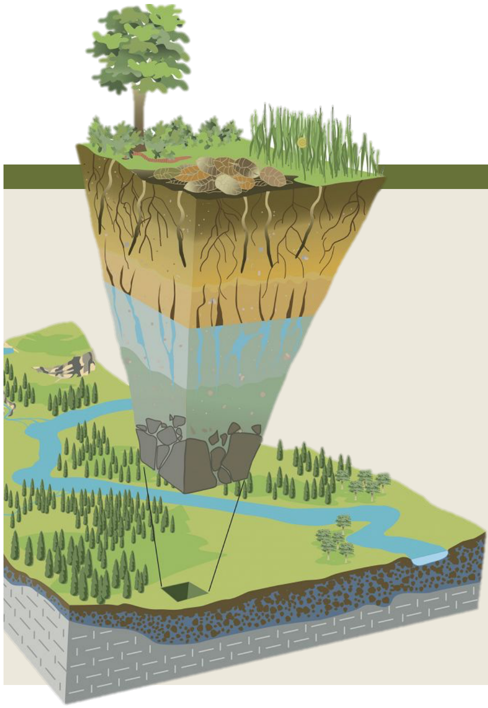

New Opportunities for Critical Zone Science

June 2017 Arlington Meeting for CZ Science White Booklet

Critical Zone Observatories
U.S. NSF National Program

CZO

Authors

Pamela Sullivan, Adam Wymore, William McDowell, and 51 other contributors (see list on pg 3).

Meeting

Over 200 researchers, students, and administrators from within and outside of the CZO program participated in the *June 2017 Arlington Meeting for Critical Zone Science* (hosted by CZO). At this NSF-sponsored event, we assessed the current state of CZ science and considered how the next iteration of a CZ science program can address key scientific, societal and educational questions about the Critical Zone. For meeting details, visit http://criticalzone.org/arlington2017

Booklet Topics

This booklet expresses the ideas generated and knowledge shared during the meeting. The document begins with an executive summary and the main content is divided into four sections:

The booklet is available at http://criticalzone.org/2017-white-booklet

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New Opportunities for Critical Zone Science

Executive Summary

Critical Zone (CZ) science has created a transdisciplinary nexus that seeks to understand the response of Earth's near surface processes to climatic and human perturbations. CZ science brings together researchers from geology, soil science, geomorphology, hydrology, meteorology, and ecology to study Earth's living skin from bedrock to the top of vegetation. CZ scientists forge theories that incorporate geological, chemical, physical, and biological insights. They focus on modern environments but integrate observations of today's fluxes with past records of tectonic, erosional and climatic processes. The CZ program provides a robust platform for convergent Earth-system and environmental science research.

CZ science has been advanced by the development of observatories. In the United States, the catalyst for this development has been the funding of Critical Zone Observatories (CZOs), a network initiated by the Earth Sciences Division of the National Science Foundation (NSF). The CZOs grew and flourished, drawing together scientists with many different perspectives to create a vigorous and engaged community. Each CZO, with its own unique questions and conceptual framework, initiated core measurements that together provided a community platform for research. By also working as a network of sites with shared values and approaches, a larger CZ science community has developed. Over the last 10-years, the US CZO program has been highlighting the importance of geology in services provided at Earth's near surface, which has also resulted in the development of CZOs internationally (e.g., China and Europe).

As noted by NSF in its "Big Ideas" planning, grand challenges of today – protecting human health; understanding the food, energy, water nexus; exploring the universe at all scales – will not be solved by one discipline alone. They require convergence, i.e. the *deep integration* of knowledge, techniques and expertise from multiple fields to form new and expanded frameworks for addressing scientific and societal challenges and opportunities. The CZ program does this, across the geological, biological and social sciences. CZ science matters to people as it allows us to understand the response of Earth's surface to extreme events (e.g., floods, droughts, fires, landslides and hurricanes) and anthropogenic disturbance (e.g., agriculture and aerosol contamination). CZ scientists forge models that incorporate all the important agents and drivers for societally important services such as agricultural production, drinking water supply, and erosion control which in turn enables decision-makers to design integrative policies and best practices. CZ scientists now stand poised to use CZ science to project changes in the Earth-surface system using quantitative models for prediction, or " Earthcasting", enabling the development of tools that will enhance societal preparedness and resilience to future climatic and anthropogenic changes.

The US CZO network has produced a number of exciting findings over the last decade; we highlight the broader impacts and intellectual merits that have thus far emerged from 10 key areas in the program:

Broader Impacts—

1. Humans depend on CZ services including food, wood and fiber production, water resources, sediment and soil production, and stream flow.
2. Anthropogenic perturbations are changing the CZ in some areas from a system that processes nutrients, a " transformer-dominated" system, to a system that simply moves nutrients through, a " transporter-dominated" system.
3. CZ structure controls hydrologic function, and in turn CZ structure evolves through physical, chemical, and biological processes controlled by water.
4. CZ architecture may be a legacy of geologic, tectonic, biotic or climatic history, and may not be in equilibrium with current forcing.
5. An emphasis on the entire CZ throughout the undergraduate, graduate and postdoctoral program attracts and develops a diverse group of scholars who bridge earth and environmental sciences seamlessly.

Intellectual Merits—

1. Rock, infalling dust and aerosols provide biota with nutrients; the geologic or atmospheric availability of elements—either beneficial nutrients or harmful toxins—may explain variations in biota distribution and health.
2. Soil moisture (water held in mobile regolith) and rock moisture (water held in weathered rock) provides water for trees; the cycling of water through the CZ has far-reaching implications for element cycling, regolith formation, below-ground biota, water budgets, and climate boundary layers.
3. Geophysical imaging and deep sampling of the subsurface can be used to map deep CZ structure, which is poorly known in most regions.
4. Models to date suggest that the spatial variation in CZ architecture across hillslopes of a given lithology depends on river incision rates, regional stress fields, solute evolution of subsurface waters, depth of freeze-thaw activity, as well as surface sediment transport processes.
5. The structure of regolith is a function of the distribution of microorganisms in the subsurface — "the weathering microbiome" —; the co-evolution of CZ structure and geo-microbiologic function is just beginning to be deciphered.

A new generation of scientists is being enthusiastically entrained by the CZO enterprise at many educational levels. Hundreds of post-docs, graduate and undergraduate students from a wide variety of backgrounds have been trained in CZ science. It is the inclusive nature of the science that provides an intellectually enthralling framework that is attractive to many, including groups such as women and minorities that are under-represented in traditional geosciences. CZ science provides a unifying conceptual framework for K-12 environmental science education, which is why it is being embraced by classrooms around the world. But the stage has only been set: the next 10 years can generate a more quantitative science led by integrative thinkers from today's younger generation.

The future of CZ science requires an intelligent mix of approaches to provide solutions to societal challenges. Specifically, this requires: 1) a set of observatories that catalyzes work across disciplines by making common measurements, developing new models, and articulating new theory; 2) new observatories in locations that cannot be understood within the current observatory network; 3) satellite sites that leverage the existing observatory network infrastructure, including sites from other networks (national and international); 4) focused questions addressed through shorter-term regional, national or international campaigns across the leveraged observatory networks, 5) synthesis initiatives, linking multiple near Earth surface networks (e.g., LTER, NEON) with the US and international CZOs, that foster the emergence of theory and prediction, and 6) outreach activities that teach nonscientists and citizens about the CZ, and engage decision makers with CZ science. These approaches will enhance the growth of CZ science, allow its practitioners to articulate the bigger patterns inherent in the CZ across space and time, and allow inclusion of physical, life, and social scientists alike.

In the rest of this document we amplify these ideas and emphasize the knowledge shared and ideas generated from the June 2017 CZO All Hands Meeting that was held in Arlington, Virginia. The document is divided into the following sections: 1) what we have learned from a decade of CZ science, 2) compelling CZ questions for the decade to come, 3) the next generation of CZ observatories and approaches, and 4) CZ education and outreach initiatives.

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1 What We Have Learned from a Decade of CZ Science:

The integrated approach of CZ science has led to several theories that now provide the platform for predictions regarding CZ structure, dynamics and evolution. Since the inception of the US CZO network, the network grew to its current configuration of nine CZOs (Fig. 1): Boulder, Calhoun, Catalina-Jemez, Eel River, Intensively Managed Landscape (IML), Luquillo, Reynolds, Shale Hills, and Southern Sierra (White et al. 2015). Here we provide examples of how our understanding of CZ form and function has evolved over the last decade, readying us for this next step. The ten transformative ideas that emerged from the CZO network are outlined and discussed below.

