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Hydrological Partitioning in the Critical Zone: Recent Advances and Opportunities for Developing Transferable Understanding of Water Cycle Dynamics

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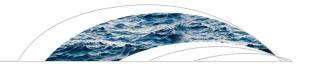
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Water Resources Research

REVIEW ARTICLE

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Special Section:

The 50th Anniversary of Water Resources Research

Key Points:

- The disparate nature of hydrologic research hinders theoretical advancement
- Coordinated research on subsurface hydrologic partitioning to ET or streamflow can address this gap
- Multiple areas of research identify extensive groundwater interaction with streamflow and atmosphere

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Hydrological partitioning in the critical zone: Recent advances and opportunities for developing transferable understanding of water cycle dynamics

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Abstract Hydrology is an integrative discipline linking the broad array of water-related research with physical, ecological, and social sciences. The increasing breadth of hydrological research, often where subdisciplines of hydrology partner with related sciences, reflects the central importance of water to environmental science, while highlighting the fractured nature of the discipline itself. This lack of coordination among hydrologic subdisciplines has hindered the development of hydrologic theory and integrated models capable of predicting hydrologic partitioning across time and space. The recent development of the concept of the critical zone (CZ), an open system extending from the top of the canopy to the base of groundwater, brings together multiple hydrological subdisciplines with related physical and ecological sciences. Observations obtained by CZ researchers provide a diverse range of complementary process and structural data to evaluate both conceptual and numerical models. Consequently, a cross-site focus on "critical zone hydrology" has potential to advance the discipline of hydrology and to facilitate the transition of CZ observatories into a research network with immediate societal relevance. Here we review recent work in catchment hydrology and hydrochemistry, hydrogeology, and ecohydrology that highlights a common knowledge gap in how precipitation is partitioned in the critical zone: "how is the amount, routing, and residence time of water in the subsurface related to the biogeophysical structure of the CZ?" Addressing this question will require coordination among hydrologic subdisciplines and interfacing sciences, and catalyze rapid progress in understanding current CZ structure and predicting how climate and land cover changes will affect hydrologic partitioning.

1. Introduction

There is a dynamic tension in water resources research where hydrology is both an applied discipline with tremendous practical relevance to society, while also a vibrant area of basic research that integrates biogeophysical processes from pore to global scales. Ensuring reliable and consistent supplies of fresh water, along with protecting infrastructure and lives from floods, is critical for sustainable development and economic growth [NRC-NAS, 2012]. This immediate relevance of hydrology to society led to the well-documented fracturing of the discipline across a gradient of applied to basic research [Burges, 1990]. Arguably, these divisions within hydrology have hindered the theoretical advancement of the discipline [e.g., Penman, 1961; Klemeš, 1986; Kirchner, 2006; Thompson et al., 2011c). Over the last several decades, however, hydrology has begun to expand from relatively narrow or applied foci to become an integrative discipline linking civil and environmental engineering, ecohydrology, physiological ecology, biogeochemistry, geology, soil science, atmospheric science, and climatology. This integration has been driven by the growing appreciation that the availability, cycling, and quality of water are intimately linked to most if not all biophysical processes [NRC-NAS, 2012] and to the observation that rapid changes in climate and land cover require both new fundamental understanding of coupled biophysical processes and new approaches to predict resource availability [Milly et al., 2008].

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Integration among various subdisciplines is leading hydrologists to reevaluate the stakeholders for their research. It is straightforward to identify stakeholders for applied research addressing readily defined societal solutions (e.g., flood control, agricultural water supply, or groundwater drawdown). However, increasing demand for water combined with rapidly changing land cover and climate requires integrated observation and modeling approaches [NRC-NAS, 2012; Montanari and Koutsoyiannis, 2012]. As the degree of integration increases, the diversity of stakeholders with questions and interests in various aspects of the water cycle also expands, requiring both new types of observations that provide insight into water stores and fluxes [e.g., Vereecken et al., 2015], and importantly, consistent representations of water cycling across scales. The development of long-term, experimental catchment study sites provides examples where the integration of physical hydrology, hydrochemistry, hydrometeorology, and biogeochemistry has spurred advances in both conceptual and quantitative models of precipitation routing and streamflow generation [e.g., Lins, 1994; Elliot and Vose, 2011; Neal et al., 2013; Lutz et al., 2012; Hooper, 2001; Peters et al., 2011; Lohse et al., 2009]. These catchment efforts echo early work by Horton [1933] by taking a systems approach linking diverse observations and conceptual models to advance trans-disciplinary and transferable research (Blöschl and Sivapalan, 1995; McDonnell et al., 2007; Sivapalan et al., 2003; Wagener et al., 2007; Troch et al., 2009]. To the extent that these place-based efforts bring diverse groups of researchers together, they continue to be successful in generating new questions, defining hypotheses, and advancing conceptual and numerical representation of water cycling.

Cross-site comparisons build upon this place-based research by quantifying and modeling behaviors that are generalizable across space and time. These efforts are critical for the advancement of transferrable understanding of hydrological processes and development of hydrological theory [Beven, 2006; Bejan, 2007]. Comparative hydrological research has identified mechanisms by which catchments store and release water [Kirchner, 2006; McNamara et al., 2011], partition precipitation [Huxman et al., 2005; Troch et al., 2009], and attenuate nutrients [Peterson et al., 2001]. As consistent hydrochemical data sets are developed across multiple locations, the concurrent application of hydrometric, hydrochemical, and isotopic data holds great promise for identifying predictive models that "get the right answer for the right reasons" [Kirchner, 2006]. For example, detailed surface water hydrochemical studies indicate tremendous heterogeneity in water residence time in the subsurface [Neal et al., 2013; Kirchner, 2003; Bishop et al., 2004) often with much longer residence times and greater groundwater contributions than predicted by operational models of river discharge [Frisbee et al., 2012]. Similarly, plant physiological ecology and ecohydrology observations suggest that subsurface water stores are highly heterogeneous in both space and time [Dawson and Ehleringer, 1991; McDonnell et al., 2003; Brooks et al., 2010; Hu et al., 2010; Thompson et al., 2011c] and provide fertile conceptual ground for integrating catchment and land surface approaches to water balance. Whether through ecohydrological or hydrochemical observations, challenging models with diverse data maximize the use of models as learning tools. Expanding upon the concept that "all models are wrong, but some are useful" [Box and Draper, 1987], a powerful focus in comparative work is on breaking the model by explicitly finding its limitations rather than validating the model for a particular application.

Both hydrochemical and ecohydrological observations suggest that the residence time and routing of water in the subsurface is highly heterogeneous in space and time, underscoring the need to explicitly include geological, geomorphological, and pedological understanding into hydrological partitioning [McDonnell, 2003]. The development of critical zone science [NRC-NAS, 2001; Amundson et al., 2007; Brantley et al., 2007, 2011] has catalyzed the establishment of a network of terrestrial environmental observatories that has the potential to meet this need. The critical zone is the outer surface of the terrestrial earth where "rock meets life" and where water cycle dynamics connect the subsurface to the atmosphere and climate. The CZ explicitly includes the vertical domain from the base of active groundwater circulation through the top of vegetation canopies and horizontally encompasses nested catchments associated with surface and subsurface structure that develops on geological times scales (Figure 1). Notably different from previous catchment studies is the broad range of relevant time scales, encompassing microbial through pedological, geomorphological, and geological processes in the CZ [Brantley et al., 2011; Chorover et al., 2011; Rasmussen et al., 2011]. The explicit focus on CZ structure (geologic, topographic, pedologic, and ecologic) and how it develops across time and space scales represents an opportunity to advance hydrologic research, and its interface with allied earth science disciplines, in both process representation and similarity analyses.

Here we briefly review research from three active, but largely independent, subdisciplines of hydrology (catchment hydrology and hydrochemistry, hydrogeology, and ecohydrology) that converge on a common

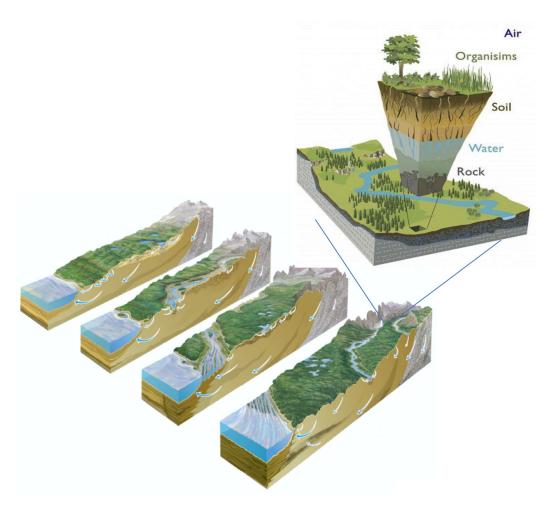


Figure 1. The critical zone (CZ) is the near-surface environment where rock, soil, water, air, and life interact. The exploded view on the inset top right represents both the vertically deeper and longer time scale foci of CZ science relative to most hydrological or ecological research. The four transects from mountains to sea illustrates the multiscale nature of CZ processes [Winter et al., 1998].

knowledge gap critical for developing transferable understanding of how precipitation is partitioned to surface water discharge or vapor flux. Specifically, all converge on the need for improved understanding of the amount and residence time of subsurface water, including both soil and groundwater. Individually, each subdiscipline brings complementary perceptual and conceptual models, spatial and temporal scales of interest, observational techniques, and numerical models. Together, these observations and models provide complementary "windows" into subsurface water storage and movement that exert strong controls on hydrologic partitioning in the CZ. We suggest that "critical zone hydrology" can serve as a catalyst for new theory, observational techniques, and closure schemes that cross time and space scales [Beven, 2006] by integrating these approaches from what largely have been disparate subdisciplines of hydrology. We further suggest the following as an integrating question of common interest to guide critical zone hydrology: "how is the amount, routing, and residence time of water in the subsurface related to the biogeophysical structure of the CZ?" The wide range of CZ disciplines utilizes an equally broad range of metrics to quantify CZ structure. Consequently, we use the structure broadly to include any quantifiable biophysical characteristic of the critical zone (e.g., lithology, topography, soils, and vegetation) that is either directly involved in, or can provide indirect insight into, water cycling.

