that more recently have been used to infer residence time and flow paths generating stream flow (166).

A major expansion in catchment-scale hydrobiogeochemical research stemmed from the recognition that atmospheric deposition of acid anions, primarily N and S compounds, were reducing surface water pH in Europe and North

America (167). The need to couple hydrological and biological processes to address this problem was motivated by the increasing knowledge that both N and S were actively cycled through biota in soil and vegetation (168) and that the routing and residence of water through catchments delivered the acidifying solutes to surface water (169). A general finding from many of these experimental catchments was that both acid-anion deposition and organic acids generated in surface soil horizons were buffered by mineral weathering of base cations (e.g., 170). These research efforts demonstrated that surface water chemistry integrated, or mirrored, both biotic and abiotic processes on the landscape (164, 171). More specifically, these studies showed that the length of time that water resided in the catchment before becoming stream flow controls the length of time that terrestrial biota had access to cycle and recycle elements and that the flow path that the water took on its way to becoming stream flow had a pronounced effect on the potential solute (e.g., weathering products).

Atmospheric N deposition also provided a natural fertilization experiment in many terrestrial ecosystems, leading to the concept of N saturation—N inputs in excess of biological demand (88). A general finding from these studies was that the timing and magnitude of  $\text{NO}_3^-$  export in streams was tightly linked to patterns of biologic demand for N in upland ecosystems, with vegetation N demand associated with long-term trends in surface water (95, 171) and soil microbial processes associated with variability in individual soil flushing events (172, 173). More recent long-term analysis of C and N in soil solution and stream flow in Hubbard Brook has linked variation in N export to changes in flow paths, from vertical flow paths to horizontal flow, and to flushing of organic soil horizons into the stream during the non-growing season and high-rainfall events (174). These findings again highlight the importance of understanding hydrologic routing of water through the catchment to explain hydrochemical responses in stream flow.

Research questions on the importance of terrestrial DOM export to stream ecosystems

and to terrestrial C balance prompted similar studies to characterize the magnitude, sources, and cycling of DOM in headwater catchments. Research focused on two complementary approaches: One characterized the landscape characteristics and related these characteristics to DOM in stream flow, and the other approach focused on the temporal dynamics of DOM in stream flow. The landscape studies demonstrated that DOM concentrations in stream flow are strongly related to catchment soil organic C pools (175) or to putative flow paths through wetland systems with high soil C content (176). Temporal studies demonstrated that DOM often exhibits a flushing response, characterized by higher DOM concentrations on the ascending limb of the hydrograph compared to the descending limb (177). Together, these studies highlighted two important points: (a) Hydrological flow paths matter for the source and residence time of DOC, and (b) the amount of DOM available to be moved along a hydrologic flow path depends on the availability of substrate and the biological processing of this DOM into mobile forms. Spectrophotometric analyses of DOM have further demonstrated that terrestrial organic matter is rapidly transported to surface water during storm events (178), and quantitative hydrologic investigations have demonstrated that riparian systems serve as hot spots of terrestrial DOM production that are flushed by upslope water (179). Similarly, plot-scale studies have shown that the amount of mobile DOM flushed during runoff events relates to organic matter supply and soil heterotrophic activity before the event (172). However, few studies have evaluated the controls on DOM production in soils simultaneously with hydrologic transport to surface water.

As catchment-based work progresses, both hydrologists and biogeochemists have focused their investigations on looking inside the black box of catchment responses to identify when and where reactions are occurring that generate the solutes observed at the catchment outlet. A number of tools and techniques have been proven helpful in refining our knowledge

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**DOM:** dissolved organic matter