1.1 Humans depend on critical zone services including food, wood and fiber production, water resources, sediment and soil production, and stream flow

Fig. 1: Critical Zone Observatories (CZOs) in the USA in 2017.

The critical zone is, experiencing unprecedented pressures, provides many goods and services — food, fiber, shelter, aggregate, water— essential to humans. CZ science provides an integrative framework for understanding how these services function and how they can be maintained for future generations (White et al. 2015). The nascent term "critical zone services", now used similarly to "ecosystem services", refers to services important to humans that rely on, or interact with, long-term geological processes and deeper systems (Field et al. 2015). While some services of the CZ can also be thought of as ecosystem services, others clearly do not fall under the rubric identified for decades by ecosystem scientists. For example, CZ services include processes related to deep groundwater and how it nourishes ecosystems with clean water, processes related to long-timescale soil formation, and processes related to mined resources.

By extending the timescales and spatial scales (particularly with depth below the surface) of ecosystem services to that of CZ services, we increase our ability to manage Earth's surface sustainably. Processes operating on geologic time scales — soil erosion, soil production, sediment movement on hillslopes and in rivers, and landscape change — support ecosystem services important on human time scales such as short-term biogeochemical processes and land use. Sustaining ecosystem services requires understanding the interaction of process operating on these two different time scales.

Long-term measurements made in an observatory context are required to identify disruptions to CZ services, and to develop an understanding of how these services respond to climate change, more localized anthropogenic forcing, and associated extreme events. These measurements and inferences will allow identification of sensitivities and thresholds in the critical zone to inform human decision-making practices and policies.

1.2 Anthropogenic perturbations are changing the critical zone in some areas from a system that processes nutrients, a "transformer-dominated" system, to a system that simply moves nutrients through, a "transporter-dominated" system

In many landscapes, intensive anthropogenic alterations have affected hydrological and biogeochemical characteristics across whole catchments. The rapid intensification of agricultural practices, for example, has fundamentally altered soil structure, leading to an almost ten-fold increase in soil erosion, and even larger increases in concentrations and fluxes of important limiting nutrients in nearby aquatic ecosystems. The agricultural heartland of the US was once a system in which streams were characterized by long residence times of water, carbon and nitrogen, but rapid land use change and landscape modification (including tillage, tiles, channelization, wetland drainage) have shifted these ecosystems to transport-dominated systems characterized by fast movement of water, sediment, and nutrients through the landscape

(Kumar et al. in review). Legacy effects and their interplay with climate gradients have accelerated this transition to transport dominance (Van Meter et al. 2016).

The IML and Calhoun CZO findings point to a cascade of hydrologic and biogeochemical patterns marking the impacts of the Anthropocene on soils and surface waters. These patterns span across all disciplines and reflect the changes that have occurred in the overall structural organization and behavior of the critical zone. Conservation practices have a positive effect on nutrient cycling in heavily managed systems (Papanicolaou et al. 2015a, Wilson et al. 2016, Woo et al. 2014) but the spatial scale of this response and the lag between human intervention and environmental response remain uncertain (see Fig. 2).

The reorganization of both surface and subsurface structure by tillage and tiles (T2 impacts) has affected the provenance of the transported material, its pathways, and delivery times to aquatic ecosystems. Flow paths through porous media have been affected by use of heavy machinery, leading to reduction of the rate of infiltration by two orders of magnitude (Papanicolaou et al. 2015b). Short-circuiting of flow pathways, developed through a vast network of subsurface tile drains and surface drainage ditches, has also led to an increase in flashiness within receiving channels, with further implications for water, sediment and nutrient transport (Abban et al. 2016). These modifications have been found to produce long-lasting effects on flux transport with enhanced fluxes of water, carbon and nitrogen characterized by shorter travel times through the system (Abban et al. 2016, Rhoads et al. 2015). The enhanced connectivity between landscape and receiving waters has resulted in a strong relationship between nutrient fluxes and riverine discharge, with geology also playing a key role on the overall response (Davis et al. 2014, Ward et al. 2016). Increased fluxes from upland areas have also led to an increase in sedimentation rates on floodplains by an order of magnitude, resulting in a redistribution of material on the landscape with increased storage in valleys (Papanicolaou et al. 2015a, Grimley et al. 2017). Bank erosion has increased and is also a significant contributor to material flux within the stream network (Abban et al. 2016, Papanicolaou et al. 2017a). Channel straightening along with clearing of vegetation for improved drainage and to increase "useful" agricultural land area has also led to a destabilization of streams in which oversteepened bed and bank slopes are generally unstable, leading to migrating knickpoints and bank collapse that both increase material loads within the stream network (Sutarto et al. 2014, Bressan et al. 2014, Papanicolaou et al. 2017b). Future efforts should focus on development of a system-level approach to understand and model the connectivity among various units of intensively managed landscapes at characteristic scales. This can be achieved by linking US and International CZOs such as those in China, where one major research focus is understanding the long-term impacts of intensive agriculture activities on CZ services.

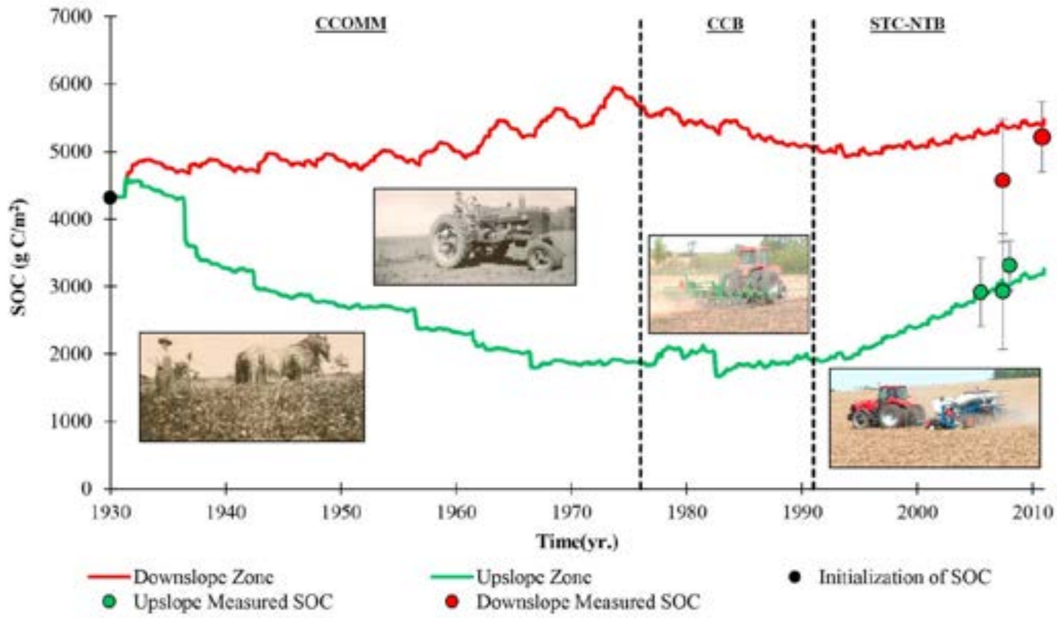


Fig. 2: Spatial heterogeneity and temporal variability of SOC in the IML. A time series of simulated values of SOC is provided for the upslope (green line) and downslope (red line) zones of a representative IML hillslope, highlighting the variability of SOC following model initialization is plotted (black dot). In addition, field measured values of SOC collected within the upslope (green circle) and downslope (red circle) zones of several hillslopes within the study watershed are compared to corresponding simulated SOC values. The chronosequence in SOC storage for the erosional zone revealed that conservation tillage and enhanced crop yields begun in 1980s reversed the downward trend in SOC losses, causing nearly 26% of the lost SOC to be regained. Figure from Papanicolaou et al. (2015a).

1.3 CZ structure controls hydrologic function, and in turn CZ structure evolves through physical, chemical, and biological processes controlled by water.

Topography influences the three-dimensional structure of the critical zone by affecting the transport rates and paths of water and sediment moving downslope. Topography also affects microclimates, organizes subsurface water flow, and constrains vegetation and snowpack distributions (e.g. Tennent et al., 2017); influencing both the reservoirs of the critical zone and setting the stage for critical zone processes. Conversely, critical zone processes from chemical and physical weathering to biological activity influence the occurrence and rates of geomorphic processes. Thus, approaching geomorphic models from within the paradigm of critical zone science requires considering how, where, and at what timescales geomorphic processes are coupled to other types of critical zone processes.