2. Catchment Hydrology and Hydrochemistry

The common observation that surface water chemistry more closely resembles soil or groundwater than precipitation has been used to draw inferences about the magnitude and mobility of stored subsurface

water. Water chemistry evolves while in contact with host rock and soil allowing simultaneous measurements of stored water quantity (e.g., water level in a well and soil moisture) and quality (e.g., major and trace ions and isotopes) to provide complementary insights into the physical, chemical, and biological processes otherwise hidden from our eyes [Kirchner, 2009]. Consequently, stream chemistry provides a powerful, integrative tool to evaluate inferences on subsurface (geological and soil) structure and water residence time drawn from physical hydrological models and observations. Mixing models [e.g., Christophersen et al., 1990; Liu et al., 2008] used by catchment hydrologists and hyporheic exchange models used by stream ecologists [e.g., Gooseff and McGlynn, 2005] utilize this approach to understand coupled hydrological and biogeochemical processes in catchment ecosystems [e.g., Mulholland and Hill, 1997; Brooks and Lemon, 2007].

It is not difficult to conceptualize a slow release of stored water modulating surface water chemistry during base flow. However, the widespread ability of catchments to release large amounts of stored water and solutes during high flows has been termed a double paradox in catchment hydrology [Kirchner, 2003]. Efforts to resolve the double paradox rely on groundwater flow through various subsurface reservoirs [Bishop et al., 2004], and emphasize the importance of variable subsurface (soil and groundwater) stores and fluxes through both macropore flow [e.g., Beven and Germann, 2013] and transmissivity feedbacks through a soil profile [Bishop et al., 2004]. Even during peak flows at small spatial scales, hydrochemistry indicates that stream water has had considerable contact with the subsurface [e.g., Williams and Melack, 1991; Frisbee et al., 2012]. Because water stored in the subsurface potentially is subject both to evapotranspiration and to discharge to surface water, these observations highlight that a critical challenge in predicting how precipitation is partitioned involves quantifying the spatial and temporal heterogeneity in subsurface water storage and movement.

Patterns of catchment-scale concentration-discharge (C-Q) relations across different tracers and catchment types reflect (bio)geochemical reactions occurring during advective water transport and, hence, how water and solutes move through the catchment. Some solute concentrations remain relatively stable even as discharge varies widely (Figure 2) [Godsey et al., 2009; Basu et al., 2010], whereas other solute concentrations vary with discharge or other controls [e.g., Agren et al., 2010; Guan et al., 2011; Shanley et al., 2011]. Furthermore, C-Q patterns for a given solute vary among sites, even during the rising versus falling limbs of the hydrograph, reflecting structural and kinetic controls. In all cases, observed concentration-discharge patterns must reflect both the timing and location of subsurface water movement, and reaction rates within both the subsurface and the stream channel [Creed et al., 2015]. Perhaps the most surprising aspect of cross-site analysis is that concentrations of many weathering and/or slow reacting solutes vary minimally as discharge varies by several orders of magnitude. These "chemostatic" C-Q relationships (Figure 2) [Godsey et al., 2009] again highlight the importance of large subsurface water or solute stores that can be mobilized rapidly in response to precipitation events but also contributions from significantly slower, by several orders of magnitude, flow paths [Kirchner et al., 2000]. Recent advances in descriptions of the timing of water movement suggest dynamic travel time distributions with long tails best describe water movement [e.g., Harman, 2015], and they also indicate strong effects of evapotranspiration fluxes and initial conditions [e.g., Heidbüchel et al., 2012; van der Velde et al., 2014]. Further work to link these travel time distributions to solute patterns in effluent stream waters is warranted. Working at different scales including subcatchment observations, such as those evaluating groundwater, soil water, and wetland concentration-discharge patterns [Brooks et al., 2005; Kim et al., 2012], may reveal more process-based information about the temporal and spatial distribution of reactions and fluxes through the unsaturated and saturated zones across the landscapes (Figure 3). By extension, these advances in understanding where and how long water resides in the subsurface will inform both hydrogeology and ecohydrological research.

Concentration-discharge relationships using multiple tracers that differ in mobility and source also provide insight into how hydrological stores and fluxes are coupled to weathering processes and biogeochemical reactions. $\delta^{18}O$ and $\delta^{2}H$ or other conservative tracers reflect how water particles move whereas other solutes (e.g., Ca, Mg, Na, and Si in many systems) reflect weathering and transport processes. Metals, including trace elements, can reflect bioligand and reduction/oxidation controls on weathering processes [*Vázquez-Ortega et al.*, 2015]. Acquisition of continuous groundwater metal samples during and between events will provide new data [*Kim et al.*, 2012] to probe these redox controls. Furthermore, additional isotopic techniques, especially in concert with geophysical approaches, can reveal important subsurface heterogeneities [*Druhan and Maher*, 2014]. Use of multiple tracers within a network of CZ observatories during extreme

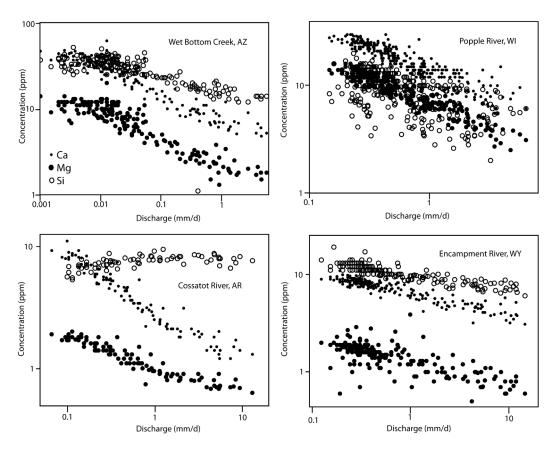


Figure 2. Concentration-discharge relationships for Si, Ca, and Na at four USGS Hydrologic Benchmark Network streams. Concentration-discharge relationships conform relatively closely to chemostatic behavior (log-log slope near zero) suggesting large pools of subsurface water and solutes.

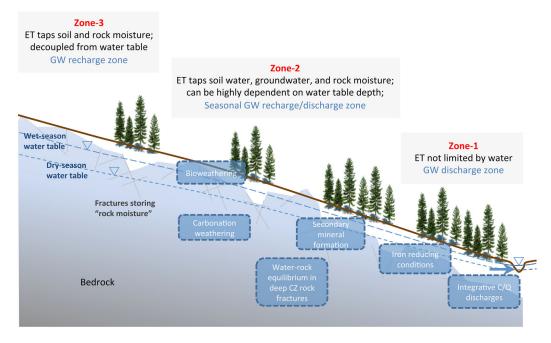


Figure 3. Conceptual model showing the relationships between three zones of groundwater depth, associated subsurface biogeochemical reactions and surface vegetation expression. The figure highlights that both streamflow and ET are dependent on how subsurface water is partitioned. Importantly, diagnostic structural elements of the CZ (regolith, vegetation, and hydrochemistry) can be used to draw complementary inferences on the partitioning of subsurface water storage.

events may be particularly fruitful for revealing short time scale responses that may be disproportionately significant on landscape evolution time scales [e.g., Burt et al., 2015]. Similarly, coupled hydrological and biogeochemical tracers can be used to infer subsurface biogeochemical redox state and reaction that develop over geological time scales [Bates et al., 2011]. Finally, hysteresis in different tracers has previously been shown to result from multiple possible combinations of controls [Chanat et al., 2002], but by using multiple tracers, the processes controlling hysteretic patterns may be able to be more clearly interpreted.

These feedbacks and relationships between hydrological and geochemical processes can elucidate longterm controls on landscape evolution and thus provide insight into how CZ structure develops. Because hydrologic fluxes may be important regulators of geologic-scale carbon fluxes and storage [Maher and Chamberlain, 2014], it is critical to understand the feedbacks between hydrologic flows and weathering fluxes across a range of climates and lithologies. Possible reduction/oxidation controls on those relationships [Riebe and Brantley, 2015; Rempe and Dietrich, 2014], set by steady or unsteady groundwater table elevations, both influence both the degree of weathering and the slope and dissection of the landscape. The time scales at which water interacts with mineral surfaces leading to observed concentrationdischarge patterns are dynamic [Maher, 2011; White and Blum, 1995; White and Brantley, 2003]. This implies that a dynamic ratio of advection to reaction time scales—a dynamic Dahmkohler number—may also be required to understand temporal and spatial heterogeneities at some time scales. Modeling the weathering and hydrological processes controlling concentration-discharge relationships at a variety of spatial and temporal scales is often a data-limited problem. A CZ observatory network offers a suite of sites to test models where the critical data exist. For example, the time that water is in contact with mineral surfaces can be better constrained along with the surface area of those minerals and the assemblage of mineral types in the catchment. However, we also will need to improve our understanding of how preferential flow paths influence the contact time that similar age water has with mineral surfaces within the catchment.

