Groundwater—The Dynamic Base of the CZ

Pamela L. Sullivan, David P. Genereux, Andrea E. Brookfield, Daniella Rempe, Randy L. Stotler, Holly R. Barnard, Leif Karlstrom, Jennifer C. McIntosh, Holly A. Michael, Karla Jarecke, Rene M. Price, Steven P. Loheide, Alissa White, and Kamini Singha

1 Introduction

Addressing the multiple and diverse threats to groundwater requires the holistic approach inherent to critical zone (CZ) science—the discipline that unites researchers across fields of earth and environmental science to study the interactions from the top of the canopy down to the depths of groundwater over timescales that span seconds to millennia [6, 24, 146]. Groundwater, the water in the saturated earth below the water table, is an important natural resource for humans and ecosystems around the world. It is the largest source of available freshwater [278], supporting over 2 billion

P. L. Sullivan (✉) · K. Jarecke
College of Earth, Ocean and Atmospheric Science, Oregon State University, Corvallis, OR, USA
e-mail: pamela.sullivan@oregonstate.edu

D. P. Genereux
Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC, USA

A. E. Brookfield · R. L. Stotler
Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, ON, Canada

D. Rempe
Department of Geological Sciences, University of Texas at Austin, Austin, TX, USA

H. R. Barnard
Institute of Arctic and Alpine Research, Department of Geography, University of CO–Boulder, Boulder, CO, USA

L. Karlstrom
Department of Earth Sciences, University of Oregon, Eugene, OR, USA

J. C. McIntosh
Department of Hydrology and Atmospheric Sciences, University of Arizona, Tucson, AZ, USA

H. A. Michael
Department of Earth Sciences, Department of Civil and Environmental Engineering, University of Delaware, Newark, DE, USA

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people on Earth [141], however, another near 2 billion people live in areas where groundwater resources are under threat [102]. Approximately 70% of groundwater withdrawals are used for irrigation [59], representing about half of all water used for irrigation purposes [70, 257]. Groundwater is important for ecosystems globally: roughly 1/3 of terrestrial vegetation relies on groundwater [69], it is the source of baseflow to surface-water systems [279, 310], and through its reactions with the aquifer matrix, it plays a key role in controlling elemental cycling and fluxes [289]. Similarly, through baseflow contributions, groundwater plays a critical role in regulating heat in many surface-water bodies [121], often supporting specific aquatic fauna habitats (e.g., spawning ground for salmon; see [50] and references within). In addition to regulating energy fluxes, both the discharge of groundwater and the recharge of surface water through groundwater-surface water interaction controls the fate and transport of contaminants and nutrients in aquatic environments [28, 261]. Thus, perturbations to groundwater recharge or extraction induced by anthropogenic activities and climate change can threaten these CZ services [78].

At the most basic level, groundwater can be recharged naturally (e.g., precipitation, groundwater-surface water interactions) or artificially (e.g., irrigation, injection wells, infiltration ponds, and leaky urban infrastructure). Inputs to groundwater may change as a result of changing climatic conditions, such as the timing, amount, and phase of precipitation. Warmer temperatures can also increase evapotranspiration, which can have cascading effects on groundwater levels and fluxes. It has been projected that roughly half of global groundwater fluxes could be sensitive to shifts in climate and human activities within 100 years, potentially limiting available resources and their capacity for climate buffering due to altered recharge patterns [57]. Because many ecosystems are dependent upon using groundwater directly or the discharge of groundwater (e.g., wetlands, streams, and lakes), changes in climate may create key tipping points that drive ecosystems into alternative stable states [51, 54, 103]. For example, changes in the delivery of groundwater to streams may shift a stream from perennial to intermittent, flowing only part of the year. Given large-enough declines in the water table, an intermittent stream may transition to ephemeral, where the stream flows for a portion of the year, typically in response to precipitation events, and may also be disconnected from the groundwater [314]. Not only does stream intermittency impact the wetted length of streams and duration of surface water flow, but the degree and duration of groundwater-surface water

R. M. Price
Department of Earth and Environment, Florida International University, Miami, FL, USA

S. P. Loheide
Department of Civil and Environmental Engineering, University of Wisconsin-Madison, Madison, WI, USA

A. White
Department of Geosciences, University of Montana, Missoula, MT, USA

K. Singha
Hydrologic Science and Engineering Program, Colorado School of Mines, Golden, CO, USA

interactions, including those that thermally regulate stream-water temperature and support aquifer recharge [143]. In environments where the rooting zone of vegetation interacts and draws water from the water table, declines in the water table could lead to drastic shifts in the vegetation productivity [47] and shifts in community composition [51, 54, 103, 174]. The effects of climate change on water table position can be exacerbated by groundwater pumping [53, 140], causing water tables to lower at rapid rates. In many regions the water extracted is considered ancient, over pumping of groundwater—old or new—means water managers are likely to face growing scarcity issues in the future [75].

Solutions to these current and future challenges rely on understanding how much water is stored within the CZ. Yet the lower boundary, hidden well below our feet, is unclear; the base of the CZ has been defined as the bottom of the groundwater [106] or deepest depth of circulating groundwater [5], which may extend to depths greater than 2–3 km in some settings (e.g., [36, 196]). Entangled in these definitions are two questions: (1) What marks the bottom? and (2) What constitutes circulating water? This debate of where to draw the hydro-biogeochemical bottom of a watershed, or the CZ, was explored in [51, 54], where the authors provided three general definitions: (1) the depth to the low-conductivity boundary or "no-flow boundary", (2) the active circulation depth, which is "tunable" to the questions at hand–what flow paths are thought to contribute to the process or pattern under investigation, and (3) the depth to saline water. Our goal here is not to declare that any one of these is the best definition but to highlight that groundwater makes up an important component and driver of CZ processes, and that groundwater systems are complex and vary in the factors that threaten their resources.

Beyond groundwater quantity, groundwater scarcity is also controlled by water quality. Two spatially extensive processes threaten groundwater quality; the first is agriculture, which occupies roughly 40% of ice-free land [85] and is often associated with the contamination of groundwater by fertilizers and pesticides (e.g., [32, 249]). Contamination is particularly problematic in environments underlain by karstified aquifer systems having large conduits that allow for rapid connectivity between surface processes and groundwater through fast flow [116]. The second factor limiting access to potable groundwater occurs in coastal environments where seawater intrudes into coastal aquifers. It only takes about 2–3% seawater to yield non-potable water. Large-scale analysis of wells in the coastline of the contiguous USA shows groundwater levels are below sea level across 15% of the area [142], supporting landward hydraulic gradients that drive salt-water intrusion into coastal aquifers. Continued increases in sea levels create added pressure, as does coastal pumping, which can lower the water table and artificially create landward hydraulic gradients [15]. On a more regional scale, there are also millions of contaminated sites worldwide affected by a range of contaminants from heavy metals to pharmaceuticals to "forever" chemicals.

Below, we delve into the many ways in which groundwater dynamics and other subsurface-water stores (i.e., vadose zone water or "rock moisture") interact and feedback to control CZ functions, such as evapotranspiration, carbon cycling, and solute generation and export to surface waters and the ocean, and how these may be impacted under a changing climate. We also explore the ways in which CZ processes in turn influence the flow paths, transit times, and quality of groundwater, affecting water resources.

2 CZ Structure Controls Vadose Zone Thickness and Therefore Groundwater Recharge

Before we explore the role of groundwater as a dynamic boundary of the CZ, we highlight that the depth to the water table and the rates of groundwater recharge are dependent on the properties of the material above the water table (Fig. 1). We can conceptualize the subsurface as a three-phase system comprised of solids, liquid, and gases. The solid components include soil, saprolite, weathered rock, unweathered bedrock, and unconsolidated sediments, where liquid (water) and gases (e.g., oxygen (O_2), carbon dioxide (CO_2), and water vapor) fill the pore space created within the solid components. Collectively, these three components determine the heterogeneous CZ structure and its consequent function. Land surface, land cover, and atmospheric conditions interact with the underlying structure to determine the timing and amount of recharge to groundwater storage that feeds streams and springs.