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of hydrologic routing and residence time and biologically mediated reactions. End-member mixing analysis (EMMA) has been used to identify the number and relative contributions of different water sources to stream flow and changes over time (166). Two strengths of EMMA are that it provides fractional contributions of source waters to the stream so these contributions can be used to compare catchment responses even in the absence of discharge, and it can be used to infer where water originates and thus where biogeochemical modifications to C and N are most likely to occur. For example, Mulholland & Hill (150) used the fingerprinting of source-water chemistry to determine that nutrients originating in the catchment were actively modified along flow paths out of the catchment, presumably as water passed through the riparian and/or hyporheic zone. Similarly, the unique isotopic composition of the N and oxygen molecules in  $\text{NO}_3^-$  has been used to determine if  $\text{NO}_3^-$  in stream water is derived from atmospheric deposition, fertilizer, or mineralized organic matter (180). Finally, McKnight and colleagues (181) have developed a simple spectrophotometric method to determine the relative contributions of terrestrially and aquatically derived organic C to DOM in streams and lakes. In all these examples, researchers are using the hydrochemical and isotopic composition of surface water to determine when and where hydrological versus biological processes dominate observed patterns in stream hydrobiogeochemistry.

Many research gaps remain in catchment hydrology, and catchment-scale science still lacks a multiscale framework for predicting watershed hydrology and functions (12). To address these conceptual gaps, McDonnell et al. (12) have argued for a classification system for catchment hydrologic residence time, flow-path distribution, and functions that allow for predictions of hydrologic patterns across scales. Identifying these hydrologic scaling laws will enhance coupled biogeochemical theory and predictions by eliminating the need for site-specific, detailed hydrologic characterization of catchments. These scaling laws should provide

a pathway for coupling tracer-based field and modeling techniques with process-oriented hydrologic models to capture flow-path distributions and water-residence times such that hydrograph and chemograph separations are in accord (182). These advancements would foster the ability of coupled hydrological and biogeochemical models to “get the right answers for the right reasons” (183).

## RESPONSES OF BIOGEOCHEMICAL CYCLES TO CHANGES IN VARIABILITY OF HYDROLOGIC CYCLES

In this section, we summarize results from a few key studies that couple water, C, and N cycling within and across different environments and examine the impact of changing hydrologic cycles on biogeochemistry. The 2007 Intergovernmental Panel on Climate Change report (6) projects increased runoff and earlier spring peak discharge in glacier- and snow-fed ecosystems as well as warming of most rivers and lakes. Increased water availability is likely in the moist tropics, whereas decreased water availability is likely in midlatitude and semiarid low-latitude ecosystems. Mountain, tundra, boreal forest, and Mediterranean ecosystems are virtually certain to experience the most severe ecological impacts (6). Below, we examine the impacts of changing climate and N deposition on changing biogeochemical cycles in snow-dominated, semiarid, and tropical ecosystems as well as groundwater systems.

### Snow- and Ice-Dominated Catchments

Climate change models predict earlier snowmelt and less spring snowpack accumulation, with higher temperatures influencing the structure and functioning of snow- and ice-dominated systems. Earlier studies by Brooks et al. (172, 173) in the Rocky Mountains showed strong snow cover controls on N export and retention. Measurements of leached N were inversely related to measurements of

overwinter CO<sub>2</sub> flux at all sites, suggesting that N was immobilized in soil heterotrophic biomass (172, 173). Consistent with these plot-scale measurements of heterotrophic immobilization, catchment N retention was positively related to catchment snow cover ( $r^2 = 0.68$ ). However, similar patterns have not been observed in warmer and wetter systems in the Sierras (184) and northern hardwood forests (185). Brooks & Williams (173) proposed a conceptual model of respiratory and N fluxes, which is based on snow duration, that provides a framework for predicting the effects of future changes in snow cover duration. More recent studies have confirmed the importance of snowpack and the microbial community on soil respiration (186). For example, Groffman et al. (187) have experimentally demonstrated that reduced snow depth and associated soil freezing increase fluxes of CO<sub>2</sub>, N<sub>2</sub>O, and methane in northern hardwood forests.

Recent studies in permafrost-dominated Arctic catchments have shown that groundwater and surface water systems are rapidly responding to changing climate conditions, resulting in detectable changes in C and N transport and cycling (188). As the surface thaw depth increases because of global warming, storehouses of C and N in frozen soils are becoming available for microbial utilization. In addition, as the residence time of groundwater increases because of increased depth and length of subsurface flow paths, more DOC and DON are converted to DIC and DIN and transported to surface waters. Walvoord & Striegl (188) reported that groundwater contributions to stream waters in Arctic catchments have increased by 0.7% to 0.9% over the past 30 years, causing marked decreases in DOC and DON and increases in DIC and DIN in surface discharge.