One finding that remains clear, however, is that the majority of stream and surface water has had considerable interactions with, or residence time within, various soil and groundwater reservoirs (Figure 3). This observation seems to hold across a wide variety of catchments and flow regimes and highlights the need for improved understanding of subsurface (geological and soil) structure and how that influences residence time and routing. Key questions then for catchment hydrology and hydrochemistry research include Where, how much, and for how long is water stored in the subsurface? How do catchments release large amounts of this water quickly? How does CZ structure control and inform these hydrological characteristics? Addressing these questions is approached most efficiently in an observatory setting where chemical and isotopic tracers can help constrain and revise physical hydrological models, physical hydrological observations and models can constrain weathering processes, and ecohydrological observations and models can inform ET fluxes.

3. Hydrogeology

Concurrent with the growing recognition in catchment hydrology and hydrochemistry of the need to look more deeply into the subsurface, hydrogeologists, who historically focused on groundwater quantity and quality in aquifers, have directed more attention toward the role of shallow groundwater in regulating near-surface CZ processes. Shallow groundwater storage and lateral convergence from hills to valleys are key controls of base flow physics and chemistry, as discussed in the previous section, but here we will focus on another aspect of groundwater influence: its role in regulating vadose zone thickness and water storage available to plants and thus evapotranspiration fluxes. The central argument here is that shallow groundwater can directly regulate the "vertical" fluxes as well, i.e., the partition of subsurface water storage toward vapor fluxes into the atmosphere.

The water for plant transpiration comes from moisture stored in the unsaturated root-zone soil above the water table (except for wetland plants adapted to prolonged root anoxia below the water table). Soil moisture is recharged during rainfall infiltration and snowmelt events, and that portion in excess of field capacity can recharge groundwater [*Graham et al.*, 2010], raising the water table (Figure 3, the higher dashed-blue line). Groundwater not only sustains river base flow, but subsidizes soil moisture and plant available water

between precipitation events. In this way, water table depth influences root-zone soil moisture and plant uptake, and this groundwater subsidy becomes increasingly important as the surface soil dries.

Seasonal variability in water table depths results from the partitioning of groundwater to either lateral drainage that sustains stream and river base flow or upward discharge into unsaturated soils that sustains evapotranspiration. A water table decline below the regolith on the upper slopes (Zone-3, Figure 3) increases the importance of "rock moisture" [Salve et al., 2012], or water stored in the rock fractures/fissures as a critical water source for trees with roots penetrating deeply into the fractures of crystalline rocks [Hellmers et al., 1955; Berndt and Gibbons, 1958; Dell et al., 1983; Jones and Graham, 1993; Rose et al., 2003], basalts [Bishop, 1962], carbonate rocks [Berndt and Gibbons, 1958; Jackson et al., 1999; Querejeta et al., 2007; Bleby et al., 2010; Schwinning, 2010] and metamorphic and sedimentary rocks [Berndt and Gibbons, 1958; Kerfoot, 1963; Lewis and Burgy, 1964; Zwieniecki and Newton, 1995, 1996; Drexhage and Bruber, 1998; Nijland et al., 2010; Raz-Yaseef et al., 2013]. In sedimentary environments with deep bedrock, this framework simplifies so that a laterally continuous saturated zone underlies the entire toposequence. In this setting, plantgroundwater interactions can be conceptualized as a sequence of three zones along the water table gradient (Figure 3) [Kollet and Maxwell, 2008; Maxwell and Kollet, 2008; Ferguson and Maxwell, 2010; Rihani et al., 2010; Soylu et al., 2011; Condon et al., 2013; Shi et al., 2013]. In Zone 1, located at the bottom of the hillslope or river channel, the water table may interact directly with surface water, although the degree of interaction may be spatially and temporally variable. Importantly for partitioning, however, the water table is close enough to the land surface that latent heat flux is not moisture limited for large portions of the year. On the other end of the water table gradient, in Zone 3, the water table is too deep to influence land surface processes, and plants here entirely rely on the amount and frequency of precipitation. In between these extremes is Zone 2, where the water table depth is in a critical "transition zone" such that there is a tight, nonlinear relationship between latent heat flux and water table depth [Kollet and Maxwell, 2008; Maxwell and Kollet, 2008]. In terms of partitioning of groundwater storage, under Zone 1, the flux is downward to recharge the groundwater, under Zone 2, the flux can be either direction depending on water status, and under Zone 3, the flux is primarily upward (groundwater discharge zone). Thus, the partitioning of groundwater stores into lateral versus vertical fluxes will depend on its accessibility to plant roots, highlighting the importance of water-plant interactions discussed in the next section.

This three-zone model can be expanded to regional and global scales to obtain a sense of the significance of the transition zone [Condon et al., 2013]. A simple extrapolation based on the model of Fan et al. [2013] suggests that ~24% of the global land area may fall into this critical transition zone where the depth to groundwater may regulate ET fluxes and land-atmosphere interactions. Field observations in Nebraska [Szilagyi et al., 2013], where the soils are relatively homogeneous and the water table gradient is largely controlled by topography, support the three-zone model. In contrast, the Valley and Ridge system in Pennsylvania [Shi et al., 2013] suggests that smaller-scale geologic complexity may play an important role in controlling water table depths. Rihani et al. [2010] investigated the effects of subsurface heterogeneity at the hillslope scale (e.g., bedrock depth, terrain shape, layered heterogeneity, and climate) and Condon et al. [2013] examined multiple types of geologic heterogeneity at large scales. Both studies found that the conceptual model of three-zone groundwater-land surface interaction holds, but the location and relative extent of the three zones are more nuanced. Targeted research across a range of CZ observatories to explore these nuances will improve our conceptual and numerical models of these regional-scale to local-scale connections through groundwater.

Because the amount of water stored in the subsurface acts as a buffer for climate variability, cross-site comparisons among water storage, geological structure, and climate in CZ sites will allow for improved predictions of locations most at risk from extended drought under future climate scenarios or buffered against atmospheric deposition. Moving forward, key questions are When and where does groundwater reside in the subsurface? and How are its dynamics related to other aspects of CZ structure? A major hurdle in addressing these questions is the opaqueness of the subsurface. It is difficult to make direct and comprehensive observations so that even the most basic information is missing, such as the transitions from soil to saprolite and competent bedrock, the structure and scales of heterogeneity (macropores and fractures), and the plant rooting depths. Applications of conventional and new geophysical tools offer unprecedented means to image the structures of the shallow subsurface [Parsekian et al., 2015], and a geophysical characterization of the subsurface should be an essential ingredient of CZ observations. Accelerated subsurface

imaging [Holbrook et al., 2014; Parsekian et al., 2015] combined with models of the development of the critical zone into distinct material properties [Lebedeva et al., 2007; Lebedeva and Brantley, 2013; Rempe and Dietrich, 2014, Slim et al., 2014] are critical steps toward understanding the partitioning of water in the subsurface. Finally, because vegetation is opportunistic in accessing subsurface water, vegetation patterns discussed below provide an additional window into subsurface structure.

4. Ecohydrological Partitioning at the Land Surface

A critical need for ecohydrology is quantifying plant water availability, often conceptualized as soil moisture but with a growing emphasis on the importance of groundwater and "rock moisture" as discussed above. In many landscapes, the majority of precipitation (P) is partitioned either to evaporation (E) or transpiration (T) rather than streamflow [Horton, 1933; Troch et al., 2009; Jasechko et al., 2013]. The extent to which these vapor fluxes represent plant water use (T) largely constrains what vegetation is present on the landscape, how productive the vegetation is in assimilating carbon, and how resilient the vegetation is to changing climate [Webb et al., 1978; Knapp and Smith, 2001; Hicke et al., 2002; Huxman et al., 2004]. Geophysical properties (CZ structure) are important controls on plant water use and productivity, particularly in water limited environments [Rodriguez-Iturbe, 2000; Newman et al., 2006; Asbjornsen et al., 2011] leading to a growing focus on understanding where in the subsurface plants obtain water. Both observational and modeling studies reveal that plant water supply is much more variable, and often much larger than estimated from near-surface soil moisture [Dawson and Ehleringer, 1991; Lee et al., 2005; Hu et al., 2010; Thompson et al., 2011c].

Beginning with vegetation and working from the "top down," these studies draw similar inferences to the hydrogeology work described above. Specifically, ecohydrologic partitioning of available water into E, T, recharge, and streamflow is intimately connected both to land surface complexity and subsurface structure [e.g., Hinckley et al., 2014; Maxwell et al., 2007] (Figure 3), which coevolve in response to long-term interaction of energy, water, and terrain [Rasmussen et al., 2011]. For example, aspect and elevation-related variability in CZ structural elements are dominant controls on water flux and storage across depth [Tesfa et al., 2009; Smith et al., 2011; Rasmussen et al., 2011], soil texture [Geroy et al., 2011], carbon and nitrogen fluxes and stocks [Kunkel et al., 2011; Perdrial et al., 2014], and the amount and diversity of biomass [Smith et al., 2011]. Until recently, however, there was minimal integration between hydrogeology and ecohydrologists as the different spatial (both X–Y and depth) and temporal scales of interest rarely resulted in collocated observations needed to evaluate coupled models of subsurface hydrology and land surface water fluxes [Brooks and Vivoni, 2008].