Typically, the pathway of water transport from the surface to the water table requires the movement of water through some thickness of unsaturated subsurface known as the vadose zone. Fluid and nutrient fluxes in the vadose zone are driven by competing forces, with upward flow driven by evapotranspiration and capillarity, and gravity driving downward flow. In interbasin arid and semi-arid environments, wetting fronts are rarely deeper than the root zone [247]. In these environments, matric potentials are often lowest near the land surface, indicating that upward fluid

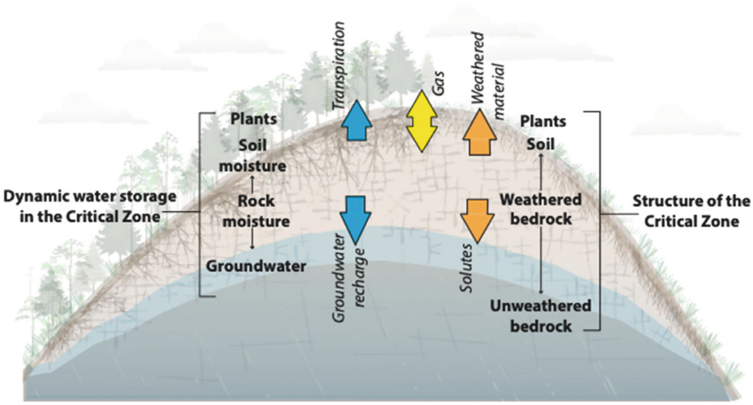

Fig. 1 A conceptual cross section through a hillslope shows the structure of the CZ (right) and water storage reservoirs within the critical zone (left). Arrows depict the fluxes of water (blue), gases (e.g., CO_2 in yellow), and products of the weathering of solid material (orange)

flows dominate [247, 295–298]. In more humid environments, matric potentials favor downward flow for longer periods of time, and water tables are closer to the surface. Downward flow dominates when water contents exceed the field capacity, where water draining beyond the root zone is potentially available for groundwater recharge. The balance of upward and downward fluxes drives the distribution and transport of nutrients and solutes in the subsurface. As external forcings change, such as shifts in the seasonal amount and intensity of precipitation or land cover/use changes, matric potential gradients in the subsurface will be altered and can change the distribution and flushing of solutes and nutrients [117, 198, 221, 222, 247, 287, 295].

The structure of the land surface, land cover, and vadose zone constrain infiltration, drainage, and fluid and solute movement in the vadose zone (Fig. 2). Drainage and recharge rates are not consistent across a landscape. Focused recharge is more likely to occur in depressions; areas where ponding frequently occurs; intermittent, ephemeral, and perennial stream beds with higher hydraulic potential than nearby aquifers; irrigated fields; or anywhere soil is wet for longer periods of time (e.g., [148, 198, 250, 291]). Gravity-induced drainage, defined by the specific yield, may also be aided by capillary flow, which acts in all directions. Ponded soils provide areas where downward pressure gradients are greater in duration and therefore able to drive fluids downward. This process also provides more opportunity to drive air out of pores, which increases the hydraulic conductivity. Infiltration and recharge are further constrained by biota, land cover and land use (e.g., [1, 240, 248, 308]). Worm, insect, and animal burrows, desiccation cracks, decayed root tubes, joints, and fractures provide pathways for rapid fluid flow past the root zone [124]. These preferential pathways essentially create a dual-porosity or dual-permeability medium, with water and solutes traveling to the water table at different rates [109, 239, 269].

In many locations, particularly in montane terrains, the vadose zone can consist of meters to tens of meters of weathered bedrock. This weathered bedrock can store exchangeable water, analogous to soil moisture, that has a distinctly different response to precipitation and drought than soil moisture [231]. Rock moisture storage may be greater than soil moisture storage, and continually expanding in active weathering environments through increases in secondary porosity (Fig. 1, [231, 294]). The influx, storage, and removal of rock moisture results in additional weathering, nutrient cycling, and geochemical mixing, likely supporting diverse and dynamic microbial populations [197, 231]. Importantly, rock moisture appears to represent water storage that mediates the rate of decline in plant-available water in droughts [231]. Consequently, plants with root systems that extend into fractured rock may be more resilient to seasonal droughts. Hahm and Rempe [111] highlighted the importance of rock moisture storage in controlling the regional distribution of plant communities, and evidence increasingly indicates that forest water use and productivity may be more closely related to rock moisture storage and topography than annual precipitation inputs [74, 276, 285]. Studies of soil moisture depletion have shown that many montane soils, particularly those on southern aspects, are thin and quick to dry, suggesting seasonally dry forests may rely on water from deeper reservoirs [11, 74, 126].

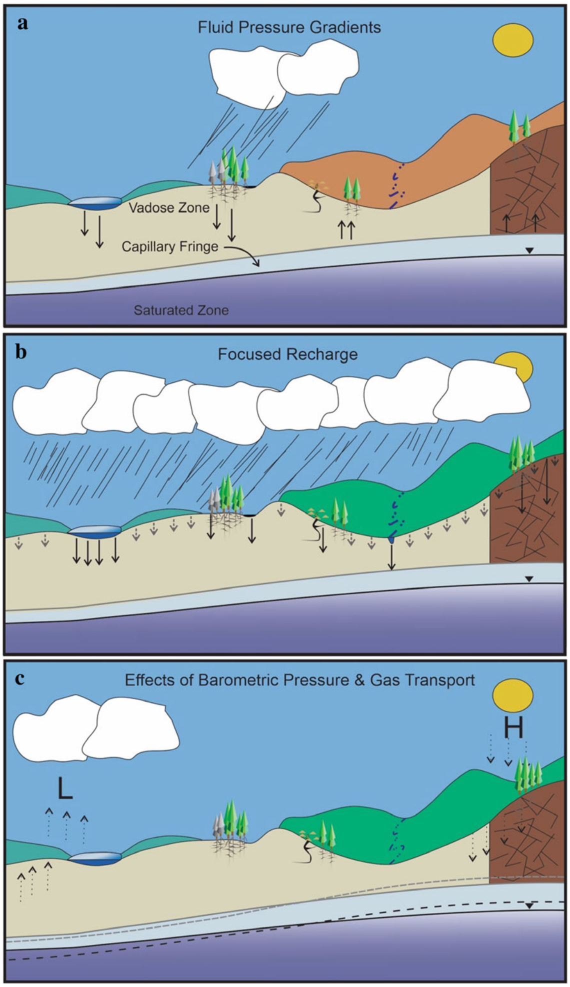

Fig. 2 Effects of changing conditions of fluid flow in the vadose zone. Note in this conceptualization surface-water bodies are disconnected from the water table and are losing water to the subsurface. **a** Fluid pressure gradients are downward beneath ponded water and during recharge events with gravity drainage, but upward during droughts and under actively transpiring plants. **b** Focused recharge pathways provide faster conduits for more water to the water table, and include ponded areas, depressions, and intermittent streams filled with water during and after a rain event, decayed root tubes, animal burrows, and joints and fractures. **c** Barometric pressure changes affect gas transport, as well as the position of both the capillary fringe and the water table. The upper dashed line, near the top of the capillary fringe, represents the location of the capillary fringe if barometric pressure conditions are constant across the watershed. Likewise, the lower dashed line represents the location of the water table under constant barometric pressure conditions. Reductions in barometric pressure result in upwards gas transport, while increases in barometric pressure result in downward gas transport

In recent decades, our understanding of how this unsaturated, weathered-bedrock vadose zone mediates fluxes to deeper groundwater has expanded rapidly as a result of innovations in sensing. Vadose-zone monitoring systems now allow monitoring of matric potential through advanced tensiometers, water content with multiple tools including flexible time-domain reflectometry, and soil and rock moisture and gas samples through sampling ports at multiple depths many meters below ground surface [65, 128, 168, 235, 236]. Near-surface geophysical tools also provide the ability to image the subsurface structure in minimally invasive ways and monitor changes across multiple temporal and spatial scales [218]. For example, shallow seismic refraction and electrical resistivity tomography have been used to map spatial variability in weathered and unweathered rock properties, and nuclear magnetic resonance documents moisture stored within the voids of weathered bedrock [81, 218, 253], which can be directly related to the structure of the vadose zone that overlies groundwater.