### Arid and Semiarid Ecosystems

These ecosystems are likely to experience warmer temperatures and changes in the timing, frequency, and magnitude of rainfall. The Southwest is the driest region in the United

States, but precipitation varies seasonally, from a winter-dominated regime in the west (e.g., Mohave Desert) to a bimodal regime in the Sonoran Desert, to summer domination to the east (Chihuahuan Desert). Many semiarid basins are glacier- or snowmelt-fed river basins, and with more than one-sixth of the world's population living in these regions and with projected population increases in the future, seasonal shifts in stream flow, and possibly reduced low flows, caused by decreased snow water storage, will likely adversely affect ecosystem and human functioning (6).

In semiarid terrestrial ecosystems, rainfall pulse size regulates ecosystem C balance by determining the duration of microbial respiration and photosynthetic activity of plants, with microbes responding to small pulse sizes and plants requiring large pulse sizes to initiate photosynthesis. Thus, semiarid ecosystems act as immediate C sources to the atmosphere following soil wetting, with subsequent periods of C accumulation if the pulse size is sufficient to initiate plant activity (189). Shifting precipitation patterns will likely alter the C and N cycling and the partitioning of gaseous and hydrologic losses with feedbacks to NPP. One of the main challenges is resolving the partitioning of the CO<sub>2</sub> efflux as plant respiration, microbial respiration, and physical displacement of soil CO<sub>2</sub> following soil wetting. Understanding the mechanistic interactions of soil water characteristics, plant ecophysiological responses, and canopy structure on the partitioning of water, C, and N fluxes will be important for understanding the effects of shifting precipitation and vegetation patterns in these water-limited ecosystems (51, 189).

Changes in the timing, distribution, and magnitude of snowmelt or monsoon precipitation are also likely to result in significant hydrobiogeochemical responses in streams and riparian systems across this region. In the San Pedro River, for example, Meixner et al. (152) found significantly elevated N loading during summers, preceded by low winter rainfall, but low N loading following high winter rainfall. These findings suggest longer and more

frequent winter droughts in the Southwest may alter the capacity of a riparian ecosystem to remove N during winter months and increase N delivery to streams.

In contrast to these fast climate features, changes in mountain groundwater recharge to rivers will not likely impact stream functioning in the short term because of the slow travel time from mountain fronts. However, human appropriation of groundwater in the Southwest is profoundly impacting groundwater recharge and thus stream flow, an impact that is likely to continue given that arid and semiarid lands are expected to experience disproportionate increases in human populations and land transformation worldwide. Pumping has resulted in groundwater decline and produced intermittent and even zero-flow conditions in the summer dry season (190). Such land-use driven changes in hydrologic conditions also are likely to reduce N removal capacity, thereby affecting water quality downstream. In a synoptic survey of stream water chemistry in the San Pedro River, Brooks & Lemon (147) observed that perennially wet (gaining) reaches were generally sinks for  $\text{NO}_3^-$ , DON, and DOC, whereas dry losing reaches were sources of  $\text{NO}_3^-$  to the stream following the monsoon season. These observations together suggest reduced hydrological connections due to groundwater lowering and prolonged drought will decrease riparian N removal capacity and negatively affect downstream water quality. To date, however, little research has focused upon the impacts and feedbacks of hydrologic alterations (human and climate driven) on riparian zone ecosystem processes and services.