The mechanisms whereby, and the conditions under which, plants access these diverse water sources remain a key challenge in ecohydrology [McDonnell, 2014]. Quantifying the role of soil physical properties in controlling plant available water remains a challenge [Vereecken et al., 2015], but recent work has highlighted the importance of terrain and deeper subsurface geophysical structure in controlling plant water availability [Hu et al., 2010]. Dominant controls on soil moisture patterns often show substantial spatial and temporal variability [Western and Blöschl, 1999; Penna et al., 2009] with spatial patterns of soil moisture controlled by lateral subsurface flow patterns that followed subsurface geologic features [Kampf et al., 2014]. Similarly, other studies [e.q., Tromp-van Meerveld and McDonnell, 2006] indicate that hillslope-scale transpiration is more strongly related to subsurface storage than surface supply, highlighting the need for a deeper and larger scale focus on CZ structure to predict multiple sources of plant available water (Figure 3). Analysis of water isotopes has been instrumental in gaining insight into where in the subsurface plants obtain water [Dawson and Ehleringer, 1991; Hu et al., 2010; Brooks et al., 2010]. The signature message from this work has been that plants are extremely opportunistic in accessing water from both deep and shallow sources. The interactions between aspect-mediated microclimate and subsurface-mediated water availability are reflected in airborne LiDAR-derived vegetation structure in Gordon Gulch in the Boulder Creek CZO (Figure 4; data from http://czo.colorado.edu/geGIS/). Located at 2600 m in Colorado, Gordon Gulch is at the boundary of energy limitation at higher elevations and water limitation at lower elevations and differences in vegetation type and size are associated with aspect, topographic convergence, and bedrock topography [Adams et al., 2014]. Further work is needed to quantify these patterns at other locations and to identify the underlying processes resulting vegetation structure.

Nonlocal sources of laterally redistributed soil moisture are important for both local and regional-scale water balances [Thompson et al., 2011b; Goulden et al., 2012]. Notably, this lateral subsidy can occur on

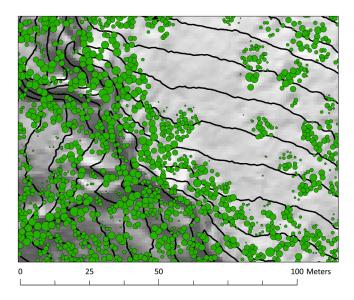


Figure 4. Vegetation structure in Gordon Gulch catchment of the BC CZO in Colorado. Circles show individual tree canopies (to scale) across a catena from N and NE facing slopes (bottom left,) and S and SW facing slopes (top right). Contour intervals are 2 m, shading represents annual solar loading computer in arc GIS using 1 m LiDAR topography. More and larger trees are found on N facing slopes reflecting lower atmospheric demand for precipitation. Higher vegetation in convergent zones and stands of large trees on the S facing slope represent subsurface controls on vegetation access to GW.

scales from hillslope to catchment, regional, and continental (Figure 1). For example, watershed scale evapotranspiration was 15% greater for a Sierra watershed if lateral redistribution of water was accounted for [Tague and Peng, 2013]. Similarly, rooting zone storage or lateral subsidy can result in watershed scale ET fluxes that are 20% or greater than expected based on local precipitation and standard soil water holding capacity estimates derived from Ameriflux tower evapotranspiration data [Thompson et al., 2011a]. At hillslope scales, emergent patterns of vegetation can be indicators of upslope redistribution and water subsidy [Hwang et al., 2012]. At catchment to regional scales, landscape indices of evapotranspiration to subsurface water storage are strongly and significantly related to remotely sensed vegetation productivity [Brooks et al., 2011; Voepel et al., 2011]. However, where this water is stored in the

subsurface, and where ET fluxes occur on the landscape remain unknown highlighting the need for coupled ecohydrological and hydrogeological research.

Beyond influencing subsurface water supply, surface CZ structure (e.g., aspect, topography, and vegetation structure) profoundly affects hydrologic partitioning by modifying microclimate and land surface atmosphere energy exchanges [Hinckley et al., 2014; Rasmussen et al., 2015]. Because seasonal snow cover in many locations persists on the land surface for an extended period of time, patterns in snow accumulation and ablation have been widely employed to provide insight into how the structure of the land surface (topography and vegetation) influences hydrologic partitioning through influences on microclimate [Marks et al., 1999; Link and Marks, 1999; Winstral et al., 2002; Erickson et al., 2005] independently of the more wellstudied effects of on vegetation. Relationships among elevation, temperature, and precipitation are widely appreciated [e.g., Aishlin and McNamara, 2011; Anderson et al., 2014], but slope and aspect exhibit significant controls on solar radiation, wind sheltering, and thereby snow accumulation and melt [Winstral et al., 2002; Erickson et al., 2005; Rinehart et al., 2008; Anderson et al., 2014], producing spatially and temporally variable water inputs to soil [Kormos et al., 2014; Harpold et al., 2014; Molotch et al., 2009; Bales et al., 2011]. Vegetation further complicates the impacts of aspect on hydrological partitioning of both snow and rain through interception, shading from solar radiation, generating longwave radiation, and reducing wind speeds that drive turbulent energy fluxes [Link and Marks, 1999; Veatch et al., 2009; Musselman et al., 2008; Gustafson et al., 2010; Rinehart et al., 2008; Molotch et al., 2009; Lundquist et al., 2013; Broxton et al., 2014; Harpold et al., 2014]. These spatial patterns in microclimatic interactions between vegetation and terrain may be mimicked following rain during the growing season [Royer et al., 2010], yet are rarely included in models.

Because of its central role in hydrologic partitioning, vegetation structure is widely used to provide insight into both subsurface hydrogeology [e.g., *Cowardin et al.*, 1979; *Brooks*, 1991; *Rango et al.*, 2006] and terrain-mediated energy balance and water demand [e.g., *Rodriguez-Iturbe*, 2000; *Ivanov et al.*, 2008a, 2008b]. To date, however, analyses of vegetation amount, composition, and activity have not yet been used to their full potential to advance understanding of hydrological partitioning. For example, Figure 4 not only high-lights both the differences in vegetation associated with surface energy balance on north versus south facing slopes but also reflects stands of vegetation on south facing slopes that have greater water availability based on subsurface geological structure. Key questions remain therefore, including Where do plants get

their water? Where on the landscape is evapotranspiration supply versus demand limited? How are these characteristics related to CZ structure? Addressing these questions will allow CZ ecohydrology to move beyond one-dimensional models of plant water use, by employing spatially explicit hydrological, microclimate, and vegetation structure. Remotely sensed vegetation structure, including high-resolution LiDAR data, can be used to infer subsurface CZ structure and water availability as well as evaluate models of groundwater flow and routing. Further, water isotopes and geochemical tracers in vegetation hold potential to fingerprint water sources and constrain water availability in space.

5. Summary

A consistent theme that emerges from the brief reviews of catchment hydrology and hydrochemistry, hydrogeology, and ecohydrology above is the importance of a potentially large and spatially variable pool of stored subsurface water that may contribute to both ET and streamflow. When combined with the ubiguitous hydrochemical observations that most stream flow has interacted extensively with subsurface stored water, the critical knowledge gaps in hydrologic partitioning in the critical zone converge on the need to quantify the size and accessibility of this reservoir to resolve interactions with both atmospheric and surface water fluxes. These knowledge gaps highlight the need for understanding spatial variability in the threedimensional "plumbing" connecting groundwater both to surface water or the atmosphere [NRC-NAS, 2012]. Growing lines of evidence indicate that surface and subsurface CZ structure is strongly related to this plumbing, and in turn the structure of the CZ develops in response to these interactions among microclimate, water, and vegetation productivity [Rasmussen et al., 2011]. Spatially variable and temporally dynamic subsurface water supply is rarely incorporated into land surface, ecohydrological, or streamflow models, representing a major gap if predictive models are going to get "the right answers for the right reasons" [Kirchner, 2006]. Ongoing changes in climate and land cover however highlight the need to improve current operational models in locations where intensive observations across CZ disciplines are not available [Milly et al., 2008]. The characterization and classification of cross-site hydrological response-based analyses of geological and geomorphological characteristics may aid in efforts toward hydrological predictions on both gauged and ungauged catchments [Sivapalan et al., 2003; Wagener et al., 2007].

Within this framework, we pose four challenges for the CZ hydrological community geared both toward improving process understanding of hydrologic partitioning and developing operational hydrologic models:

(1) Identify the interactions among terrain, lithology, vegetation, and water that control subsurface weathering and allow prediction of subsurface structure. This represents an ongoing, multidisciplinary effort to understand how and why structure develops. (2) Quantify the amount, residence time, and movement of subsurface water to better predict plant available water and stream flow generation. This work will utilize the growing knowledge on how CZ subsurface structure develops to reconcile ongoing disciplinary questions including partitioning of plant water sources and the rapid release of stored water. (3) Evaluate the role of terrain complexity in modifying microclimatic influences on water demand. Combined with improved understanding of where plants obtain water, this work will address when and where partitioning to vapor flux is under primary control of subsurface supply versus climatic demand. (4) Develop focused or targeted observations across a larger range of spatial scales to place site-specific work in regional context. These efforts will use the patterns associated with the rapidly increasing spatial and temporal data on CZ structure to predict dominant processes/controls and thereby sensitivity to change in the vast majority of locations that are not extensively instrumented and studies.