The coupling between geomorphic process and shallow properties of the critical zone has long been recognized. For example, the relationship between landscape and soils has received considerable study, ranging from Jenny's identification of topography as a primary control on soil formation (Jenny, 1941) to discussion of aspect as a control on soil formation (e.g., Rech et al. 2001, Langston et al. 2015, Pelletier and Swetnam, 2017). Feedbacks between chemical and physical weathering and the erosion of landscapes have been more broadly explored than potential feedbacks between landscape evolution and fluxes of solutes (Anderson et al. 2012). Soil evolution in settings dominated by aeolian transport has been modeled and compared to soil formation by bedrock weathering (Cohen et al. 2015). Yet the relationships between geomorphic process and critical zone form and function in other landscapes characterized by net sediment deposition remain an area of emerging research (Patton et al. in review). Hillslope evolution models utilize relationships between soil production and soil depth (e.g., Heimsath et al. 1997). Models considering the role of vegetation and animals on soil formation and hillslope sediment transport is an area of active research (e.g., Gabet and Mudd, 2010, Hoffman and Anderson, 2014, Yoo et al. 2005).

In the deeper portions of the critical zone the relationships between geomorphology and other critical zone processes present opportunities for significant new advances in understanding and represent an area of growing research. Anderson et al. (2013) model rock damage via frost cracking to depths of 10 m and its impact on hillslope evolution. Pelletier et al. (2013) present a coupled model of soil formation, hillslope and fluvial transport developed in the context of the climate and vegetation gradients of the Sky Islands region of Arizona. Rempe and Dietrich (2014) couple groundwater flow and rock weathering to hillslope evolution. These studies focus on regions of bedrock uplift with little study of the geomorphic interactions with the deep critical zone in depositional areas. Landscape evolution is likely an important control on the deep critical zone. Advancing knowledge of the deep CZ requires understanding the relationships between topography and the structure and function at depth (Riebe et al. 2017).

1.4 CZ architectures may be a legacy of geologic, tectonic, biotic or climate history, rather than in equilibrium with current forcing.

Landscapes are shaped by weathering and erosion processes that are affected by climate, baselevel, or tectonic uplift. In some cases, landscapes may be legacies of past conditions. Glacial climates prevailed for most of the Quaternary, the last 2.5 Myr of Earth history. Many landscapes and their CZ architectures were shaped by processes active during glacial climates (e.g. glacial erosion and deposition or periglacial processes) that are not present today. For instance, deposits from the Laurentide Ice Sheet thickly mantle bedrock in IML-CZO sites (Yan et al. 2017), while the headwaters of Boulder Creek CZO were scoured by Pleistocene alpine glaciers (Dühnforth and Anderson 2011). A perhaps more subtle legacy of glacial climates is found outside glacial limits, in terrain where periglacial processes held sway during periods of glacial climate. Frost cracking, solifluction, and other periglacial processes drive mechanical weathering and sediment transport on hillslopes via mechanisms that may not occur under modern climates. The role of periglacial processes shaping present CZ architecture has been explored in Shale Hills CZO (West et al. 2014), which lies south of the terminus of the Laurentide Ice Sheet, and in ice-marginal areas in Boulder Creek CZO (Anderson et al. 2013). Frost cracking is a mechanical weathering process that can operate at significant depths below the ground surface, creating porosity that affects modern hydrologic function.

While glacial climates bring to mind the direct influence of glaciers and permafrost, even regions lacking freezing conditions were affected by the global climate shifts during the Quaternary. Cooler and drier conditions were widespread during glacial periods, but shifts in the jet stream brought greater rainfall and lakes to some regions (e.g. Lake Bonneville in the western United States, a lake filling the present Dasht-e Kavir desert in Iran, and periods of "green Sahara" and pluvial lake expansion in Africa). Because soils, weathered profiles, and topography often represent >10 kyr of evolution, the impact of Quaternary climate and ecosystems should be considered when evaluating current conditions.

Changing baselevel, whether due sea level change (e.g., Luquillo CZO), climate or tectonic driven exhumation (e.g. Boulder Creek CZO), tectonic uplift (Eel CZO) or land use change (e.g. Calhoun CZO), affects fluvial incision, which in turn affects adjacent hillslopes. Fluvial knick points are recognized as important perturbations whose influence persist as hillslopes, groundwater systems, and soils adjust to new conditions (Anderson et al. 2012, Brocard et al. 2016). Figure 3 shows influence of knickzone propagation (by a wave of rapid channel incision) on surrounding hillslopes and groundwater systems, using Boulder Creek as an example. In general, any perturbation to landscape lowering rates will ripple influence throughout the landscape as groundwater flow, weathering rates, and mobile regolith transport rates respond. Critical zone architecture will therefore reflect climate over the residence time of material within it, and the history of fluvial or shoreline elevations that set baselevel for the landscape.

CZ architecture is also driven by biota, both past and contemporary (and may not be in equilibrium with current forcings). The geomorphological and geochemical influence of multiple generations of vegetation can help to govern the evolution of CZ architecture. For example, tree throw (arborturbation) — the upheaval of soil and sometimes bedrock in the root mass of a fallen tree — has been identified as a major process in the overturn and downslope transport of soil and shallow bedrock in mountainous regions. In shale dominated landscapes (e.g., SSHCZO), tree throw associated sediment fluxes rates often exceed those of soil creep by several orders of magnitude, while the depth to a root limiting layer and the distance from the center of a root wad to the center of an excavated pit increase across a shale north to south climosequence– suggesting that deeper roots excavate more soil and deeper soils generally exist in warmer climates.

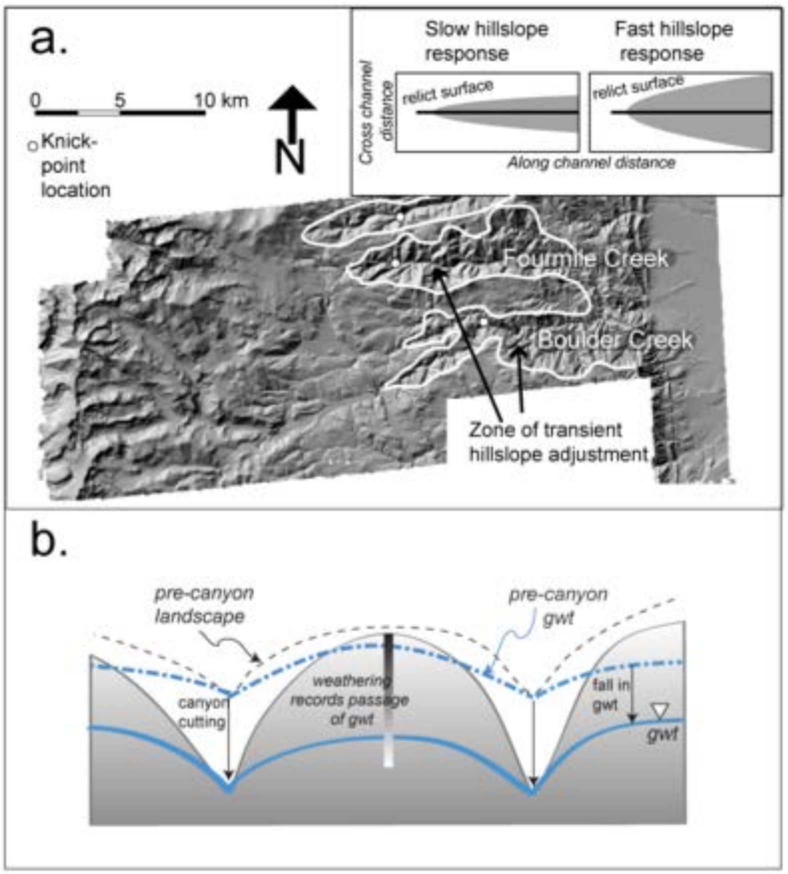


Fig. 3: Influence of knickpoint migration upstream in Boulder Creek CZO (from Anderson et al., 2012). a) Lidar hillshade shows topography from headwaters of Boulder Creek (left side of image) to edge of the Plains (right side of image). White dots show approximate location of current knickpoint in main channels, while white line outlines region of hillslopes adjusting to the fluvial downcutting associated with knickpoint migration. Inset shows theoretical width of areas of transient hillslopes downstream of knickpoint for different hillslope response speeds, based on Mudd and Furbish, 2007. b) Sketch showing influence of rapid fluvial incision on hillslope profiles and groundwater systems.