It is worth emphasizing that water moves in both fluid and vapor phases in the vadose zone (Fig. 2) and that reactive gases influence chemical reactions, nutrient availability, and solute transport (e.g., [158]). Gas transport is a complex process affected by both diffusion and pressure gradients of the gases, as well as a dissolved component in fluid [189]. The pneumatic diffusivity of gas in the subsurface is analogous to the hydraulic conductivity, and in the vadose zone, tends to be greater in matrices with large pore spaces (e.g., sands and gravels), with transport more likely in large capillaries and at low water contents [101, 301]. Because pressure gradients provide an important driving force for gas transport, changes in barometric pressure are integral to movement of gases in the vadose zone, even affecting the thickness of the capillary fringe and the position of the water table, which can affect groundwater flow directions and velocity [189, 264, 301]. Complex subsurface composition and pore structure can result in insertion and venting of gases in response to barometric pressure changes to great depths and long distances (i.e., 100 s m) [67, 169, 210]. Daily, seasonal, and climatic changes also affect connections and transport of gases, with increased water content, snowfall, and seasonal soil freezing reducing the prevalence and changing the locations in which barometric pressure gradients between the atmosphere and subsurface cause gas to flow into or out of the vadose zone (barometric pumping; [127, 188, 302]).

Recent investigations have expanded our understanding of vadose zone water storage, flow, and partitioning through the hydrologic cycle at multiple scales, and the effects on the connections of groundwater to the critical zone. Remote estimations collected over very large regions by the Gravity Recovery and Climate Experiment (GRACE) have revealed increases in total water storage in some areas despite significant on-going declines in water table elevation; these increases are driven by rising storage in the vadose zone [29]. Even as groundwater levels fall, the pores in the newly acquired vadose-zone storage do not completely drain [148]. Total water-storage estimates in conjunction with other ground-based observations indicate that groundwater removal in the Central Valley, CA, USA resulted in more uplift of the Sierra Nevada than tectonic uplift over a four-year drought period as an elastic response to the loss of water mass [8]. Yet ~70% of the uplift over this same four-year period, and 40–60% over an eleven-year period in which seven years are drought, is a result of drought-driven water loss deep in the vadose zone, alluvial aquifers, and crystalline basement [8]. Meanwhile, groundwater pumping in the Central Valley is resulting in localized subsidence of the land surface as decreasing fluid pressures increase effective stress, resulting in compaction of soils and permanent loss in aquifer and vadose-zone storage [73]. Groundwater-induced uplift and subsidence also reorganizes surface drainage and affects overland flow and sources of water for evapotranspiration [252]. The role of groundwater in frozen CZ systems, which might limit depth of flow profoundly, also remains an area ripe for additional research [232]. Work to date emphasizes the profound connection between subsurface water and the structure and functioning of the critical zone, and yet leaves us needing to fill several key knowledge gaps:

- How does the combined surface and subsurface topography drive spatial heterogeneity in water storage and flux patterns in and through the vadose zone to groundwater?
- To what degree can rock moisture support forest productivity under more variable weather conditions in the future (e.g., more severe drought)?
- How does an increasing depth to the water table interact with barometric pressure changes to affect fluid and gas fluxes and recharge rates through the vadose zone?

3 Groundwater and Plant Relationships

Plants rely on vadose-zone water stores for meeting transpiration demands that in turn have cascading impacts on groundwater recharge by influencing matric potentials. More directly, groundwater is responsible for an average of 10% of transpired water and up to 47% in lowlands [21, 49, 190, 201]. Thus, understanding the interconnections between transpiration—an inevitable consequence of photosynthesis and plant growth—and groundwater fluxes is thought to be one of the most important and emerging challenges in hydrology [207]. Transpiration is the largest water flux from the terrestrial surface and can be representative of vegetation productivity and how resilient it is to climate change [30]. A growing number of studies have shown that land–atmosphere feedbacks depend on regional groundwater [7, 77, 157]. For example, Maxwell and Kollet [191] found that the depth to the water table determines the relative sensitivity of areas to changes in temperature and precipitation. Similarly, Tromp-van Meerveld [285] indicate that hillslope-scale transpiration and tree basal area are more strongly related to subsurface storage than surface-water supply, highlighting the need for a larger-scale focus on subsurface structure to predict multiple sources of plant-available water and net carbon accumulation in forests.

Complex topography drives the hydrologic and microclimate dynamics of catchments and consequently the spatial and temporal variation of forest carbon accumulation and growth. Because surface topography is not always representative of subsurface processes, it has been difficult to identify mechanisms that determine the spatial distribution of aboveground biomass and its temporal feedbacks with groundwater fluxes. Dominant controls on subsurface moisture patterns often show substantial variability [220, 303], with spatial patterns of soil moisture controlled by lateral subsurface flow patterns that follow subsurface geologic features [147]. While the importance of soil properties in controlling plant-available water is well known (Billings et al. 22, Chap. 2 in this book), recent work has highlighted the importance of terrain and deeper subsurface physical structure in controlling plant water availability [134, 276]. The carbon accumulated in forests is a direct input into natural-resource dependent economies, consequently, quantifying the relationship between transpiration, groundwater, and accumulated carbon is essential to understanding the potential economic impacts to forestry resulting from climate change as well as the potential impacts on downslope agricultural water availability and agriculture-related economics [20, 30, 41]. Furthermore, understanding the relationship between transpiration, productivity, groundwater, and soils is essential for quantifying the magnitude and likelihood of success of so-called natural climate solutions that aim to sequester atmospheric carbon by enhancing forest primary productivity and increase in subsurface carbon stocks [133, 138, 164]. Consequently, it is expected that the terrain complexity will shape forest resilience and related downstream economic impacts with changing climate conditions.

While terrain complexity drives spatial heterogeneity in water availability, it is a species' ability to obtain resources—including nutrients, light, and water—in a given environment that controls its likelihood to thrive, or at least survive. In the face of competition with other species, water availability is one of the primary limits on plant productivity. Thus, a plant's strategy for obtaining water can give it an advantage under specific sets of environmental conditions (e.g., [259]). In environments where groundwater is deep relative to the root zone, all root water uptake occurs in the vadose zone and contributes to the unsaturated subsurface component of evapotranspiration (Sect. 2). However, some roots can access the water table and take up water from the saturated zone. This direct use of groundwater has long been recognized as a source of water for wetland species and phreatophytes [237, 270, 272, 273], and often, these are groundwater dependent ecosystems (GDEs), see review by [214] where their composition and function is controlled by the presence of and depth to groundwater. This connection is clearly demonstrated where diel water-table fluctuations are a diagnostic indicator of groundwater use by vegetation. When evaporative demand is high during the daylight hours, the water table falls, but as root water uptake slows in the evening, water is replenished due to groundwater flow from depth or from areas higher in the landscape [35, 115, 175]. Since the 1930s, diel fluctuations in the water table signal has been occasionally used to quantify evapotranspiration from groundwater [200, 305], but the use of diel signals to explore plant-water interactions has gained much more frequent use in recent decades [13, 35, 114, 187] and several methods have been introduced that allow for sub-daily estimates of evapotranspiration from groundwater [107, 145, 176]. In addition, the groundwater component of evapotranspiration has been quantified with isotopic methods, whereby the isotopic composition of xylem water can be portioned into end-member sources from both the vadose and saturated zones [12] (Fig. 3).