To address these challenges, hydrologists must view colleagues in related fields as stakeholders who help define the spatial and temporal scales of research, which often may be outside those typically used in disciplinary research. In this way, the CZ community can advance basic hydrological theory and provide consistent and widely transferrable information to societal stakeholders charged with decision-making in a rapidly changing world.

References

Adams, H. R., H. R. Barnard, and A. K. Loomis (2014), Topography alters tree growth–climate relationships in a semi-arid forested catchment, *Ecosphere*, 5(11), Article 148.

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- Ågren, A., M. Haei, S. J. Köhler, K. Bishop, and H. Laudon (2010), Regulation of stream water dissolved organic carbon (DOC) concentrations during snowmelt; the role of discharge, winter climate and memory effects, *Biogeosciences*, 7, 2901–2913.
- Aishlin, P., and J. P. McNamara (2011), Bedrock infiltration and mountain block recharge accounting using chloride mass balance, *Hydrol. Processes*. 25, 1934–1948.
- Amundson, R., D. D. Richter, G. S. Humphreys, E. G. Jobbágy, and J. Gaillardet (2007), Coupling between biota and earth materials in the critical zone, *Elements*, 3(5), 327–332.
- Anderson, B. T., J. P. McNamara, H. P. Marshall, and A. N. Flores (2014), Insights into the physical processes controlling correlations between snow distribution and terrain properties, *Water Resour. Res.*, 50, 4545–4563, doi:10.1002/2013WR013714.
- Asbjornsen, H., et al. (2011), Ecohydrological advances and applications in plant–water relations research: A review, J. Plant Ecol., 4(1–2), 3–22, doi:10.1093/jpe/rtr005.
- Bales, R. C., J. W. Hopmans, A. T. O'Geen, M. Meadows, P. C. Hartsough, P. Kirchner, C. T. Hunsaker, and D. Beaudette (2011), Soil moisture response to snowmelt and rainfall in a Sierra Nevada mixed-conifer forest, *Vadose Zone J.*, 10, 786–799.
- Basu, N. B., et al. (2010), Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity, *Geophys. Res. Lett.*, *37*, L23404, doi:10.1029/2010GL045168.
- Bates, B. L., J. C. McIntosh, K. A. Lohse, and P. D. Brooks (2011), Influence of groundwater flowpaths, residence times and nutrients on the extent of microbial methanogenesis in coal beds: Powder River Basin, USA, Chem. Geol., 284(1), 45–61.
- Bejan, A. (2007), Constructal theory of pattern formation, Hydrol. Earth Syst. Sci., 11, 753–768.
- Berndt, H. W., and R. D. Gibbons (1958), Root distribution of some native trees and understory plants growing on three sites within Ponderosa pine watersheds in Colorado, Rocky Mountain Forest and Range Experiment Station, Stn. Pap. 37, For. Serv., U.S. Dep. of Agric., Fort Collins, Colo.
- Beven, K. (2006), Searching for the holy grail of scientific hydrology: Qt = H(t)A as closure, Hydrol. Earth Syst. Sci., 10, 609-618.
- Beven, K., and P. Germann (2013), Macropores and water flow in soils revisited, Water Resour. Res., 49, 3071–3092, doi:10.1002/wrcr.20156.
- Bishop, D. M. (1962), Lodgepole pine rooting habits in the Blue Mountains of Northeastern Oregon, Ecology, 43(1), 140–142.
- Bishop, K., J. Seibert, S. Koher, and H. Laudon (2004), Resolving the Double Paradox of rapidly mobilized old water with highly variable responses in runoff chemistry, *Hydrol. Processes*, 18(1), 185–189.
- Bleby, T. M., A. J. McElrone, and R. B. Jackson (2010), Water uptake and hydraulic redistribution across large woody root systems to 20 m depth, *Plant Cell Environ.*, 33, 2132–2148.
- Blöschl, G., and M. Sivapalan (1995), Scale issues in hydrological modelling: A review, Hydrol. Processes, 9(3-4), 251-290.
- Box, G. E., and N. R. Draper (1987), Empirical Model-Building and Response Surfaces, John Wiley, N. Y.
- Brantley, S. L., M. B. Goldhaber, and K. V. Ragnarsdottir (2007), Crossing disciplines and scales to understand the critical zone, *Elements*, 3(5), 307–314.
- Brantley, S. L., et al (2011), Twelve testable hypotheses on the geobiology of weathering, Geobiology, 9, 140–165.
- Brooks, J. R., H. R. Barnard, R. Coulombe, and J. J. McDonnell (2010), Ecohydrologic separation of water between trees and streams in a Mediterranean climate, *Nat. Geosci.*, 3(2), 100–104, doi:10.1038/ngeo722.
- Brooks, P., and E. R. Vivoni (2008), Mountain ecohydrology: Quantifying the role of vegetation in the water balance of montane catchments, *Ecohydrology*, 1(3), 187–192.
- Brooks, P. D. (1991), Identification of vegetation community structure and groundwater flow patterns in the Riparian zone along South Boulder Creek. MS thesis. Univ. of Colo., Boulder.
- Brooks, P. D., and M. M. Lemon (2007), Spatial variability in dissolved organic matter and inorganic nitrogen concentrations in a semiarid stream, San Pedro River, Arizona, J. Geophys. Res., 112, G03505, doi:10.1029/2006JG000262.
- Brooks, P. D., C. M. O'Reilly, S. A. Diamond, D. H. Campbell, R. Knapp, D. Bradford, P. S. Corn, B. Hossack, and K. Tonnessen (2005), Spatial and temporal variability in the amount and source of dissolved organic carbon: Implications for ultraviolet exposure in amphibian habitats, *Ecosystems*, 8(5), 478–487.
- Brooks, P. D., P. A. Troch, M. Durcik, E. Gallo, and M. Schlegel (2011), Quantifying regional scale ecosystem response to changes in precipitation: Not all rain is created equal, *Water Resour. Res.*, 47, W00J08, doi:10.1029/2010WR009762.
- Broxton, P. D., A. A. Harpold, J. A. Biederman, P. A. Troch, N. P. Molotch, and P. D. Brooks (2014), Quantifying the effects of vegetation structure on snow accumulation and ablation in mixed-conifer forests, *Ecohydrology*, doi:10.1002/eco.1565, in press.
- Burges, S. J. (1990), Water resources research: Past, present, and future, Water Resour. Res., 26(7), 1321–1322
- Bur, T. P., F. Worrall, N. J. K. Howden, and M. G. Anderson (2015), Shifts in discharge-concentration relationships as a small catchment recover from severe drought, *Hydrol. Processes*, 29, 498–507.
- Chanat, J. G., K. C. Rice, and G. M. Hornberger (2002), Consistency of patterns in concentration-discharge plots, *Water Resour. Res.*, 38(8), doi:10.1029/2001WR000971.
- Chorover, J., P. A. Troch, C. Rasmussen, P. D. Brooks, J. D. Pelletier, D. D. Breshars, T. E. Huxman, S. A. Kurc, K. A. Lohse, and J. C. McIntosh (2011a), How water, carbon, and energy drive critical zone evolution: The Jemez-Santa Catalina Critical Zone Observatory, *Vadose Zone* 1, 10(3) 884–899
- Christophersen, N., C. Neal, R. P. Hooper, R. D. Vogt, and S. Andersen (1990), Streamwater chemistry as a mixture of soil water endmembers—Towards developement of second generation acidification models, *J. Hydrol.*, 116, 307–320.
- Condon, L. E., R. M. Maxwell, and S. Gangopadhyay (2013), The impact of subsurface conceptualization on land energy fluxes, *Adv. Water Resour.*, 60(0), 188–203, doi:10.1016/j.advwatres.2013.08.001.
- Cowardin, L. M., V. Carter, F. C. Golet, and E. T. LaRoe (1979), Classification of wetlands and deepwater habitats of the United States, report, U.S. Dep. of the Interior, U.S. Fish and Wildlife Serv., Washington, D. C.
- Creed, I. F., D. M. McKnight, B. A. Pellerin, M. B. Green, B. A. Bergamaschi, G. R. Aiken, D. A. Burns, S. E. Findlay, J. B. Shanley, and R. G. Striegl (2015), The river as a chemostat: Fresh perspectives on dissolved organic matter flowing down the river continuum, *Can. J. Fish. Aquat. Sci.*, 72(8): 1272–1285, doi:10.1139/cjfas-2014-0400.
- Dawson, T. E., and J. R. Ehleringer (1991), Streamside trees that do not use stream water, *Nature*, 350, 335–337.
- Dell, B., J. R. Bartle, and W. H. Tacey (1983), Root occupation and root channels of Jarrah forest subsoils, Aust. J. Bot., 31(6) 615–627.
- Drexhage, M., and F. Bruber (1998), Architecture of the skeletal root system of 40-year-old *Picea abies* on strongly acidified soils in the Harz Mountains (Germany), *Can. J. For. Res.*, 28, 13–22.
- Druhan, J. L., and K. Maher (2014), A model linking stable isotope fractionation to water flux and transit times in heterogeneous porous media, *Procedia Earth Planet. Sci.*, 10, 179–188.
- Elliott, K. J., and J. M. Vose (2011), The contribution of the Coweeta Hydrologic Laboratory to developing an understanding of long-term (1934–2008) changes in managed and unmanaged forests, For. Ecol. Manage., 261(5), 900–910.