1.5 An emphasis on the entire CZ throughout the undergraduate, graduate and postdoctoral programs attracts and develops a diverse group of scholars who bridge Earth and environmental sciences seamlessly

Students (graduate and undergraduate) and postdoctoral scholars represent nearly 60% of the individuals conducting research at the CZOs (in 2015; CZO National Office) with increasing recruitment over time (Fig. 4). The focus of their study reaches well beyond the traditional Earth science disciplines, ranging from biodiversity, microbial ecology, agriculture, engineering, meteorology, soil science, watershed biogeochemistry and plant science, among others. This breadth reflects the transdisciplinary nature, education, and training provided by the CZO program and how this new generation of Earth and environmental scientists works across disciplines. Now more than 25 faculty members, trained at US based CZOs, have been hired at US and international universities including appointments at large land-grant RI universities and smaller teaching intensive 4-year colleges. Early career faculty are now advising and teaching new students at their home institutions. This means that new research and graduate training initiatives are being offered across institutions and the transdisciplinary concepts of CZ science are being integrated into undergraduate curricula. One exemplary effort is Roanoke College where CZ science is being used as an integrative framework and core theme for their Environmental Studies program. These efforts have resulted in the broader dissemination of CZ science across institutions and an increased exposure to the framework and science of the critical zone to a new generation of CZ practitioners.

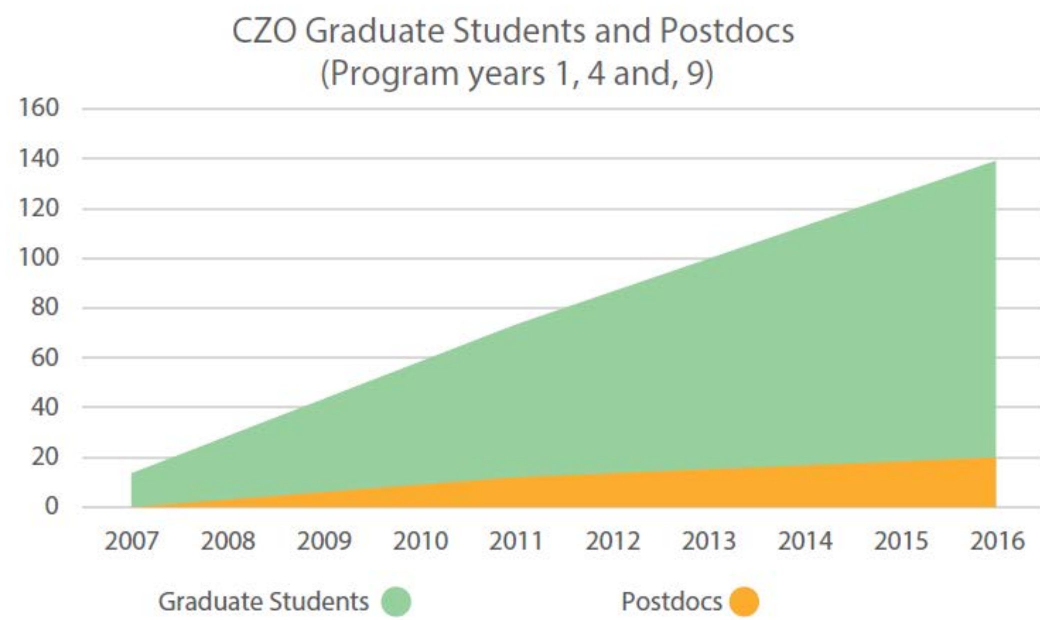


Fig. 4: Cumulative growth of graduate students and post-doctoral researchers receiving training in Critical Zone science. Data were collected from the US Critical Zone National Office and reflect reporting from across the US Critical Zone Observatories. Figure does not represent a complete data set. Actual growth across the entire international CZO program is likely to be much greater than expressed in this figure (Wymore et al. 2017a).

Reflecting this diverse training, early career faculty are now bridging CZ science with other disciplines. These faculty have developed a new course on CZ science as well as incorporating CZ concepts into established courses. For example, through funding support from the NSF-funded InTeGrate program at the Science Education Resources Center at Carleton College, a semester-long university-level CZ course was developed and taught at five different US institutions (White et al. 2017). These institutions ranged from large R1 universities to smaller liberal arts college and across departments and degree programs ranging from Natural Resources, to Geography and Geology, Hydrology, Environmental Engineering, and

Biology. Other faculty are incorporating CZ concepts and knowledge into established courses and as a result are enhancing the multidisciplinarity of traditionally siloed curricula. Two examples are a Watershed Hydrology course at the University of Minnesota and a Geochemistry of Natural Waters at the University of Vermont. Collectively, these efforts introduce CZ science to literally hundreds of new students each year promoting more and more cross-disciplinary and system-thinking in future cohorts of environmental scientists (Wymore et al. 2017a). Future training efforts should continue to diversify participation of students and post-doctoral researchers as well as working with secondary school instructors. Critical zone science is a natural integrator of the natural sciences and could offer an ideal unifying framework for high school-level science courses. Support for these training and outreach efforts will need to continue if CZ science is to be sustained into the future.

The CZO program has also facilitated the development and distribution of stand-alone resources for teachers at the K-12 and undergraduate levels that can be incorporated into classroom and instructional laboratory settings. These range from hands on activities, to activities that use CZO data, to individual teaching modules, videos, and on line virtual field experiences (Duggan-Haas et al., 2015, 2016, 2017; Moore et al. 2017). These resources demonstrate CZ concepts, and in many case the value of CZ services to a wide audience.

1.6 Rock, infalling dust and aerosols provide biota with nutrients; the geologic or atmospheric availability of elements—either beneficial nutrients or harmful toxins—may explain variations in biota distribution and health.

Natural dust inputs have been shown to sustain ecosystems in places where nutrient supply from bedrock weathering is insufficient to do so (e.g., Chadwick et al. 1999, Pett-Ridge 2009, McClintock et al. 2015, Aciego et al. 2017). These ecosystems include slowly-eroding and phosphorus-poor tropical ecosystems (Pett-Ridge 2009, McClintock et al. 2015). On the other hand, a number of anthropogenic emissions impact the critical zone. The fate of anthropogenic atmospheric nitrogen deposition depends on slope aspect in the Colorado Front Range, due to aspect controls on CZ structure and hydrologic function (Hinckley et al. 2014, 2017). Additionally, mining and smelting have increased global emissions of heavy metals to the atmosphere (Herndon et al. 2011, 2014, 2015, Kraepiel et al. 2015, Ma et al. 2014). These metals are subsequently deposited back to Earth's surface over broad areas, leaving behind a record of human activities and disrupting biogeochemical cycles (e.g., Fig. 5). CZO work on atmospheric deposition and metal mobility at the Earth’s surface has been highlighted in National Academy of Sciences publications tackling problems related to the apportionment of metal contamination in soils and household yards (NAS, 2017).