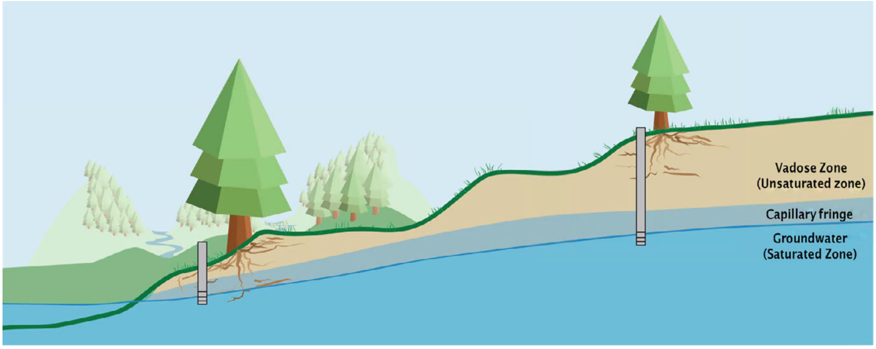

Fig. 3 Shallow groundwater subsidizes tree transpiration and growth in temperate forests when and where the water table is in the vicinity of plant roots. Trees growing where groundwater is shallow (left), experience more stable soil moisture regimes, sustained transpiration, and less year-to-year variability in growth whereas trees growing in areas of deep groundwater (right) experience greater climate-driven variability in moisture status and reduced growth, particularly in drier years. Figure modified from Cirruzi and Loheide [47]

Groundwater-dependent ecosystems in arid regions stand out as green oases within dry landscapes and have been used as indicators in prospecting for groundwater [237]. If shallow groundwater did not exist in these drylands, these ecosystems would not exist. However, this focus on groundwater-dependent ecosystems neglects other ecosystems that are not completely reliant on groundwater, but occasionally benefit from it. For example, Miller et al. [202] observed groundwater use in an oak savanna in a Mediterranean climate of California, [47] documented a groundwater component of evapotranspiration in temperate forests of northern Wisconsin, and Chimner and Resh [42] determined that Bur oak in Nebraska were obtaining 70–88% of their water from groundwater. Furthermore, Soylu et al. [262] and Zipper et al. [315] found that even maize uses shallow groundwater, which subsidizes both transpiration and crop yield. With this growing recognition that a much broader array of ecosystems use groundwater when and where it is available, even if the ecosystems' form and function may not rely on the presence of groundwater, it is time that we start to acknowledge groundwater-*influenced* ecosystems and better understand the interplay between groundwater and these ecosystems in the CZ.

The influence of groundwater extends beyond providing an additional source of water to support transpiration and subsidize growth [47, 178, 315], it is also a primary control on the distribution of ecosystems across the landscape and the spatial patterning and composition of vegetation within a given ecosystem. The range of hydrologic conditions that a plant can tolerate is its hydrologic niche. Individual species realize their hydrologic niches on the landscape based on their water requirements and tolerance for anaerobic conditions that inhibit root respiration. Shallow groundwater can help subsidize root water uptake by minimizing water stress while simultaneously increasing oxygen stress or water logging, which can lead to reduced productivity and even plant mortality. Individual species have evolved to have differing ability to benefit from increased water availability through adaptations such as deep tap roots and dimorphic root structures while other species better tolerate low-oxygen conditions through development of arenchema (a spongy tissue in the stem capable of transporting oxygen into the subsurface) and adventitious roots. It is these, and other, adaptations that increase the likelihood of an individual species to dominate under specific groundwater regimes by outcompeting others. The hydrologic niche of a species or vegetation community can be represented at a basic level by summary statistics of the groundwater regime that supports that vegetation, such as the mean water-table depth and range [3]. However, it is often extremes that drive plant mortality, and Henzey et al. [125] found that the 7-day high water level was the strongest predictor of riparian vegetation composition, likely because shallow groundwater of this duration can induce oxygen stress in unadapted plants, diminishing their competitiveness under these conditions. Furthermore, approaches such as those of Silvertown et al. [258] and Lowry et al. [179] recognize that the magnitude and duration of both wet and dry conditions control the ability of vegetation to thrive in shallow groundwater environments and have used water table hydrographs to integrate the area above and below thresholds of oxygen and water stress, respectively, as descriptors of the hydrologic regime and predictors of vegetation composition. Lastly, approaches such as that of the UK Environmental Agency [290] and vegetation threshold hydrographs of Loheide and Gorelick [174] incorporate the seasonality of groundwater levels in determining the suitability of a specific groundwater regime to support a vegetation type. These advances in our ability to quantitatively articulate the hydrologic niche of different vegetation types has enabled coupling of hydrologic and ecologic models to predict the two-way interactions and trajectory of ecohydrologic systems in response to restoration, management, climatic/land use change, and geomorphic evolution [46, 112, 173, 174, 229].

Another mechanism by which plants connect groundwater to the vadose zone is through hydraulic redistribution, the passive movement of water by roots from areas of high to low moisture content in the subsurface [37]. Root access to a continuous water source like groundwater may be particularly influential on strong upward hydraulic redistribution when the partial recovery of soil moisture in the upper soil layers is advantageous for plants to maintain shallow root function and sustain transpiration [105, 161, 167], such as during seasonal drought [61]. Hydraulic redistribution has been documented for a wide range of species, both woody and herbaceous, spanning arid to cool temperate regions as well as seasonally dry Mediterranean and tropical climates [139, 211]. This injection of water, however fleeting (typically wetting and drying daily), can increase dry-season transpiration and gross ecosystem productivity [60], stimulate microbial decomposition of organic carbon [89] and the production of CO_2 [110], and enhance the mobility of nutrients for root uptake [243]. Furthermore, the connectivity between groundwater and the vadose zone, as facilitated by hydraulic redistribution, can alter the water status of neighboring plants. For example, hydraulic redistribution of groundwater by deeply rooted sugar maple supplied understory species with up to 60% of their water [58] and hydraulic redistribution of groundwater by mesquite trees supported 14% of transpiration in shallow-rooted grasses [167]. These results highlight that the movement of groundwater through the process of hydraulic redistribution can impact both short-term drought resilience of plant communities as well as long-term above- and below-ground exchange of water, carbon, and nutrients as neighboring plant communities establish. Although still in a research stage, geophysical methods like self-potential, which measure naturally occurring electrical potentials in the ground and are thus sensitive to any source that creates a voltage (e.g., water movement and redox gradients), are being developed to characterize subsurface water flow around roots [293].

Finally, it is important to note that where roots mine water they also influence biogeochemical conditions directly through root exudation and solute uptake and indirectly via root-associated microbial activity [129]. Specifically, the root systems (roots and their microbes) respire CO_2, exude organic acids, and produce enzymes, all of which help plants meet their nutritional demands for growth [38, 120, 281]. Regardless of the substrate being mined, be it organic matter or mineral, the decomposition and dissolution of material can both generate and destroy pore space depending on the degree of expansion or compaction (e.g., Bazilevskaya et al. [14]). Over timescales of decades to millennia, these changes alter the subsurface hydraulic properties and therefore infiltration and groundwater recharge rates (Sullivan et al. [274] review and references therein).

Decades of research clearly demonstrate the importance of groundwater on supporting vegetation productivity, the ability of the CZ to accumulate carbon, and the ability of vegetation to control where groundwater flows. However, we are still left with several major knowledge gaps:

- When and where do plants rely on groundwater?
- How is the spatial distribution of aboveground biomass linked to patterns of groundwater uptake by vegetation?
- How will changes in land cover and plant function alter belowground biogeochemical functioning and thus terrestrial fluxes of carbon and nutrients to aquatic environments?
- Does hydraulic redistribution measurably alter soil carbon and weathering fluxes at the watershed scale?

4 Groundwater-Surface Water Interactions

Groundwater's contributions to streams, termed baseflow, sustain streams during dry seasons and drought, and provide valuable nutrients and thermal diversity to support healthy instream habitats [45, 155]. This exchange of water between the surface and subsurface is bi-directional, with conditions allowing for stream water to also recharge groundwater systems, which then often may return to surface flow down-gradient, defining the hyporheic zone (Boano et al. 2014). This flux of surface water into groundwater brings with it solutes such as nitrate (NO_3^-), dissolved organic carbon (DOC) and O_2, which enhance microbial activity in the subsurface (e.g., [108, 312, 313]). Consequently, groundwater-surface water interactions give rise to biogeochemical hotspots beneath streams (e.g., [17, 119]). Subsurface flow paths through the hyporheic zone are a major contributor to ecosystem health and stability, yet the controls on these flow paths are an unsolved problem in hydrology due, in part, to their spatial and temporal complexity [23]. One such example of complexity emerges from our understanding of oxygen consumption in such systems. In surface water, O_2 is thermodynamically favored for respiration, and we expect that hyporheic pore waters transition from bulk oxic to bulk anoxic conditions as the O_2 is respired (e.g., [39]). However, recent theoretical and experimental studies indicate the presence of anaerobic denitrification products, namely nitrous oxide (N_2O)—a potent greenhouse gas and an intermediary product in the microbially mediated reduction of NO_3^- to N_2 gas [66, 284] —and dinitrogen (N_2) in bulk oxic sediment [25, 118, 312]. Bulk oxic conditions should inhibit anaerobic processes, and yet products of anaerobic processes exist.