- Erickson, T. A., M. W. Williams, and A. Winstral (2005), Persistence of topographic controls on the spatial distribution of snow in rugged mountain terrain, Colorado, United States, *Water Resour. Res.*, 41, W04014, doi:10.1029/2003WR002973.
- Fan, Y., H. Li, and G. Miguez-Macho (2013), Global patterns of groundwater table depth, *Science*, 339(6122), 940–943, doi:10.1126/science.1229881.
- Ferguson, I. M., and R. M. Maxwell (2010), The role of groundwater in watershed response and land surface feedbacks under climate change, *Water Resour. Res.*, 46, W00F02, doi:10.1029/2009WR008616.
- Frisbee, M. D., F. M. Phillips, G. S. Weissmann, P. D. Brooks, J. L. Wilson, A. R. Campbell, and F. Liu (2012), Unraveling the mysteries of the large watershed black box: Implications for the streamflow response to climate and landscape perturbations, *Geophys. Res. Lett.*, 39, L01404, doi:10.1029/2011GL050416.
- Geroy, I. J., M. M. Gribb, H. P. Marshall, D. G. Chandler, S. G. Benner, and J. P. McNamara (2011), Aspect influences on soil water retention and storage, *Hydrol. Processes*, 25, 3836–3842.
- Godsey, S. E., J. W. Kirchner, and D. W. Clow (2009), Concentration–discharge relationships reflect chemostatic characteristics of US catchments, *Hydrol. Processes*, 1864, 1844–1864.
- Gooseff, M. N., and B. L. McGlynn (2005), A stream tracer technique employing ionic tracers and specific conductance data applied to the Maimai catchment, New Zealand, *Hydrol. Processes*, 19(13), 2491–2506.
- Goulden, M. L., R. G. Anderson, R. C. Bales, A. E. Kelly, M. Meadows, and G. C. Winston (2012), Evapotranspiration along an elevation gradient in California's Sierra Nevada, J. Geophys. Res., 117, G03028, doi:10.1029/2012JG002027.
- Graham, C. B., W. van Verseveld, H. R. Barnard, and J. J. McDonnell (2010), Estimating the deep seepage component of the hillslope and catchment water balance within a measurement uncertainty framework, *Hydrol. Processes*, 24(25), 3631–3647, doi:10.1002/hyp.7788.
- Guan, K., S. E. Thompson, C. J. Harman, N. B. Basu, P. S. C. Rao, M. Sivapalan, A. I. Packman, and P. K. Kalita (2011), Spatiotemporal scaling of hydrological and agrochemical export dynamics in a tile-drained Midwestern watershed, *Water Resour. Res.*, 47, W00J02, doi:10.1029/ 2010WR009997.
- Gustafson, J. R., P. Brooks, N. Molotch, and W. Veatch (2010), Estimating snow sublimation using natural chemical and isotopic tracers across a gradient of solar radiation, *Water Resour. Res.*, 46, W12511, doi:10.1029/2009WR009060.
- Harman, C. J. (2015), Time-variable transit time distributions and transport: Theory and application to storage-dependent transport of chloride in a watershed, *Water Resour. Res.*, 50, 1–30, doi:10.1002/2014WR015707.
- Harpold, A. A., N. P. Molotch, K. N. Musselman, R. C. Bales, P. B. Kirchner, M. Litvak, and P. D. Brooks (2014), Soil moisture response to snow-melt timing in mixed-conifer subalpine forests, *Hydrol. Processes*, 29, 2782–2798.
- Heidbüchel, I., P. A. Troch, S. W. Lyon, and M. Weiler (2012), The master transit time distribution of variable flow systems, Water Resour. Res., 48, W06520, doi:10.1029/2011WR011293.
- Hellmers, H., J. S. Horton, G. Juhren, and J. O'Keefe (1955), Root systems of some chaparral plants in Southern California, *Ecology*, 36, 667–678.
- Hicke, J. A., G. P. Asner, J. T. Randerson, C. Tucker, S. Los, R. Birdsey, J. C. Jenkins, and C. Field (2002), Trends in North American net primary productivity derived from satellite observations, 1982–1998, *Global Biogeochem. Cycles*, 16(2), 1019, doi:10.1029/2001GB001550.
- Hinckley, E. L. S., B. A. Ebel, R. T. Barnes, R. S. Anderson, M. W. Williams, and S. P. Anderson (2014), Aspect control of water movement on hillslopes near the rain–snow transition of the Colorado Front Range, *Hydrol. Processes*, 28, 74–85.
- Holbrook, W. S., C. S. Riebe, M. Elwaseif, J. L. Hayes, D. L. Harry, K. Basler-Reeder, A. Malazian, A. Dosseto, P. C. Hartsough, and J. W. Hopmans (2014), Geophysical constraints on deep weathering and water storage potential in the Southern Sierra Critical Zone Observatory, Earth Surf. Processes Landforms, 39, 366–380.
- Hooper, R. P. (2001), Applying the scientific method to small catchment studies: A review of the Panola Mountain experience, *Hydrol. Processes*, 15(10), 2039–2050.
- Horton, R. E. (1933), The role of infiltration in the hydrologic cycle, Trans. AGU, 14, 446-460.
- Hu, J., D. J. Moore, S. P. Burns, and R. K. Monson (2010), Longer growing seasons lead to less carbon sequestration by a subalpine forest, *Global Change Biol.*, 16(2), 771–783.
- Huxman, T. E., et al. (2004), Convergence across biomes to a common rain-use efficiency, Nature, 429(6992), 651–654.
- Huxman, T. E., B. P. Wilcox, D. D. Breshears, R. L. Scott, K. A. Snyder, E. E. Small, K. Hultine, W. T. Pockman, and R. B. Jackson (2005), Ecohydrological implications of woody plant encroachment, *Ecology*, 86(2), 308–319.
- Hwang, T., L. E. Band, J. M. Vose, and C. Tague (2012), Ecosystem processes at the watershed scale: Hydrologic vegetation gradient as an indicator for lateral hydrologic connectivity of headwater catchments, *Water Resour. Res.*, 48, W06514, doi:10.1029/2011WR011301.
- Ivanov, V. Y., R. L. Bras, and E. R. Vivoni (2008a), Vegetation-hydrology dynamics in complex terrain of semiarid areas: 2. Energy-water controls of vegetation spatiotemporal dynamics and topographic niches of favorability, Water Resour. Res., 44, W03430, doi:10.1029/2006WR005595.
- Ivanov, V. Y., R. L. Bras, and E. R. Vivoni (2008b), Vegetation-hydrology dynamics in complex terrain of semiarid areas: 1. A mechanistic approach to modeling dynamic feedbacks, *Water Resour. Res.*, 44, W03429, doi:10.1029/2006WR005588.
- Jackson, R. B., L. A. Moore, W. A. Hoffmann, W. T. Pockman, and C. R. Linder (1999), Ecosystem rooting depth determined with caves and DNA, *Proc. Natl. Acad. Sci. U. S. A.*, 96, 11,387–11,392.
- Jasechko, S., Z. D. Sharp, J. J. Gibson, S. J. Birks, Y. Yi, and P. J. Fawcett (2013), Terrestrial water fluxes dominated by transpiration, *Nature*, 496(7445), 347–350.
- Jones, D. P., and R. C. Graham (1993), Water-holding characteristics of weathered granitic rock in chaparral and forest ecosystems, *Soil Sci. Soc. Am. J.*, 57(1), 256–261.
- Kampf, S., J. Markus, J. Heath, and C. Moore (2014), Snowmelt runoff and soil moisture dynamics on steep subalpine hillslopes, *Hydrol. Processes*, 29, 712–723.
- Kerfoot, O. (1963), The root systems of tropical forest trees, Commonw. For. Rev., 42(1(111)), 19–26.
- Kim, H., J. K. B. Bishop, T. J. Wood, and I. Y. Fung (2012), Autonomous water sampling for long-term monitoring of trace metals in remote environments, *Environ. Sci. Technol.*, 46(20), 11,220–11,226.
- Kirchner, J. W. (2003), A double paradox in catchment hydrology and geochemistry, Hydrol. Processes, 17(4), 871–874.
- Kirchner, J. W. (2006), Getting the right answers for the right reasons: Linking measurements, analyses, and models to advance the science of hydrology, Water Resour. Res., 42, W03S04, doi:10.1029/2005WR004362.
- Kirchner, J. W. (2009), Catchments as simple dynamical systems: Catchment characterization, rainfall-runoff modeling, and doing hydrology backward, Water Resour. Res., 45, W02429, doi:10.1029/2008WR006912.
- Kirchner, J. W., X. Feng, and C. Neal (2000), Fractal stream chemistry and its implications for contaminant transport in catchments, *Nature*, 403(6769), 524–527.