Alterations in hydrological conditions, including reduced flow permanence on account of stream diversion and groundwater pumping, are also thought to drive the pervasive riparian vegetation shift from cottonwood-willow (*Populus fremontii*-*Salix gooddingii*) gallery forests to tamarisk-dominated (*Tamarix ramosissima*) stands. Lite & Stromberg (191) developed a hydrological threshold model predicting this riparian state transition in the San Pedro River on the basis of occurrence data for indicator

species of the two states. A lower composite hydrologic condition index (i.e., lower water table, increased water table fluctuation, and less flow permanence) is predicted to increase vulnerability of native riparian species such as cottonwood to drought and favor the drought-tolerant tamarisk. Their findings and those of others (192) suggest that maintaining or restoring the hydrologic flow regime is critical to reinforcing the native vegetative state of the ecosystem. In spite of advances in understanding the hydrologic drivers behind movement between states, the consequences of groundwater lowering and of the associated riparian-community shift for biogeochemical processes remain poorly understood and understudied.

### Wet Tropical Ecosystems

In the moist tropics, global climate change models predict increased water availability, with decreased water availability and increased droughts in midlatitudes as well as the possible conversion of forest to savanna (193). Atmospheric models predict increased N deposition in the tropics because of agricultural and industrial intensification (17). The responses of these systems to changes in hydrology, N deposition, and their interaction with land-use change remain highly uncertain. Some of our best insights to tropical forest responses to changes in water availability come from gradient analysis. In a study along a precipitation gradient (2200–5050 mm rainfall) in the Hawaiian islands, Schuur et al. (58) examined the effects of climate on tropical forest ANPP, decomposition, C storage, and nutrient losses. They showed that increased C storage at the wetter sites was associated with steeper declines in decomposition compared to forest ANPP. Decreased decomposition rates corresponded with low soil reduction-oxidation potentials and suggested that soil  $\text{O}_2$  availability was limiting to microbes. Decline in net primary productivity corresponded with decreased N availability owing to slower decomposition and nutrient release. Other studies across this gradient have documented thresholds in N trace gas fluxes

(as  $N_2O$ ), whereby N trace gas fluxes decreased with decreasing N availability at the wettest sites (194). These studies and others (57, 195) suggest that one of the most important effects of variation in water on C and N cycling in wet tropical ecosystems is the control on the diffusion of  $O_2$  into the soil; changes in water availability in the tropics will strongly affect decomposition and nutrient availability with important feedbacks to productivity and trace gas emissions (195).

### Response of Groundwater Systems to Land-Use and Climate Change

Studies in the High Plains aquifer system (Figure 6) document how hydrologic systems respond to land-use change and climate variability on annual and longer-term timescales (196, 197). Periods of enhanced precipitation and infiltration (e.g., the warm phase of El Niño-Southern Oscillation) mobilizes soil N pools and transports DOC and DON to the water table, whereas periods of colder and drier conditions can cause N accumulation in shallow soils. Conversion of rangelands to irrigated croplands can also induce these changes in chemical reservoirs of the vadose and phreatic zones (107, 197). Because of the relatively long transit times from the water table to stream discharge, changes in C and N pools and water sources in groundwater systems, caused by changes in climate and/or land use, may not appear in surface waters for several decades or more (e.g., 198). For example, if fertilizer use is substantially decreased in agricultural watersheds, high  $NO_3^-$  concentrations may persist in groundwater-fed streams, especially if aquifers are C limited.

Groundwater systems may still be equilibrating from past climate change events, such as the Last Glacial Maximum or more recent Holocene periods of cold and wet conditions. Recharge beneath Pleistocene continental ice sheets stimulated C cycling via methanogenesis in organic-rich Paleozoic shales in deep basinal aquifer systems by significantly diluting the formation of water salinity (117). Sub-

glacial waters may have been oxic to anoxic, depending upon the availability of electron acceptors/donors and organic substrates at the base of glaciers. Sediments deposited by glacial or fluvial processes provide important organic matter and mineral substrates for denitrification, as well as preferential flow paths for water and for C and N transport. Böhlke et al. (199) reported that oxic groundwaters in the Great Plains aquifer system were recharged in the Holocene, during periods of increased precipitation. Recent fertilizer use in agricultural watersheds has greatly modified these prior redox conditions by substantially increasing the flux of  $O_2$ , C, N, and water to groundwater systems.