To explain this apparent paradox, the hypothesis of anoxic 'microzones' in groundwater was developed (e.g., [132]). These locations act as anaerobic reaction sites and thus, important sinks of N [79, 118]. Microzone formation and their functions is an emerging topic, with most papers published in the last few years (e.g., [26, 244, 182]). While the well-connected pore space within the streambed water may remain oxic, anoxic microzones form due to heterogeneity in sediment or organic carbon availability [44, 113, 244]. These previously uncharacterized zones along hyporheic flowpaths may help predictions of unexplained water-quality phenomena such as anaerobic denitrification and production of N_2 and N_2O within bulk oxic hyporheic zones. Briggs et al. [26]'s numerical models suggested that pore-network structure controls residence times and thus microzone formation, where zones of lower hydraulic conductivity will have longer porewater residence times and higher respiration rates. However, they did not explore varying nutrient conditions or the role of bioclogging on how these zones may evolve through time. Roy Chowdhury [44] developed one of the first numerical models that combined hydraulics and microbial conditions to explore microzone formation. These models indicated microzone existence and distributions are not controlled by residence time alone, but by interactions between hydraulic flux, nutrient concentrations and biomass, and are thus dynamic in space and time. Under all conditions explored that considered biomass growth, anoxic microzones would perish after only a few days as bioclogging would largely occur in the downwelling parts of the hyporheic zone, shifting the system from advection- to diffusion-dominated transport and removing all oxic regions in the hyporheic zone. Similarly, Hampton et al. [113]'s experiments demonstrate that hydrologic fluxes systematically shift the location of the bulk oxic-anoxic interface and that there are transport and reaction timescales that favor incomplete denitrification such that N_2O production rates may be higher at intermediate residence times rather than the shortest or longest ones. The role of the hyporheic zone and the presence of anoxic microzones on processing metals in the environment also remains an important area of research [90, 91, 130].

On top of these issues, changes in climate are altering groundwater levels and fluxes, which can have concurrent and cascading effects on groundwater-surface water interactions and may magnify or mitigate issues critical to ecosystem health and stability. For example, agricultural intensification has increased application of both irrigation and fertilizer use across the world. Despite worldwide efforts to reduce watershed inputs of nitrate and phosphorus and quantify legacy nutrient stores, agricultural lands are predicted to expand in the future to try to meet the food demands of an increasing population. An implication of the legacy nutrients and the expansion of agriculture is the continued storage and release of nutrients to surface-water systems. Concurrently, irrigation practices—including shifts between irrigation methods from flood to sprinkler, etc. —and changing climatic conditions affect both groundwater and surface-water systems, which will affect hyporheic flows (e.g., [260, 309]). These impacts on flow regimes and hyporheic flow are relatively understudied and the importance of their effects are generally unknown. Numerical models can be used to understand how water resources will respond to changes in water use, climate, and land use, amongst other disturbances, and help predict and mitigate potential consequences of these changes. However, numerical models represent our basic knowledge of how a system functions based on the data we physically collect can help to constrain them. Thus, advances in understanding how groundwater-surface water interactions will change in the Anthropocene and the influence these changes may have on hyporheic zone dynamics depend on being able to address some of the outstanding knowledge gaps, such as:

- How does the hyporheic zone control the fate and transport of metals?
- How will changes in land cover, land use, irrigation practices, and climate impact baseflow?
- How can we readily capture the spatial and temporal heterogeneous shifts in groundwater-surface water interactions?

5 Groundwater in the Deep CZ

Groundwater extends to kilometers depth in the Earth's crust [135], comprising the largest store of water on the continents [76]. Here we focus on the meteoric component of groundwater in the CZ, defined as waters that come from precipitation, in contrast to magmatic, metamorphic, or marine-derived fluids. Groundwater-flow systems within unweathered parent materials (e.g., fractured bedrock) are often distinct (i.e., chemistry, fluid circulation patterns, transit times) from water in overlying regolith [55]. There is evidence that meteoric recharge circulates over 1–2 km depth in sedimentary and crystalline bedrock based on geophysical and geochemical observations from boreholes and thermal springs [36, 196, 223, 238, 292] (Fig. 4), implying that the CZ may extend much deeper in some settings than commonly assumed. Groundwater circulation down to these depths is primarily driven by topography, with variable influence from hydraulic anisotropy associated with three-dimensional geology (e.g., [48, 238]); solute transport may be dominated by advection or diffusion depending on the permeability structure (e.g., [159]).

Deep CZ groundwater may represent the regional water table or can be part of stacked aquifer systems (e.g., layered volcanic or sedimentary rocks), in which case there are multiple geochemically distinct stores of groundwater [255, 304]. For example, in volcanic settings, layered lava flows with highly anisotropic hydraulic permeabilities likely dictate groundwater flow pathways [184], and can also lead to long-lived perched aquifers. Layered permeability associated with complex lithology

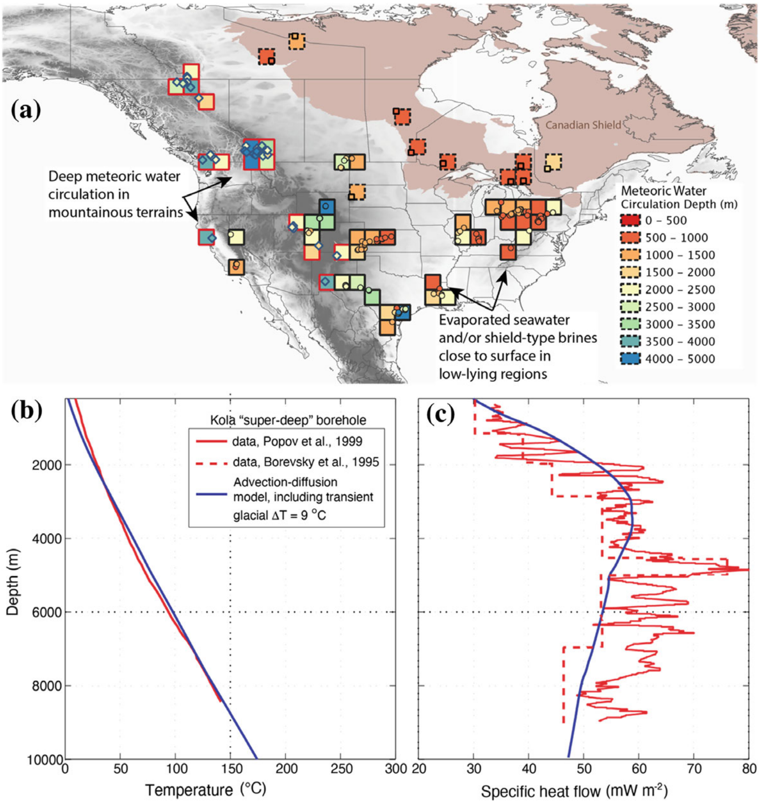

Fig. 4 **a** Depth of meteoric water circulation across North America based on water stable-isotope signatures (modified from [196]). **b**, **c** Data and representative model fits (modified from Vogt et al. [292]) from the "super-deep" borehole SG-3 on the Kola peninsula at the northern rim of the Fennoscandian Shield near the Finnish-Russian border. **b** Measured temperature versus depth (red curve), fit with a transient heat advection–diffusion model over the last 80 ka that includes a boxcar-shaped 9 °C surface temperature decrease associated with the Last Glacial Maximum. **c** Inferred vertical specific heat flow from two studies of the Kola temperature data (red curves) and model fit. Through a Bayesian inverse approach, Vogt et al. [292] infer notable vertical variations in permeability and fluid flow to depths of 7 km in this continental setting, and non-negligible coupling between paleoclimate and fluid advection in near-surface temperatures

has been inferred in deep boreholes within cratons as well (e.g., Vogt et al. [292]) and could play a role in deep CZ circulation generally. Multiscale fault and fracture networks, whether they arise from primary bedrock structure or faulting/tectonic deformation, also play a primary role in aqueous fluid transport even at kilometer depths [68]. The permeability of fault or fracture networks can evolve through geologic time as groundwater reacts with the rocks (increasing permeability, as in karst) or secondary minerals are precipitated (reducing permeability). Faults and fractures are not static and may open or close in response to gradual deformation of the solid Earth, or to rapid perturbation such as earthquakes [136, 268, 299].