- Klemeš, V. (1986), Dilettantism in hydrology: Transition or destiny?, Water Resour. Res., 22(9S), 1775–188S.
- Knapp, A. K., and M. D. Smith (2001), Variation among biomes in temporal dynamics of aboveground primary production, *Science*, 291(5503), 481–484.
- Kollet, S. J., and R. M. Maxwell (2008), Capturing the influence of groundwater dynamics on land surface processes using an integrated, distributed watershed model. Water Resour. Res., 44, W02402, doi:10.1029/2007WR006004.
- Kormos, P. R., D. Marks, J. P. McNamara, H. P. Marshall, A. Winstral, and A. N. Flores (2014), Snow distribution, melt and surface water inputs to the soil in the mountain rain–snow transition zone, *J. Hydrol.*, *519*, 190–204.
- Kunkel, M. L., A. N. Flores, T. J. Smith, J. P. McNamara, and S. G. Benner (2011), A simplified approach for estimating soil carbon and nitrogen stocks in semi-arid complex terrain, *Geoderma*, 165, 1–11.
- Lebedeva, M. I., and S. L. Brantley (2013), Exploring geochemical controls on weathering and erosion of convex hillslopes: Beyond the empirical regolith production function, *Earth Surf. Processes Landforms*, 38(15), 1793–1807, doi:10.1002/esp.3424.
- Lebedeva, M. I., R. C. Fletcher, V. N. Balashov, and S. L. Brantley (2007), A reactive diffusion model describing transformation of bedrock to saprolite, Chem. Geol., 244, 624–45.
- Lee, J.-E., R. S. Oliveira, T. E. Dawson, and I. Fung (2005), Root functioning modifies seasonal climate, *Proc. Natl. Acad. Sci. U. S. A.*, 102(49), 17,576–17,581.
- Lewis, D. C., and R. H. Burgy (1964), The relationship between oak tree roots and groundwater in fractured rock as determined by tritium tracing, *J. Geophys. Res.*, 69(12), 2579–2588, doi:10.1029/JZ069i012p02579.
- Link, T. E., and D. Marks (1999), Distributed simulation of snowcover mass and energy-balance in the boreal forest, *Hydrol. Processes*, *13*, 2439–2452.
- Lins, H. F. (1994), Recent developments in water, energy, and biogeochemical budgets research, Eos Trans. AGU, 75(38), 433–439.
- Liu, F. J., R. Parmenter, P. D. Brooks, M. H. Conklin, and R. C. Bales (2008), Seasonal and interannual variation of streamflow pathways and biogeochemical implications in semi-arid, forested catchments in Valles Caldera, New Mexico, *Ecohydrology*, 1(3), 239–252.
- Lohse, K. A., P. D. Brooks, J. C. McIntosh, T. Meixner, and T. E. Huxman (2009), Interactions between biogeochemistry and hydrologic systems. *Annu. Rev. Environ. Resour.*, 34, 65–96.
- Lundquist, J. D., S. E. Dickerson-Lange, J. A. Lutz, and N. C. Cristea (2013), Lower forest density enhances snow retention in regions with warmer winters: A global framework developed from plot-scale observations and modeling, *Water Resour. Res.*, 49, 6356–6370, doi:10.1002/wrcr.20504.
- Lutz, B. D., P. J. Mulholland, and E. S. Bernhardt (2012), Long-term data reveal patterns and controls on stream water chemistry in a forested stream: Walker Branch, Tennessee. *Ecol. Monogr.*, 82(3), 367–387.
- Maher, K. (2011), The role of fluid residence time and topographic scales in determining chemical fluxes from landscapes, *Earth Planet. Sci. Lett.*, 312, 48–58.
- Maher, K., and C. P. Chamberlain (2014), Hydrologic regulation of chemical weathering and the geologic carbon cycle, *Science*, 343, 1502–1504.
- Marks, D., J. Domingo, D. Susong, T. Link, and D. Garen (1999), A spatially distributed energy balance snowmelt model for application in mountain basins. *Hydrol. Processes*. 13(12–13), 1935–1959.
- Maxwell, R. M., and S. J. Kollet (2008), Interdependence of groundwater dynamics and land-energy feedbacks under climate change, *Nat. Geosci.*, 1(10), 665–669.
- Maxwell, R. M., F. K. Chow, and S. J. Kollet (2007), The groundwater-land-surface-atmosphere connection: Soil moisture effects on the atmospheric boundary layer in fully-coupled simulations, *Adv. Water Resour.*, 30(12), 2447–2466, doi:10.1016/j.advwatres.2007.
- McDonnell, J., M. Sivapalan, K. Vaché, S. Dunn, G. Grant, R. Haggerty, C. Hinz, R. Hooper, J. Kirchner, and M. Roderick (2007), Moving beyond heterogeneity and process complexity: A new vision for watershed hydrology, *Water Resour. Res.*, 43, W07301, doi:10.1029/2006WR005467
- McDonnell, J. J. (2003), Where does water go when it rains? Moving beyond the variable source area concept of rainfall-runoff response, *Hydrol. Processes*, 17(9), 1869–1875.
- McDonnell, J. J. (2014), The two water worlds hypothesis: Ecohydrological separation of water between streams and trees?, WIREs Water, 1, 323–329.
- McNamara, J. P., D. Tetzlaff, K. Bishop, C. Soulsby, M. Seyfried, N. E. Peters, B. Aulenbach, and R. Hooper (2011), Storage as a metric of catchment comparison, *Hydrol. Processes*, 25, 3364–3371, doi:10.1002/hyp.8113.
- Milly, P. C. D., J. Betancourt, M. Falkenmark, R. M. Hirsch, Z. W. Kundzewicz, D. P. Lettenmaier, and R. J. Stouffer (2008), Climate change—Stationarity is dead: Whither water management?, *Science*, 319(5863), 573–574.
- Molotch, N. P., P. D. Brooks, S. P. Burns, M. Litvak, R. K. Monson, J. R. McConnell, and K. Musselman (2009), Ecohydrological controls on snowmelt partitioning in mixed-conifer sub-alpine forests, *Ecohydrology*, 2(2), 129–142.
- Montanari, A., and D. Koutsoyiannis (2012), A blueprint for process-based modeling of uncertain hydrological systems, *Water Resour. Res.*, 48, W09555, doi:10.1029/2011WR011412.
- Mulholland, P. J., and W. R. Hill (1997), Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: Separating catchment flow path and in-stream effects, Water Resour. Res., 33(6), 1297–1306.
- Musselman, K., N. Molotch, and P. Brooks (2008), Effects of vegetation on snow accumulation and ablation in a mid-latitude sub-alpine forest, *Hydrol. Processes*, 22(15), 2767–2776.
- Neal, C., et al. (2013), High-frequency precipitation and stream water quality time series from Plynlimon, Wales: An openly accessible data resource spanning the periodic table, *Hydrol. Processes*, 27(17), 2531–2539.
- Newman, B. D., B. P. Wilcox, S. R. Archer, D. D. Breshears, C. N. Dahm, C. J. Duffy, N. G. McDowell, F. M. Phillips, B. R. Scanlon, and E. R. Vivoni (2006), Ecohydrology of water-limited environments: A scientific vision, *Water Resour. Res.*, 42, W06302, doi:10.1029/2005WR004141.
- Nijland, W., M. van der Meijde, E. A. Addink, and S. M. de Jong (2010), Detection of soil moisture and vegetation water abstraction in a Mediterranean natural area using electrical resistivity tomography, *Catena*, *81*(3), 209–216.
- NRC-NAS (2001), Basic Research Opportunities in Earth Sciences, Natl. Acad. Press, Washington, D. C.
- NRC-NAS (2012), Challenges and Opportunities in Hydrologic Sciences, Natl. Acad. Press, Washington, D. C.
- Parsekian, A. D., K. Singha, B. J. Minsley, W. S. Holbrook, and L. Slater (2015), Multiscale geophysical imaging of the critical zone, *Rev. Geophys.*, 53, 1–26, doi:10.1002/2014RG000465.
- Penman, H. (1961), Weather, plant and soil factors in hydrology, Weather, 16(7), 207–219.
- Penna, D., M. Borga, D. Norbiato, and G. Dalla Fontana (2009), Hillslope scale soil moisture variability in a steep alpine terrain, *J. Hydrol.*, 364(3), 311–327.