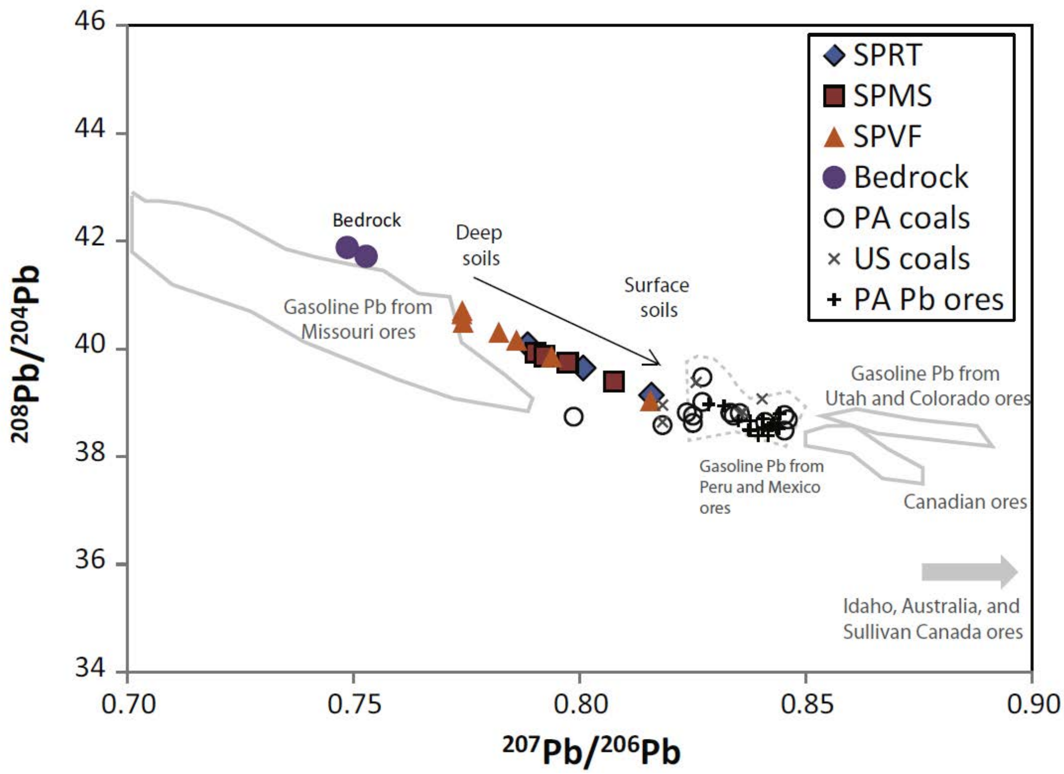


Fig. 5: Isotopic signatures of soils from the Susquehanna Shale Hills CZO (SPRT, SPMS, SPVF) in comparison to various sources of lead (grey-circled areas). Solid symbols are samples from soil or bedrock, and open symbols refer to samples of Pennsylvania coal or coal from elsewhere in the U.S. Soil lead derived from bedrock and atmospherically deposited lead from local coal burning and iron/lead ore smelting, largely released during the early industrial revolution. (From Ma et al. 2014).

Dust is particularly significant for longer timescale processes. Cosmogenic radionuclide dating of alluvial terraces in the U.S. High Plains reveals complex histories of fluvial planation and incision, and intermittent loess cover that affects soil development (Foster et al. 2017). CZO researchers have recently upended the assumption that dust is relatively unimportant in mountain ecosystems (i.e., where bedrock conversion to soil provides continuous nutrient supply) (Aciego et al. 2017, Arvin et al. in review). The measured aeolian fluxes, cosmogenic nuclides, and bulk geochemistry demonstrate that dust dominates over bedrock in nutrient supply to Sierra Nevada ecosystems (Aciego et al. 2017). Across a suite of mid-elevation sites, the dust-deposited flux of plant-essential P is on par with the P supply rate from conversion of bedrock to soil (Fig. 6). The ecological significance of dust is further supported by analyses of neodymium (Nd) isotopes in pine needles, dust, and bedrock, which demonstrate that dust contributes as much as 88% of Nd (a potential tracer of P) to vegetation at one site (Arvin et al. in review). This study is also an example of an emerging CZO approach ("CZ-Tope") that emphasizes the interpretation of multiple isotopic systems on the same samples from observatory sites (Sullivan et al. 2016).

CZO research builds on efforts to understand the global impact of dust (Maldope 1963, Pewe, 1981, Prospero et al. 1981, Muhs et al. 1990, Pye 1995, Neff et al. 2008) by delving into the mechanistic impact of dust on ecosystem and soil formation processes using tools and knowledge that spans multiple disciplines. For example, CZO researchers have observed that in more than 1300 mountain sites, spanning diverse climates and rock types, dust deposition is often on par with bedrock conversion to soil (Arvin et al. in review). New analyses show that dust fluxes may often contribute to large overestimation in denudation rates from cosmogenic nuclides, exposing potentially profound errors in previously measured landscape evolution patterns (Arvin et al. in review). Together, these analyses suggest that the paradigm of dust as a relatively minor contributor to mountain soils and ecosystems needs to be revised.

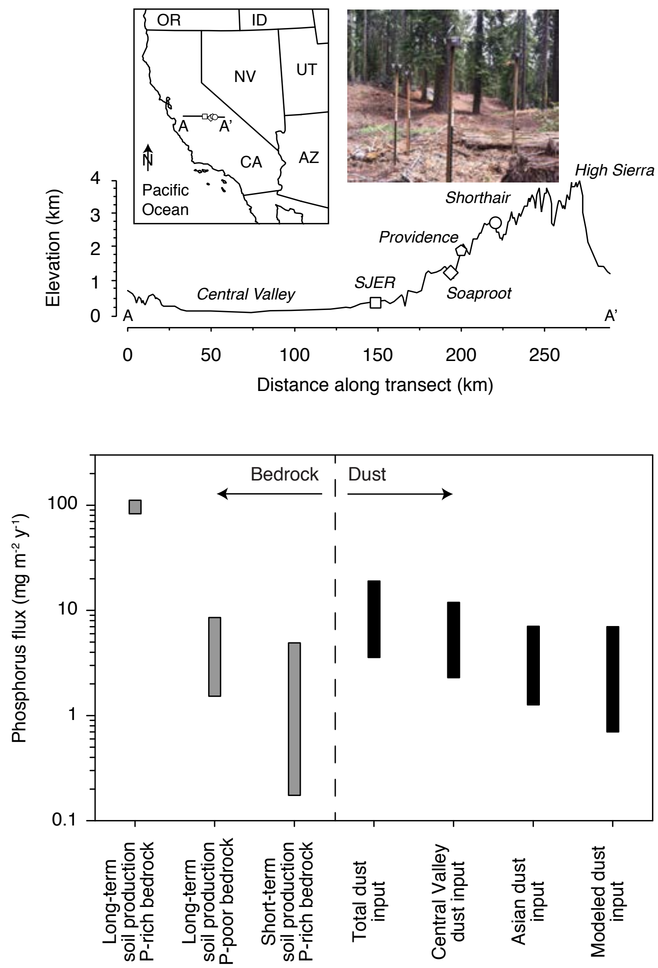


Fig. 6: (Top) Study sites are distributed along an elevation transect through the Sierra Nevada, California. Central Valley dust sources differ at sites by as much as 70 km in distance and 2300 m in elevation. Image (inset) shows array of dust collectors at the mid-elevation Providence site. (Bottom) Fluxes of the plant-essential macronutrient phosphorus at the Providence Creek site due to erosion (gray bars) and aeolian deposition (black bars). Bars span ranges in fluxes from multiple measurements. Total dust flux is the sum of fluxes from Asian and Central Valley sources. On soil-mantled slopes, P input from dust accounts for 10-20% of the supply of bedrock P. On bare rock slopes, P supplied from bedrock is much lower and commensurate with the fluxes from the Asian and Central Valley dust sources. The fluxes of P implied by catchment-wide sediment yields are generally lower than the estimated dust fluxes, implying that the modern ecosystem is strongly influenced by the day-to-day contributions of dust from Asia and the Central Valley. Adapted from Figs. 1 and 5 of Aciego et al. (2017).

1.7 Soil moisture (water held in mobile regolith) and rock moisture (water held in weathered rock) provides water for trees; the cycling of water through the critical zone has far-reaching implications for element cycling, regolith formation, below-ground biota, water budgets, and climate boundary layers.

Hydrologic studies of upland landscapes on bedrock in CZOs demonstrate that significant flow and storage of water occurs within the weathered and fractured bedrock that lies beneath the soil layer (Anderson et al. 1997, Manning et al. 2013, Brantley et al. 2013, Flinchum et al. in review). A new picture of the CZ is emerging that emphasizes the tens to hundreds of meters of regolith that underlies ridge and valley landscapes (sensu Riebe et al. 2017) (Fig. 7). These observations collectively suggest that hydrologic fluxes through weathered bedrock are a common and significant component of the terrestrial hydrologic cycle in landscapes developed on bedrock. This storage of exchangeable water in the fractures and matrix of weathered bedrock (Fig. 7), termed 'rock

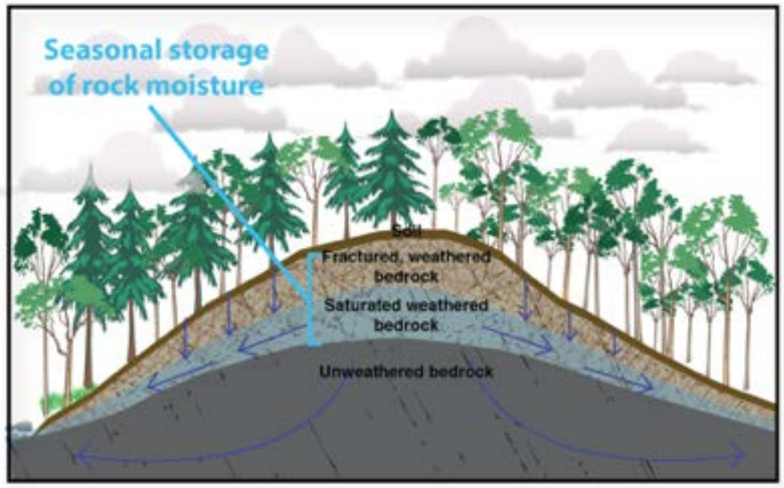


Fig. 7: A conceptual hillslope profile depicting the structure of the CZ extending into weathered bedrock. The weathered bedrock region hosts rock moisture storage in the fractures, matrix, and fracture-fill. Fractured bedrock groundwater drains to streams.