Permeability and deep CZ processes likely coevolve with the topography at the surface that drives deep fluid circulation. For example, where a > 1 km deep CZ is inferred in the Oregon Cascades on the basis of isothermal borehole temperature-depth profiles [137, 275], a state shift in surface hydrographs and topographic form is also seen. Development of fluvial channels and ridge/valley topography initiates only on lava flows ~1 Myr in age or older, as high vertical transport capacity exhibited by younger flows evidently shifts to a state of dominant horizontal permeability (lava flow tops/bottoms) [144]. The heterogeneous permeability structure of the deep CZ, within unweathered bedrock or consolidated materials, can lead to variable groundwater residence times or transit times. For example, in some cases groundwater age distributions indicate relatively young waters (<60 years, based on the presence of modern age tracers, such as tritium) mixed with older groundwater (<50,000 years old, based on radiocarbon) up to ~1 km depth [19, 87, 141, 304].

Weathering within saturated fractured bedrock or porous media is controlled by the transit times and heterogeneous flowpaths of groundwater and its chemistry. Weathering reactions are commonly mediated by microbial communities that may leverage surficial inputs of dissolved gases (e.g., O_2, CO_2) and photosynthetically derived carbon or, at some (unknown) depth, be entirely cutoff from near-surface inputs [2, 16, 163]. These deeper microbial communities rely on lithogenic sources of energy to fuel chemolithoautotrophic growth and directly or indirectly enhance weathering reactions [2, 165, 208, 256]. Recharge events, such as deep infiltration of spring snowmelt, can enhance microbial activity and mineral weathering by creating hydrologic connectivity to the near-surface and delivering freshwater and carbon sources to the deep CZ [163, 213] that alter chemical potential and equilibrium. Thus, while it is generally thought that at increasing depths in the CZ, mineral weathering often becomes transport limited by the relatively long transit times of deeper flow systems [181] there are exceptions. This can lead to the development of weathering fronts from the "bottom up" towards the surface in locations where more permeable layers are present at depth.

Actively circulating groundwater that re-emerges at the surface on timescales of years to millennia can transport solutes derived from weathering in the deep CZ to streams [34, 160, 228, 254]. The depth of actively circulating groundwater varies as a function of topographic gradients, fluid density, and permeability distributions (e.g., fracture orientation, presence of confining units), with the greatest circulation depths (~1–4 km) in mountainous terrains [86, 196]. The contribution of groundwater, in terms of water volume, solutes and/or dissolved gases to streams varies as a function of the local climate, catchment characteristics (e.g., relief, geometry and subsurface architecture), and location within the catchment. In general, groundwater contributions to surface waters increase with decreasing elevation and increasing spatial scales [52, 88]. Groundwater has also been shown to contribute notably to streamflow even during high discharge events [283]. Deep CZ groundwater may be disconnected from streamflow seasonally or more permanently in areas where the regional water table is below the stream channel. Infiltration events or wetter periods that increase the water table elevation can lead to greater groundwater-surface water connectivity [195].

To date, most of our observations of groundwater in the deep CZ have come from a few, spatially disparate measurements (e.g., boreholes, wells, springs). More recent geophysical studies have enabled broader spatial and temporal resolution, and in some cases depth resolution, of the physical architecture (e.g., fracture distribution) of the deeper CZ and groundwater transport (St. Clair et al. 2015; Riebe et al. 2017; Holbrook et al. 2014; Parsekian et al. 2014), but often still only to some 10 s of meters. One tool that covers large spatial areas and extend to significant depths is airborne electromagnetic (AEM) surveys, which can unravel features of the subsurface architecture up to ~500 m depth in high resistivity rocks such as basalts (e.g., [80]) and up to ~300 m low resistivity materials such as sedimentary units (e.g., [204]).

Recent scientific drilling campaigns to collect core materials and install monitoring wells, guided by geophysical results, have helped to illuminate the CZ down to approximately 40 to 150 m (e.g., [33, 55, 131, 205]). Direct observations have been made of fluid and rock chemical composition, microbial activity, and rock hydraulic and electric properties, informing CZ structure and function. The use of downhole sensors to measure real-time groundwater levels and chemistry (e.g., pH, temperature, CO_2, O_2) have provided vital information on deep CZ dynamics (e.g., [185, 242, 304]). In addition, more thorough analysis of groundwater-age distributions, applications of isotopic tracers, and development of reactive solute-transport models, have greatly improved our understanding of groundwater flowpaths, transit times, and weathering reactions [186, 265]. Similar scientific or commercial drilling and fluid and rock characterization has been done previously in a few terrestrial locations to several km. These locations may provide opportunities for the CZ community to probe processes deeper and possibly more isolated from the surface both at present and in the geologic past (e.g., [64, 65]).

Scientists are just beginning to illuminate the deep CZ–from the water table to the ‘bottom’ of the CZ–to understand its processes, dynamics, and hydrologic connections with near-surface environments, with many outstanding questions remaining, including:

- How do near-surface inputs of water, gases, carbon, nutrients, solutes and energy influence porosity development and groundwater storage in the deep CZ?
- What is the depth of actively circulating groundwater that delivers lithogenic solutes from the deep CZ to surface waters and how does it vary depending on climate, landscape characteristics and subsurface architecture?

- How do we measure and incorporate subsurface heterogeneity into our models of deep CZ processes, particularly in fracture-dominated systems? And, how do we account for 'hot spots' of weathering that may occur at relatively small spatial scales (e.g., within fractures), but account for a large portion of solute fluxes at the hillslope to catchment scales?
- What are the feedbacks between long-term landscape evolution, surface hydrology, and deep CZ processes?

6 Interbasin Flows: Their Importance for Understanding Large-Scale Linkages in the CZ

An important and relatively under-studied aspect of groundwater flow in the CZ is "interbasin groundwater flow" (IGF), groundwater flow beneath surface topographic divides from recharge in one hydrologic basin (watershed or catchment) to discharge in another. IGF is one consequence of regional groundwater flow at the scale of tens to hundreds of kilometers.

Occurrence of IGF relies on the existence of "losing" and "gaining" catchments, the places where IGF flowlines start and end, respectively. As such, IGF represents an important connection between hydrogeology and catchment science. IGF complicates the often assumed or hoped-for condition that a small watershed is a self-contained unit of study for water resources, with inputs and outputs only across its upper surface and a stream export. The connection between IGF and catchments is often seen as an unwanted complication in catchment science, but is usually discovered and studied through catchment research. For example, IGF has been studied using measurements and models of watershed hydrology and water budgets [96, 206, 217, 251, 311], and chemical or isotopic signals in catchments where IGF discharges to streams and springs, including major ions and isotopes of oxygen, helium, carbon, chlorine, and strontium [88, 92, 95, 98, 99, 267].

Hydrogeologists have long been aware of rapid long-distance and hard-to-predict subsurface interbasin flow associated with obvious geological heterogeneities in karst aquifers. Toth [288] opened up the field by showing that IGF can occur even in homogeneous isotropic media, if the system is thick enough and if there are water table variations (sinusoidal in his paper) imposed on a regional trend in hydraulic head. This motivated decades of diverse work in regional groundwater flow, groundwater-surface water interaction, and catchment science aimed at better understanding IGF and its implications for water quality, design and interpretation of hydrologic studies, ecosystem C and N budgets, and more. Exploring and synthesizing work on IGF, Fan [71] argued that we as a community should conceptualize catchments as semi-closed hydrologic units that are nested on top of the larger regional hydrogeologic system.