- Perdrial, J. N., J. McIntosh, A. Harpold, P. D. Brooks, X. Zapata-Rios, J. Ray, T. Meixner, T. Kanduc, M. Litvak, and P. A. Troch (2014), Stream water carbon controls in seasonally snow-covered mountain catchments: Impact of inter-annual variability of water fluxes, catchment aspect and seasonal processes, *Biogeochemistry*, 118(1–3), 273–290.
- Peters, N. E., J. K. Böhlke, P. D. Brooks, and T. P. Burt (2011), Hydrology and biogeochemical linkages, in *Treatise on Water Science*, edited by P. Wilderer edited, pp. 271–304, Academic, Oxford, U. K.
- Peterson, B. J., et al. (2001), Control of nitrogen export from watersheds by headwater streams, Science, 292(5514), 86–90.
- Querejeta, J. I., H. Estrada-Medina, M. F. Allen, and J. J. Jiménez-Osornio (2007), Water source partitioning among trees growing on shallow karst soils in a seasonally dry tropical climate, *Oecologia*, 152, 26–36.
- Rango, A., S. L. Tartowski, A. Laliberte, J. Wainwright, and A. Parsons (2006), Islands of hydrologically enhanced biotic productivity in natural and managed arid ecosystems, *J. Arid Environ.*, 65(2), 235–252.
- Rasmussen, C., P. A. Troch, J. Chorover, P. Brooks, J. Pelletier, and T. E. Huxman (2011), An open system framework for integrating critical zone structure and function, *Biogeochemistry*, 102(1–3), 15–29.
- Rasmussen, C., J. D. Pelletier, P. A. Troch, T. L. Swetnam, and J. Chorover (2015), Quantifying topographic and vegetation effects on the transfer of energy and mass to the critical zone, *Vadose Zone J.*, 15, 1–16, doi:10.2136/vzj2014.07.0102.
- Raz-Yaseef, N., L. Koteen, and D. D. Baldocchi (2013), Coarse root distribution of a semi-arid oak savanna estimated with ground penetrating radar, *J. Geophys. Res. Biogeosci.*, 118, 135–147, doi:10.1029/2012JG002160.
- Rempe, D. M., and W. E. Dietrich (2014), A bottom-up control on fresh-bedrock topography under landscapes, *Proc. Natl. Acad. Sci. U. S. A.*, 111, 6576–6581.
- Riebe, C. S., and S. L. Brantley (2015), Going deep to quantify limits on weathering in the critical zone, *Earth Surf. Processes Landforms*, in press
- Rihani, J. F., R. M. Maxwell, and F. K. Chow (2010), Coupling groundwater and land surface processes: Idealized simulations to identify effects of terrain and subsurface heterogeneity on land surface energy fluxes, Water Resour. Res., 46, W12523, doi:10.1029/ 2010WR009111.
- Rinehart, A. J., E. R. Vivoni, and P. D. Brooks (2008), Effects of vegetation, albedo, and solar radiation sheltering on the distribution of snow in the Valles Caldera, New Mexico, *Ecohydrology*, 1(3), 253–270.
- Rodriguez-Iturbe, I. (2000), Ecohydrology: A hydrologic perspective of climate-soil-vegetation dynamics, Water Resour. Res., 36(1), 3–9
- Rose, K. L., R. C. Graham, and D. R. Parker (2003), Water source utilization by *Pinus jeffreyi* and *Arctostaphylos patula* on thin soils over bedrock. *Oecologia*. 134(1), 46–54.
- Royer, P. D., D. D. Breshears, C. B. Zou, N. S. Cobb, and S. A. Kurc (2010), Ecohydrological energy inputs in semiarid coniferous gradients: Responses to management-and drought-induced tree reductions, For. Ecol. Manage., 260(10), 1646–1655.
- Salve, R., D. M. Rempe, and W. E. Dietrich (2012), Rain, rock moisture dynamics, and the rapid response of perched groundwater in weathered, fractured argillite underlying a steep hillslope, *Water Resour. Res.*, 48, W11528, doi:10.1029/2012WR012583.
- Schwinning, S. (2010), The ecohydrology of roots in rocks, Ecohydrology, 3, 238–245.
- Shanley, J. B., W. H. Mcdowell, and R. F. Stallard (2011), Long-term patterns and short-term dynamics of stream solutes and suspended sediment in a rapidly weathering tropical watershed, *Water Resour.*, 47, 1–11.
- Shi, Y., K. J. Davis, C. J. Duffy, and X. Yu (2013), Development of a coupled land surface hydrologic model and evaluation at a critical zone observatory, *J. Hydrometeorol.*, 14(5), 1401–1420, doi:10.1175/jhm-d-12–0145.1.
- Sivapalan, M., K. Takeuchi, S. Franks, V. Gupta, H. Karambiri, V. Lakshmi, X. Liang, J. McDonnell, E. Mendiondo, and P. O'connell (2003), IAHS decade on Predictions in Ungauged Basins (PUB), 2003–2012: Shaping an exciting future for the hydrological sciences, Hydrol. Sci. J., 48(6), 857–880
- Slim, M., J. Taylor Perron, S. J. Martel, and K. Singha (2014), Topographic stress and rock fracture: A two-dimensional numerical model for arbitrary topography and preliminary comparison with borehole observations, Earth Surf. Processes Landforms, 40, 512–529, doi: 10.1002/esp.3646.
- Smith, T. J., J. P. McNamara, A. N. Flores, M. M. Gribb, P. S. Aishlin, and S. G. Benner (2011), Small soil storage capacity limits benefit of winter snowpack to upland vegetation, Hydrol. Processes, 25, 3858–3865.
- Soylu, M. E., E. Istanbulluoglu, J. D. Lenters, and T. Wang (2011), Quantifying the impact of groundwater depth on evapotranspiration in a semi-arid grassland region, *Hydrol. Earth Syst. Sci.*, 15(3), 787–806, doi:10.5194/hess-15-787-2011.
- Szilagyi, J., V. A. Zlotnik, and J. Jozsa (2013), Net recharge vs. depth to groundwater relationship in the Platte river valley of Nebraska, United States, *Groundwater*, 51(6), 945–951, doi:10.1111/gwat.12007.
- Tague, C., and H. Peng (2013), The sensitivity of forest water use to the timing of precipitation and snowmelt recharge in the California Sierra: Implications for a warming climate, *J. Geophys. Res. Biogeosci.*, 118, 875–887, doi:10.1002/jgrg.20073.
- Tesfa, T. K., D. G. Tarboton, D. G. Chandler, and J. P. McNamara (2009), Modeling soil depth from topographic and land cover attributes, Water Resour. Res., 45, W10438, doi:10.1029/2008WR007474.
- Thompson, S. E., C. J. Harman, P. A. Troch, P. D. Brooks, and M. Sivapalan (2011a), Spatial scale dependence of ecohydrologically mediated water balance partitioning: A synthesis framework for catchment ecohydrology, *Water Resour. Res.*, 47, W00J03, doi:10.1029/2010WR009998.
- Thompson, S. E., C. J. Harman, A. G. Konings, M. Sivapalan, A. Neal, and P. A. Troch (2011b), Comparative hydrology across AmeriFlux sites: The variable roles of climate, vegetation, and groundwater, *Water Resour. Res.*, 47, W00J07, doi:10.1029/2010WR009797.
- Thompson, S. E., C. Harman, R. Schumer, J. Wilson, N. Basu, P. Brooks, S. Donner, M. Hassan, A. Packman, and P. Rao (2011c), Patterns, puzzles and people: Implementing hydrologic synthesis, *Hydrol. Processes*, 25(20), 3256–3266.
- Troch, P. A., G. F. Martinez, V. R. N. Pauwels, M. Durcik, M. Sivapalan, C. Harman, P. D. Brooks, H. Gupta, and T. Huxman (2009), Climate and vegetation water use efficiency at catchment scales, *Hydrol. Processes*, 23(16), 2409–2414.
- Tromp-van Meerveld, H., and J. McDonnell (2006), On the interrelations between topography, soil depth, soil moisture, transpiration rates and species distribution at the hillslope scale, *Adv. Water Resour.*, 29(2), 293–310.
- van der Velde, Y., I. Heidbüchel, S. W. Lyon, L. Nyberg, A. Rodhe, K. Bishop, and P. A. Troch (2014), Consequences of mixing assumptions for time-variable travel time distributions, *Hydrol. Processes*, 29, 3460–3474.
- Vázquez-Ortega, A., J. Perdrial, A. Harpold, X. Zapata-Ríos, C. Rasmussen, J. McIntosh, M. Schaap, J. D. Pelletier, P. D. Brooks, and M. K. Amistadi (2015), Rare earth elements as reactive tracers of biogeochemical weathering in forested rhyolitic terrain, Chem. Geol., 391, 19–32.
- Veatch, W., P. Brooks, J. Gustafson, and N. Molotch (2009), Quantifying the effects of forest canopy cover on net snow accumulation at a continental, mid-latitude site, *Ecohydrology*, 2(2), 115–128.

- Vereecken, H., J. A. Huisman, H. J. Hendricks Franssen, N. Brüggemann, H. R. Bogena, S. Kollet, M. Javaux, J. van der Kruk, and J. Vanderborght (2015), Soil hydrology: Recent methodological advances, challenges, and perspectives, *Water Resour. Res.*, *51*, 2616–2633, doi:10.1002/2014WR016852.
- Voepel, H., B. Ruddell, R. Schumer, P. A. Troch, P. D. Brooks, A. Neal, M. Durcik, and M. Sivapalan (2011), Quantifying the role of climate and landscape characteristics on hydrologic partitioning and vegetation response, *Water Resour. Res.*, 47, W00J09, doi:10.1029/2010WR009944
- Wagener, T., M. Sivapalan, P. Troch, and R. Woods (2007), Catchment classification and hydrologic similarity, *Geogr. Compass*, 1(4), 901–931. Webb, W., S. Szarek, W. Lauenroth, R. Kinerson, and M. Smith (1978), Primary productivity and water-use in native forest, grassland, and desert ecosystems, *Ecology*, 59(6), 1239–1247.
- Western, A. W., and G. Blöschl (1999), On the spatial scaling of soil moisture, J. Hydrol., 217(3), 203-224.
- White, A. F., and A. E. Blum (1995), Effects of climate on chemical_weathering in watersheds, *Geochim. Cosmochim. Acta*, *59*, 1729–1747. White, A. F., and S. L. Brantley (2003), The effect of time on the weathering of silicate minerals: Why do weathering rates differ in the laboratory and field?, *Chem. Geol.*, *202*, 479–506.
- Williams, M. W., and K. A. Melack (1991), Solute chemistry of snowmelt and runoff in an alpine basin, Sierra Nevada, *Water Resour. Res.*, 27(7), 1575–1588.
- Winstral, A., K. Elder, and R. E. Davis (2002), Spatial snow modeling of wind-redistributed snow using terrain-based parameters, J. Hydrometeorol., 3(5), 524–538.
- Winter, T. C., J. W. Harvey, O. L. Franke, and W. M. Alley (1998), Ground water and surface water: A single resource, *U.S. Geol. Surv. Circ.*, 1139, 79 pp.
- Zwieniecki, M. A., and M. Newton (1995), Roots growing in rock fissures: Their morphological adaptation, Plant Soil, 172, 181–187.
- Zwieniecki, M. A., and M. Newton (1996), Seasonal pattern of water depletion from soil–rock profiles in a Mediterranean climate in southwestern Oregon, Can. J. For. Res., 26, 1346–1352.