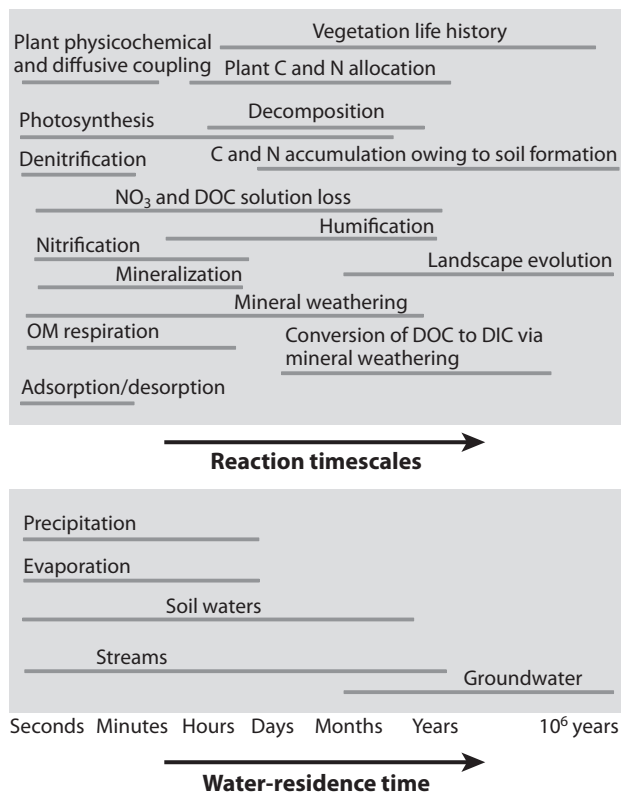
### CONCLUSIONS

Fundamental interactions of water, C, and N cycles occur at the land-atmosphere interface and at transitions in soils, groundwater, and streams (Figure 2). Common among all environments is that hydrological transitions result in disproportionately high rates of C and N cycling. Key couplings occur among fast processes (such as plant physiology and energy balance) and slow processes (such as community structure, life history, morphology characteristics, and nutrient availability) to constrain energy and material exchange at the land-atmosphere interface. Although these couplings provide a multiscale model for predicting biogeochemistry, knowledge gaps remain at this interface and across the disciplines. For example, challenges remain in partitioning evaporation and transpiration at the interface, and changes in this partitioning may feedback into soil moisture and transport within the soil regolith volume. Thresholds in soil water availability (controlled by the variability of precipitation, soil physical properties, and SOM) influence substrate availability, drainage, and redox state to control soil biogeochemical reactions and the gaseous and soil solution loss pathways. Spatiotemporal transitions in properties (such as perched water tables, fluctuating or rising water tables, wetting and drying events, and

flow-path boundaries or interfaces) are redox active because oxidized and reduced species come into close proximity to each other and because of the convergence of limiting substrates along flow paths. One of many current challenges for linking hydrology and biogeochemistry in the soil regolith is to understand how soil moisture and soil solution fluxes

influence the residence time of C, N, and water with feedbacks to groundwater and streams as well as to the atmosphere. In groundwater, the recharge rates, depth and length of flow paths, and supply of reactants control the coupling of C and N processes. However, to advance understanding of the coupling of hydrology and biogeochemistry across these fields, we need information about spatiotemporal variability in recharge. In streams, hydraulics, and material spiraling, exchange of subsurface and surface reactive volumes and hydrologic connectivity strongly influence hydrologic and biogeochemical couplings. One of the main challenges of streams is to understand and predict the spatiotemporal variability of water and solute sources. At the catchment scale, future research is needed to develop a multiscale predictive hydrology framework—a system that will classify catchment hydrologic residence time, flow-path distribution, and functions (12).

Climate-driven changes in hydrologic cycles are likely to impact hydrologic and biogeochemical couplings through changes in residence time and routing of water as well as by changes in phase. Residence time and flow paths across these different environments are highly variable and fundamentally affect reactions within them (**Figure 7**). Changes in these primary drivers of hydrologic and biogeochemical couplings (such as rainfall distribution) will likely alter the distribution of reaction timescales and movement of energy and material across these environments. Conversely, dramatic changes in slow processes at the land-atmosphere interface and in soils will also result in disturbances in hydrologic and biogeochemical couplings that will likely propagate within and across these zones through changes in reaction timescales of C and N and water-residence time. As such, loss of glaciers and permafrost reservoirs, dramatic vegetation change, and disturbances, such as pest outbreaks or fires, are likely to introduce unexpected changes in landscape processes integrated at the catchment scale.