One conundrum that IGF creates for biogeochemists is how to interpret water chemistry data, both in places where IGF is recognized, and where it occurs but goes unrecognized. For example, chemical weathering rates are sometimes estimated from the rate of stream export of major ions, expressed as solute mass per watershed area per year (e.g., [104]). Such weathering estimates could be biased high in gaining watersheds and low in losing watersheds unless the IGF is known and accounted for. Solute fluxes by IGF may be large: in a lowland rainforest in Costa Rica, IGF accounted for 90–99% of the major ion inputs to the Arboleda watershed, and atmospheric deposition only 1–10% [96]. Oviedo-Vargas [215] found high rates of CO_2 emission from the Arboleda stream to air. This result might be wrongly interpreted in terms of ecosystem respiration or another biogeochemical process if it were not known that the cause is IGF; the stream receives old groundwater with elevated CO_2 from outgassing of the underlying volcanic system. More broadly, in terms of the overall C budget of this lowland rainforest (Fig. 5) [97, 215], the Arboleda watershed has a net ecosystem exchange (NEE) of about 250 g C per m^2 of watershed per year (a net input of carbon from the atmosphere). With stream degassing of 300 gC/m^2yr (thought not to be captured by the NEE estimate) and stream export of 700 gC/m^2yr, the watershed would appear as a net C source if IGF is not considered (250–700–300 = −750 gC/m^2yr). Including the C input from IGF (860 gC/m^2yr) changes the interpretation of the watershed from a large source to a small sink (about 110 gC/m^2yr), a fundamentally different view of the ecosystem C budget and its connection to climate.

The degree to which IGF is sensitive to changing climatic conditions is relatively unknown. Schaller and Fan [251] used a hydrologic budget approach to assess whether 1555 watersheds in the 48 states of the contiguous U.S. were losing or gaining water by IGF. IGF was more prominent in drier climates; the largest deviations from a "closed" water budget (i.e., a budget with no IGF) occurred in watersheds with lower annual rainfall, especially below 500 mm [251]. Groundwater simulation results in a regional-scale vertical cross section showed that a lower water-table position under low recharge led to groundwater discharge that was less evenly distributed regionally among local elevation minima (small valleys) and more focused as IGF farther downgradient at lower elevation in the region. In other words, lower recharge led to drying of higher-elevation groundwater-discharge areas, and a greater proportion of

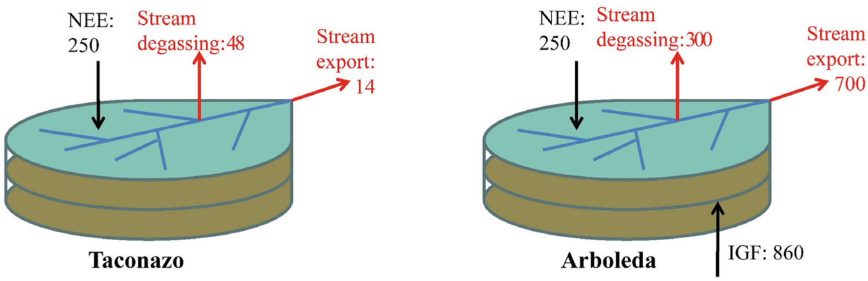

Fig. 5 Carbon flux schematic for adjacent lowland rainforest watersheds at La Selva biological station in Costa Rica, updated from [97]. The arboleda receives inputs by IGF, the Taconazo does not. Black arrows are inputs, red are outputs. Units are g C per m^2 of watershed area per year. Stream export includes both DIC and DOC. NEE represents an average for 1998–2000 data from Loescher et al. [172], stream degassing values are from Oviedo Vargas et al. [215]

discharge as IGF. These findings may be particularly relevant to changing groundwater conditions under drier climates, for example in the western U.S. And impacts may involve feedbacks from groundwater to climate; for example, persistent groundwater discharge (often associated with IGF discharge areas) may slightly increase annual rainfall and notably reduce the amplitude of year-to-year variation in rainfall, through precipitation recycling feedbacks between wetter soils and evaporation [21].

Given the strong controls IGF has on spatial redistribution of water and nutrients, which impacts CZ functioning, several key knowledge gaps should be addressed:

- How can and should IGF influence the interpretation of water chemical data?
- What is the connection between IGF and climate?
- How sensitive is CZ functioning to shifts in IGF?

7 Coastal Groundwater Process in the CZ

Coastlines are a key interface between land and sea where hydrodynamics and strong geochemical and ecosystem gradients intensify critical zone processes. Groundwater plays an important role in these processes [245], as aquifers host zones of mixing between water of terrestrial and marine origin with a wide range of residence times and geochemical characteristics. Groundwater is also a major flux to coastal surface waters, rivaling or exceeding rivers in volumetric discharge [162] and contributing substantial solute loads [277] that affect marine ecosystems [166].

Coastal systems are complex, with ecological and biogeochemical processes tightly coupled to hydrological forcings that act on timescales from seconds (i.e., waves) to millennia (i.e., glacial-cycle sea-level change). An example of this coupling is apparent in intertidal beach aquifers. There, storms, tides, and waves cause runup of seawater that infiltrates the beach face, mixes with through-flowing freshwater, and circulates seaward (Fig. 6, processes 1 and 2). Beneath the freshwater is another mixing zone where saltwater convection is driven by density gradients along a deeper freshwater-saltwater interface (Fig. 6, process 3). Infiltrating seawater contributes oxygen and organic matter, whereas through-flowing freshwater is often anoxic, low in carbon, and high in iron, nutrients, and other land-derived solutes. Mixing of these waters within the beach groundwater system creates redox gradients and reaction zones that successively support reactions such as aerobic oxidation, denitrification, and iron and sulfur cycling [40, 150] and corresponding microbial communities [192]. The geochemical system is strongly connected to the physical system, as hydrologic setting and subsurface characteristics determine the rate and extent of geochemical transformations [100, 122]. Hydrologic transience also enhances mixing and reactivity. For example, movement of the intertidal circulation cell (Fig. 6) due to tidal and seasonal shifts causes contact between mobile and immobile reactants [152].

Groundwater also plays an important role in the evolution of ecosystems at the land-sea margin. Long-timescale dynamics like sea-level rise and land-use change as well as short-timescale oscillations and events such as tides, seasons, and storms,

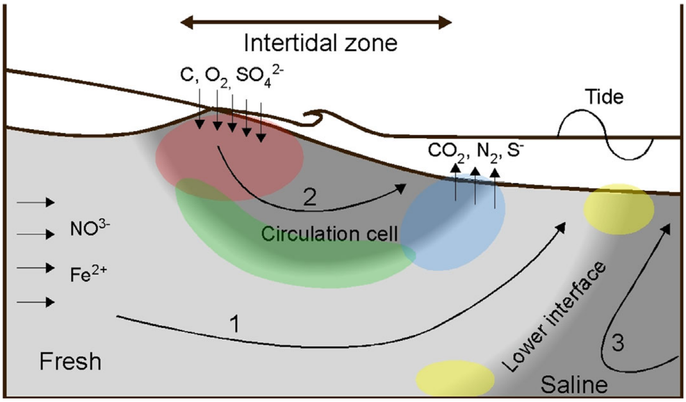

Fig. 6 Processes governed by the interaction of fresh and saline groundwater in an intertidal beach aquifer. Darker shading indicates saline water. Flow paths are shown as numbered black arrows: (1) freshwater driven by the upland hydraulic gradient; (2) intertidal saltwater circulation driven by tides and waves, and (3) offshore circulation driven by density gradients. Key geochemical zones influenced by freshwater-saltwater mixing and circulation are shaded in color. Red: swash zone where seawater carrying reactants such as carbon, oxygen, and sulfate infiltrate into the beach leading to aerobic respiration; Green: zone where denitrification and other mixing-driven reactions occur. Blue: discharge zone where reduced species carried in anoxic groundwater (e.g., Fe(II) react with oxygenated saltwater forming precipitates (e.g., Fe(oxy)hydroxides); Yellow: zones where carbonate dissolution alters aquifer porosity and permeability [123]. Adapted from and Heiss et al. [245]

are actively changing coastal environments [94, 286]. Tree mortality, reduction in crop yields, and other ecosystem changes occur as a result of flooding and salinization [4, 282, 307]. Rising sea level raises the hydrologic base level, increasing water table elevations, shrinking vadose zones and drowning plant roots. Increases in groundwater and soil salinity are driven by sea-level rise, inland hydrologic shifts such as pumping, and episodic extreme high tides and storms. The episodic events superposed on longer-timescale changes can reduce ecosystem resilience to a tipping point of large-scale change [149, 286]. While ghost forests [153] and crop damage are stark features of the landscape, concurrent inland migration of salt marshes brings ecosystem services [56] such as flood mitigation [93] and carbon sequestration [43], and counteracts marsh loss due to drowning and erosion [154].