moisture' by Salve et al. (2012), has significant implications for global cycling of solutes and water. Perhaps one of the best datasets showing the nature of the deep regolith derives from a 70 m borehole from the Calhoun CZO that has been used to document variations in porosity related to weathering and fracturing (Holbrook et al. in review). At the humid Shale Hills site, Hasenmueller et al. (2017) identified the role of the shale rock matrix as a nutrient source for vegetation rooted in rock. In the interbeded shale/siltstone deposits of the Eel River CZO and the granites of the Southern Sierra CZO, a prolonged dry season leads to the dependence of deeply rooted vegetation on rock moisture (Bales et al. 2011, Rempe, 2016).

The uptake of water by biota is often associated with the uplift of nutrients (Jobaggy and Jackson 2004), such as potassium (K), from depth. When plant material decays, the release of uplifted nutrients can alter the trajectory of mineral formation leading to the reincorporation of K into 2:1 clays (Austin et al. in review) or enhance the rate of secondary clay formation (Sullivan et al. in review). In addition, the life history strategies of biota and their feedback on soil formation can be greatly dictated by the nutrient availability of the bedrock. For example, at the Southern Sierra CZO difference in the bedrock phosphorus concentrations drives mountain ecosystem patterns and the evolution of the landscape (Hahm et al. 2014). Together these phenomena suggest important feedback exist between water, nutrient resource access and soil formation that are still not well understood.

Physical mechanisms are becoming increasingly recognized as key drivers of critical zone architecture (i.e., porosity), and may dominate over chemical processes in some settings (Brantley et al. 2017, Hayes et al. in review). In the last decade, great strides have been made in identifying and describing the individual physical mechanisms that dictate CZ architecture. Physical processes initiated at the surface or near-surface include frost cracking (Anderson et al. 2013, Rempel et al. 2016), tree sway (Marshall et al. 2016), and topographic stress (St. Clair et al. 2015). A host of recent models and near-surface geophysics (e.g., Rempe and Dietrich 2014, Marshall et al. 2015, St. Clair et al. 2015, Rempel et al. 2016) have greatly expanded our knowledge of how specific tectonic, climatic, and abiotic and biotic stresses vary spatially in terms of shaping the vertical and lateral subsurface structure of the critical zone. For example, frost cracking predicts aspect-dependent cracking intensity that generally decreases as a function of depth to ~ 5 m, with local climate factors combined with the pre-existing pore spaces in rock dictate just where in that 5-m zone the rock damage (increase in porosity) is most intense (Anderson et al. 2013, Marshall et al. 2015, Rempel et al. 2016).

Physical stresses on bedrock may also be imparted as a result of chemical reactions, where oxidation of iron-bearing minerals and re-precipitation of hydrous iron oxides results in a volumetric expansion at the (micro)mineral scale (Fletcher et al. 2006). Only recently are we learning the extent to which microfracturing along grain boundaries connects pore space in largely "unweathered" rock (Jin et al. 2010, Bazilevskaya et al. 2015, Gu et al. 2016, in preparation), providing some of the foundational architecture for CZ development. Teasing apart the relative contributions of thermally, biologically, and chemically-driven physical processes on the initiation of porosity development (i.e., the initial transformation of bedrock to regolith) remains a fundamental problem for critical zone scientists.

It is key to understand how porosity develops in rock layers as many tree species utilize rock moisture (Schwinning 2010). Yet in land-surface models (LSM), which simulate land-atmosphere exchange of water, rock moisture is an unconstrained water source and thus limits the accuracy of predictions of climate dynamics. Novel LSM parameterizations of rock moisture are in development (e.g. Vrettas and Fung 2015, Brunke et al. 2016,), but the limited number of direct observations of rock moisture makes it difficult to constrain physical processes in such models. Long-term, direct measurements of rock moisture are required to fill this gap. For example, at ERCZO rock moisture datasets demonstrate that partitioning of rainfall between evapotranspiration (green water) and runoff (blue water) is strongly influenced by deeply rooted vegetation accessing rock moisture (Fig. 8). There is evidence from Reynolds Creek CZO (RCCZO) that the amount of “green water” accessible to plants is controlled by lithology. Detailed water and energy balance data collected on two watersheds with volcanic (basalt and rhyolite) geology have shown a close correlation between the amount and timing of water passing through the root zone (1 to 2 m) and streamflow (Seyfried et al. 2009, Chauvin et al. 2011). The rapid response of groundwater implies a highly permeable substrate with very low effective porosity, consistent with volcanic geology, which may limit the rock moisture reservoir, and thus available water for plant use. Understanding when and how rock moisture governs reservoirs of ET and runoff is essential for accurate climatic and hydrologic predictions.

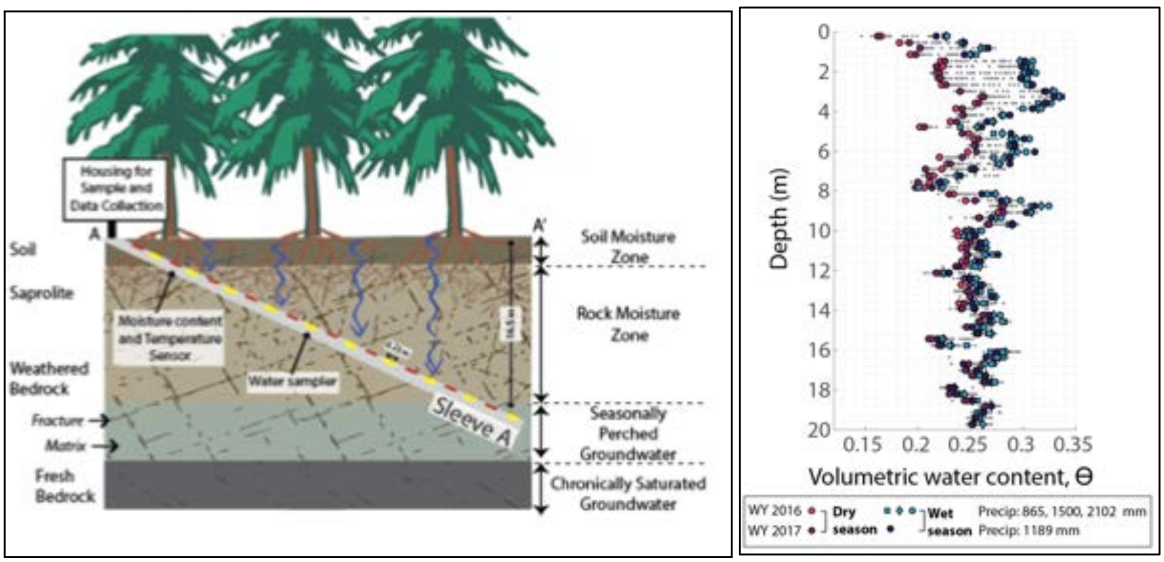


Fig. 8: Investigation of the ecohydrological and geochemical implications of rock moisture at the Eel River CZO. (Left) The Vadose Zone Monitoring System directly samples the freely draining and tightly held water in the variably saturated weathered bedrock. (Right) Rock moisture monitoring via neutron probe surveys in boreholes across the ERCZO reveals an annually consistent addition and depletion of rock moisture (Rempe, 2016). In the seasonally dry climate, initial rains refill the rock moisture reservoir to > 12 m deep, with all remaining precipitation traveling to a seasonally perched groundwater system in fractured bedrock. Stored rock moisture is then depleted by deeply rooted vegetation over the dry season.