**Figure 7**

Interactions of reaction timescales and water-residence times influencing key couplings of hydrology and biogeochemistry in different environments within catchments. Changes in primary hydrologic drivers (such as rainfall distribution) will likely alter the distribution of reaction timescales and movement of energy and material across environments (water-residence time effects on reaction timescales). Conversely, dramatic changes in slow processes at the land-atmosphere interface (such as vegetation change or soils) will also result in disturbances in hydrobiogeochemical couplings that will likely propagate within and across different fields through changes in reaction timescales of C and N (longer-reaction timescale mechanisms effect shorter-reaction timescale processes) and water-residence time (longer-reaction timescales affect water-residence time and feedbacks). Abbreviations: C, carbon; DIC, dissolved inorganic carbon; DOC, dissolved organic carbon; DOM, dissolved organic matter; N, nitrogen;  $\text{NO}_3$ , nitrate.

## SUMMARY POINTS

1. Fundamental couplings of water, C, and N occur at the land-atmosphere interface and among transitions in the soil regolith, groundwater, stream, and catchment, yet couplings across scales and research fields remain poorly understood and represent a grand challenge in linking hydrology and biogeochemistry. Common among all environments is that hydrological transitions, either episodic changes in water availability or hydrologic transport of reactants, result in disproportionately high rates of C and N cycling.
2. At the land-atmosphere interface, couplings occur among fast processes (such as eco-physiology, energy balance, and C sequestration) and slow properties (such as vegetation structure, evolutionary morphology, and nutrient availability) to control biosphere material and energy exchange.
3. In soils, thresholds in mineralization and soil water content (controlled by the climate, soil physical properties, and organic matter development) couple water and C and N cycles in such a way as to influence the hydrologic residence time of C and N.
4. In groundwater, recharge rates, depth and length of flow paths, and supply of reactants control coupling of C and N.
5. In the stream, hydraulics and material spiraling, exchange of subsurface and surface reactive volumes, and hydrologic connectivity act as primary drivers influencing hydrologic and biogeochemical coupling in streams.
6. Changes in hydrologic transitions, either episodic changes in water availability or hydrologic transport of reactants, will likely result in disturbances of hydrobiogeochemical couplings. Loss of glaciers in glacier-fed watersheds, loss of permafrost reservoirs, dramatic vegetation change, and disturbances (such as pest outbreaks or fires) are likely to introduce unexpected changes in landscape processes integrated at the catchment scale.

## FUTURE ISSUES

1. Although advances have been made at understanding couplings at the land-atmosphere interface and provide a multiscale model for prediction of biogeochemistry, knowledge gaps remain in partitioning evaporation and transpiration at this interface. Changes in this partitioning or changes in structure on account of droughts or pest outbreaks may feedback into soil moisture and transport within the soil regolith environment and to streams.
2. In the soil environment, we still lack understanding of how soil moisture and soil solution fluxes influence the residence time of C, N, and water and how this feeds back to groundwater and streams as well as to the atmosphere. Moreover, we lack understanding of how lower boundary conditions (e.g., topographic bedrock boundary, fractured bedrock, water table) influence subsurface flow and biologically mediated reduction-oxidation reactions and weathering processes.

3. To make advancements across environments associated with groundwater, we need to develop predictions of the response of groundwater systems to changing boundary conditions (e.g., recharge rates owing to climate change and changes in inputs of C and N). We also need to address in situ the study of microbial, geochemical, and hydrologic reactions as well as scaling issues.
4. Research gaps in streams include understanding the effects of longer-term storage of floodwater and material to predict the response of stream and river systems to decadal-scale climate changes.

## DISCLOSURE STATEMENT

The authors are not aware of any biases that might be perceived as affecting the objectivity of this review.

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