An example of the strong two-way coupling between subsurface hydrology and geochemistry occurs in coastal carbonate aquifers. Due to their typically high hydraulic conductivity, coastal carbonates are particularly susceptible to saltwater intrusion (i.e., inland movement of the lower freshwater-saltwater interface; Fig. 6). Coastal CZ processes in carbonates involve mineral dissolution, precipitation and diagenetic reactions that can lead to a redistribution of porosity and hydraulic conductivity as well as a release of phosphorus which can stimulate ecosystem productivity. Carbonate mineral dissolution in regions where groundwater has varying salinity have been well documented to result from undersaturated conditions with respect to carbonate minerals, particularly calcite and aragonite, upon mixing two groundwaters with different ionic strengths, temperatures, and concentrations of calcium, carbonate, carbon dioxide [306]. Large-scale dissolution of carbonate minerals along coastlines is geomorphically exhibited as caves and coves, such as those in the Yucatan Peninsula [9, 10]. These observations of carbonate dissolution were supported by hydrogeochemical modeling of variable-density groundwater in coastal carbonate aquifer systems by [241] and later by [233]. Their results determined porosity and permeability in the aquifer increased in two regions: (1) at the top of the aquifer where the brackish groundwater discharges near the coastline, and (2) at the base of the aquifer along the toe of the saltwater intrusion front (Fig. 6). The enhanced dissolution at the top of the aquifer is consistent with the development of coastal caves in Mexico [9]. The dissolution at the top of the aquifer near the groundwater discharge zone is amplified by the development of a convection cell, which results in a positive mineral-dissolution feedback loop where the increase in aquifer permeability leads to increased seawater intrusion into the aquifer and further dissolution.

Other reactions observed in coastal carbonate CZ regions exposed to seawater intrusion include calcite precipitation and aragonite neomorphism (conversion of aragonite to calcite), processes that can lead to a decrease in the porosity and hydraulic conductivity and reduce carbonate weathering in the CZ [9]. From example, supersaturated conditions with respect to calcite were observed in brackish groundwaters collected in Florida [212] and Spain [311]. A variety of hypotheses have been put forth to describe the differences in saturation states observed between the various carbonate CZs affected by saltwater intrusion such as groundwater-table fluctuations, water-to-rock ratio or initial porosity/permeability distribution, changes in the partial pressures of carbon dioxide, and the amount of organic carbon present [212, 233, 311].

Saltwater intrusion into coastal carbonate CZs has been found to release phosphorus from the carbonate bedrock/soils stimulating primary production. The release of phosphorus from the bedrock occurs by two processes, desorption upon exposure to very low concentrations of salt, and the dissolution of calcium carbonate minerals with different mixtures of fresh and saltwater [82, 83, 224]. Saltwater intrusion and the associated release of phosphorus has been found to stimulate primary production along the carbonate CZ of the Florida coastal Everglades [156, 225]. In freshwater conditions, the limestone bedrock has a strong affinity to adsorb phosphorus, most likely contributing to the naturally oligotrophic conditions in the Everglades [84]. However, as sea-level continues to rise, greater portions of the freshwater aquifer will be exposed to saltwater thereby increasing the availability of phosphorus in this CZ. Overall, this will push the system further away from oligotrophy and alter biotic processes critical to the functions of the Everglades.

These examples highlight the complex role of groundwater in the coastal CZ. Improved understanding of the feedbacks between hydrology, ecology, geochemistry, and geomorphology of these systems through observational networks and development of coupled process models [300] will allow us to tackle questions such as:

- How do physical forcings, geochemical gradients, and geomorphological settings alter landscapes and elemental fluxes along the land-sea margin?
- How will future changes in climate and land use alter coastal systems, and what are the dominant timescales of change?
- How are ecosystem processes co-evolving with porosity and hydraulic conductivity of coastal carbonate CZ systems exposed to seawater intrusion?
- How does the release of phosphorus from coastal carbonate aquifers contribute to ecosystem processes in CZ areas?

8 CZ Vision for Addressing Society's Water and Ecological Problems

Illustrated above is the fact that groundwater is a vital natural resource for humans and ecosystems around the world, and that a CZ approach is fundamental to tackling current and future groundwater threats and feedbacks to other environmental systems. Ensuring access to potable groundwater is also critical to global economic health. For example, groundwater is a major contributor to streamflow generation, which plays an important economic role in regional fisheries. Streamflow also strongly interacts with silviculture and agriculture practices; thus the management of one resource economy influences the other. Knowledge of where plants access water in the subsurface, the amount of water stored in diverse lithologies, and the sensitivities of these fluxes to more variable weather patterns creates the need to co-develop land-use practices that are evaluated and updated to account for emerging technologies, social and economic needs, and our understanding of CZ science. Hidden within this hydrologic problem are the impacts on terrestrial carbon dynamics. Layered throughout the world is the legacy of land ownership and Indigenous rights. Intertwined within our natural systems is constructed infrastructure, altered flows, and chemical controls. Developing groundwater solutions for such complex systems requires bringing diverse minds to the table and thinking about the entire system from the top of the canopy down to the depths of circulating groundwater.

Groundwater and vadose-zone moisture play a fundamental role in sustaining life on Earth. The contents and questions outlined above can be simplified into three areas highlighted by the U.S. National Academies *Earth and Time Report* (2021): (1) How does the CZ influence climate? (2) How is the water cycle changing and what does this mean for CZ function? And (3) What role do hydrologic changes play in altering how biogeochemical cycles evolve? Addressing these questions requires coordination among national and international agencies, institutions of higher education, and profit and non-profit organizations. For example, uniting existing geophysical and drill-core data repositories from mineral extraction companies and national geological agencies with satellite (e.g., GRACE) and airborne (e.g., AEM) geophysical data and targeted field observations could allow us to construct transferable knowledge on Earth's near surface geologic architecture and what controls it. Offering managers, stakeholders, and policy makers the foundation for developing sustainable groundwater extraction plans.

One important component to deriving solutions are observatories—places where groundwater is measured along with other CZ variables (e.g., geologic structure, rooting distributions, net primary productivity) to develop a process-based understanding. Groundwater is among the most difficult CZ variables to measure, characterize, and predict. Thus, observatories play an important role in both the collection of physical measurements and a place where scientists from diverse disciplinary and methodological backgrounds can get together to co-develop and synthesize these perspectives, and generate new hypotheses and models for improved application outside of the narrow confines of the observatories themselves. Additionally, observatories are locations where we can understand the impacts of climate or weather (e.g., drought, fire, flooding) and land-cover disturbance on groundwater resources, and untangle the effects of compound or co-occurring disturbances. For example, how will groundwater quantity and quality respond to drought and insect infestation followed by fire in a forested terrain? Or how do we manage groundwater resources in areas where streamflow is declining, mean annual precipitation is increasing, warmer temperatures are prompting higher evapotranspiration rates, and the biota are shifting from grass to woody dominance? Given that the response of biota and climate-carbon cycle feedbacks appears to be accelerating at the global scale [170, 266] the need for observatories that quantify the impact of these changes on groundwater is necessary for projecting water security into the future.

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