The dynamics and transit time of rock moisture have obvious implications for hydrologic models, but also remain a poorly constrained component of the reactive transport models that are needed to provide a robust framework for predicting the routing and flux of water and solutes (e.g., Fan and Bras, 1998, Troch et al. 2003, Ebel et al. 2008). For example, the chemical composition and timing of streamflow is often inferred to be a result of water transport through weathered bedrock (e.g. Anderson and Dietrich, 2001, Kim et al. 2017, Winnick et al. 2017). A key limitation to improvement of these models is the paucity of direct observations within the weathered bedrock zone that are available to constrain and test such models. At the Eel River CZO (Druhan et al. 2017) advances in direct, high frequency measurements of geochemical and hydrologic fluxes within weathered bedrock have revealed the importance of weathered bedrock in regulating the geochemical composition of CZ waters (Fig. 7).

The vadose zone in the upland catchments in the Jemez CZO (New Mexico, USA) extend tens of meters into the fractured rhyodacite and tuff (Olyphant et al. 2016). Although half of the precipitation at this site is delivered as monsoon rains in the summer, water isotopes and trace element signatures indicate that in these catchments spring snowmelt is the dominant source of deep groundwater recharge and, hence, deep CZ weathering (Fig 9.; Harpold et al. 2014, Vazquez-Ortega et al. 2015, Zapata-Rios et al. 2016). A similar dynamic is observed in upper montane forested Gordon Gulch catchment in Boulder Creek CZO (Hinckley et al. 2014, Anderson et al. 2014, Langston et al. 2015, Anderson et al. in prep). Snowmelt that percolates through soil and fractured bedrock is stored for years in a deep groundwater reservoir that is only displaced into streams by propagation of a pressure wave pulse during the wet season (i.e., during snowmelt).

Such models will not only help in understanding subsurface flow but also in understanding chemistry and discharge of rivers. In particular, CZO researchers are starting to quantify how hydrologic factors govern the C-Q relationship of the conservative (e.g. Cl^-) and geogenic (e.g. Mg^{2+}) species concentrations in rivers (Li et al. 2017b). Results suggest that the C-Q relationship is strongly driven by the distribution of source waters and subsurface flow patterns such as shown in Fig. 9. When the mass influx into streams primarily comes from soil lateral flow (interflow in the model), chemostatic behavior occurs. In contrast, when stream solutes mostly come from relatively constant groundwater – derived baseflow, chemodynamic behavior (dilution) dominates. These findings highlight the importance of subsurface water distribution in regulating C-Q relationships and thus the export of dissolved mass from watersheds. Yet in other lithological settings the C-Q behavior of geogenic solutes is controlled by changes in sampling of different "sources" in the CZ as hydrologic pathways change, including interaction with different mineral assemblages that alter to yield solutes (Kurtz et al. 2011) and soil process that generate metal-oxide and metal-organic colloids (Trostle et al. 2016; Aguirre et al. 2017; McIntosh et al. 2017).

Variations in tectonic regime, topographic relief, and bedrock mineralogy promote differences in emergent CZ properties, such as porosity and nutrient availability (e.g., Bazilevskaya et al. 2015, Hahm et al. 2014, St Clair et al. 2015) and impact on subsurface flow (Brantley et al. 2017). The interdisciplinary nature of CZ science has merged traditionally divergent disciplines (e.g., geophysics, geochemistry) to begin to tease out the relative contributions of primary bedrock mineralogy and tectonic forcings on CZ evolution. As a result, a variety of climatological, biological, chemical, and physical mechanisms are being quantified in the context of their role in producing pore space and mineral weathering within the CZ.

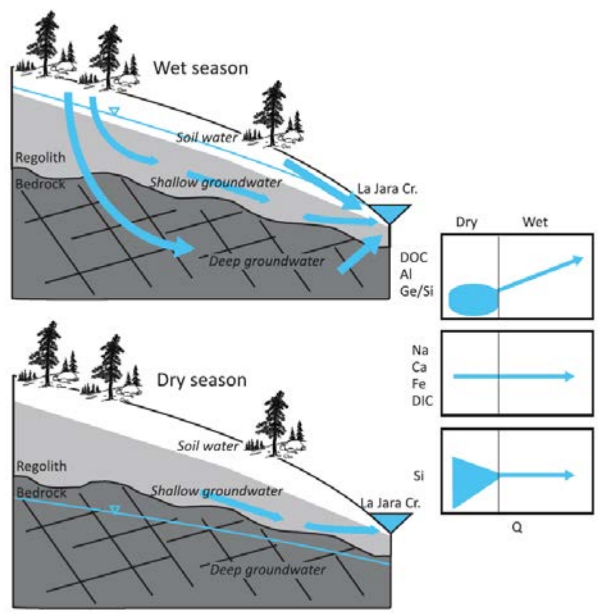


Fig. 9: Dry season discharge from the vadose zone superimposed with wet season discharge from the deep groundwater stores help to explain the chemostatic concentration-discharge behavior of major elements in surface waters (McIntosh et al. 2017).

All of these processes drive fracture development in the subsurface, allowing pathways for meteoric fluid and gas infiltration into the subsurface. Employing the CZ reference frame to our understanding of the role of fractures in the evolution of subsurface CZ architecture. We are beginning to connect the dots between fracture density and fracture orientation to the heterogeneous development of nested weathering fronts across a single watershed (Sullivan et al. 2016).

1.8 Geophysical imaging and deep sampling of the subsurface can be used to map deep CZ structure, which is poorly known in most regions

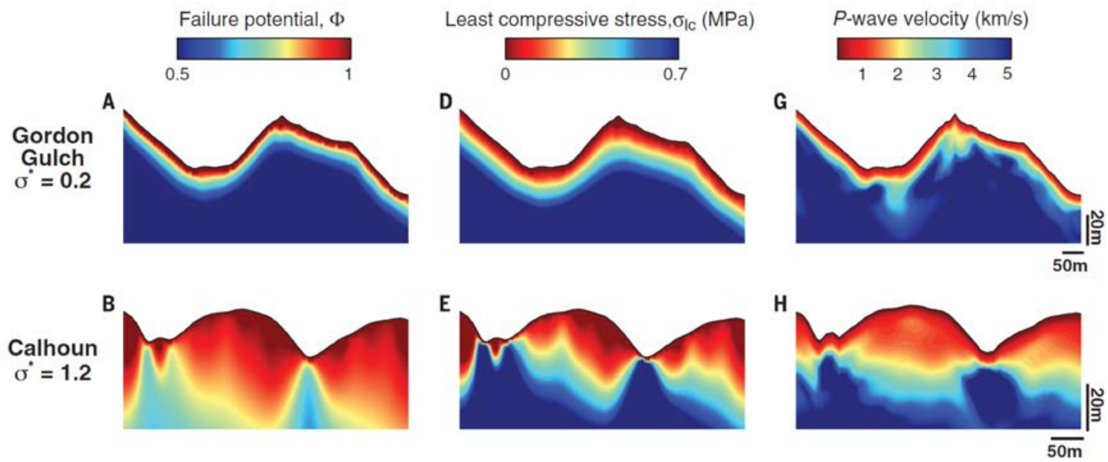
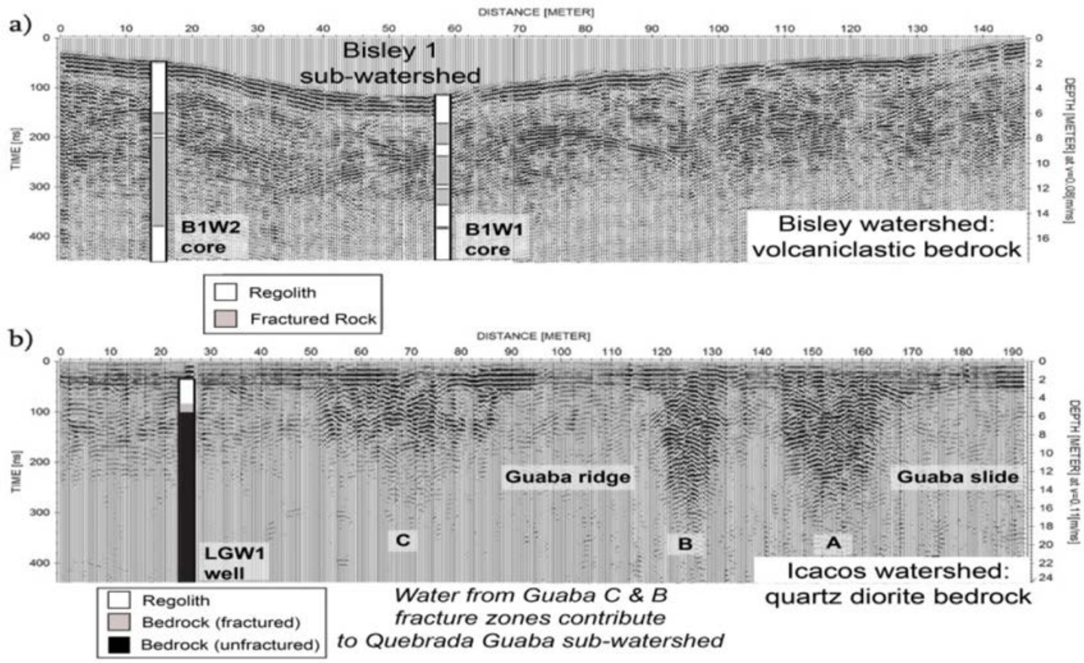


Fig. 10: A figure comparing the modeled failure potential (A, B), modeled magnitude of the least compressive stress (D,E) and measured P-wave velocity (G, H) for Gordon Gulch in the Boulder CZO and Calhoun CZO. In this figure from St. Clair et al. (2015), the depth of fracturing and weathering is very different in Gordon Gulch where the regional stress is not compressive versus Calhoun where the site experiences regional compression. St Clair et al. argued that the decrease in P-wave velocity is related to deep fracturing and weathering that occurs because of the regional stress regime and the topography. As shown in the figure, such seismic imaging is now being used to map reaction fronts and fracture densities in the subsurface, allowing better understanding of subsurface water flow and rock mechanics properties without drilling.

Multiple, complementary near-surface geophysical measurements are being used to elucidate CZ structure, as are approaches that combine geophysical and geochemical approaches to decipher the feedback between CZ structure and function (i.e., Holbrook et al. 2014, Parsekian et al. 2015, St. Clair et al. 2015, Orlando et al. 2016). Multiple methods such as ground-penetrating radar (GPR), electrical resistivity imaging (ERI), seismic and electromagnetic (EM) induction are being used to describe landforms in the range of meters to 100s of meters in order to charaterize CZ subsurface structure at the catchment scale (Van Dam 2012). For example, St. Clair et al. (2015) demonstrated how an array of seismic and electrical resistivity surveys can characterize stress fields. Those authors argued that regional stress fields may explain the distribution of bedrock fractures and weathering below the surface in regions of compression (Fig. 10). Likewise, at the Luquillo CZO, Orlando et al. (2016) showed the correspondence between valley areas and the presence of chaotic reflectors and diffraction hyperbolas in GPR profiles associated with the presence of lineations interpreted as fractures. Surveys were later expanded in the area (Hynek et al. 2016, Comas et al. in preparation) (Fig. 11), further showing the correspondence between these areas of enhanced reflections in the GPR, with decreases in terrain conductivity, and increases in magnetic susceptibility. These geophyscial features have been attributed to deep fracture zones in the quartz diorite that promote deep weathering.

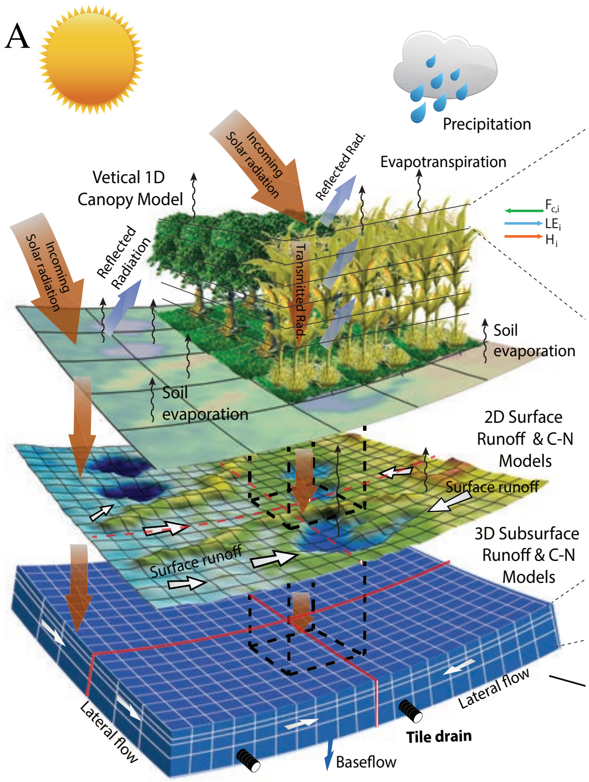


- **Fig. 11**: In a figure from the Luquillo CZO, ground penetrating radar (GPR) velocity-time plots provide images of the subsurface in (a) volcaniclastic rocks and (b) quartz diorite. The GPR plots were ground truthed against boreholes as shown in the figure. The two lithologies, weathering side by side in neighboring watersheds, present different mechanisms of weathering at this geomorphological scale (both panels show GPR images across approximately 200 m). In the volcaniclastic sedimentary rocks, the higher prevalence of fractures is inferred to result in relatively homogeneous depths of weathering (high density of GPR reflectors) whereas the quartz diorite is inferred to demonstrate localized zones of deeply weathered fractures. Without greater understanding of fracture distributions, it is impossible to understand the spatial and depth distributions of regolith. From Hynek et al. (2016).

Observations from multiple CZOs have also developed some cross-cutting conceptual models of water flow at depth. Several CZOs have noted that more than one lateral flow of water occurs underneath hills such that water can flow laterally even in the vadose zone. This is a common occurrence when local zones of perched saturation allow such lateral flow. One hypothesis states that such lateral flow zones may be preferentially aligned with sharp mineral reaction fronts where one mineral dissolves or is replaced by another mineral. Such reaction fronts – especially where clay minerals accumulate – may be zones of changing porosity and permeability that promote perched saturation. Since reaction fronts are often observed in a sequence or "nested" in the subsurface of a hill top (Brantley et al. 2013), the development of models that predict the depths of fronts may promote development of better models of water flow under hills. Brantley et al. (2017) proposed a conceptual model relating chemical reaction fronts to water flow paths where within regolith-rock profiles, a one order magnitude of change in permeability can shunt water downslope creating a saturated unit above the water table, referred to as interflow, while deeper in the profile water also moves laterally downslope when it reaches the groundwater table. A very promising new idea is that we can use geophysical imaging to map these subsurface reaction fronts and in turn use the fronts to make predictions about porosity and permeability and subsurface fluid flow (Brantley et al. 2017).

1.9 Models to date suggest that the spatial variation in critical zone architecture across hillslopes of a given lithology depends on river incision rates, regional stress fields, solute evolution of subsurface waters, depth of freeze-thaw activity, as well as surface sediment transport process

The CZOs are now providing a platform for models from distinct disciplines that "talk" to each other (Duffy et al. 2014), and have thus fostered a variety of multi-disciplinary simulations ranging from complex, processes-based numerical models describing interactions of hydrology, biology, contaminant fate and transport and isotope geochemistry (Druhan et al. 2014), to simple analytical solutions that provide general conceptual frameworks (Rempe and Dietrich 2014).



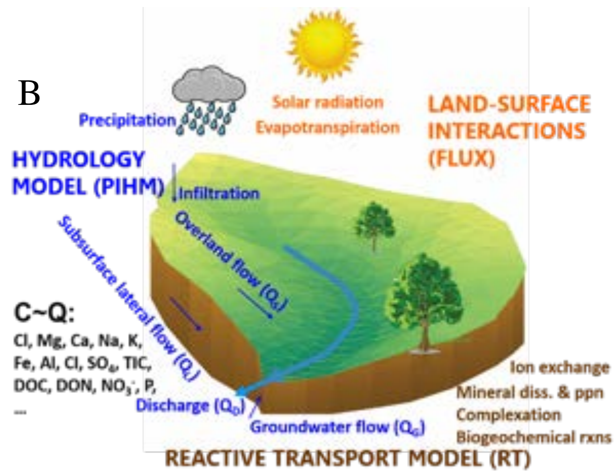


Fig. 12: (**A**) Dhara 3D hybrid computing model incorporating impacts of micro-tomographic variability using a multi-layer approach (Le et al. 2015). (**B**) Processes in RT-Flux-PIHM. The integration allows process-based, spatially explicit, systematic understanding of contaminant fluxes at the local and watershed scales (Li et al. 2017a). The watershed is the Susquehanna Shale Hills (SSHCZO), PA.

Two examples of multi-disciplinary models developed within the context of the CZO network are the newly developed open source 3D CPU-GPU hybrid *Dhara* model that couples both above- and below – ground processes (Le et al. 2015), and the watershed hydrogeochemical model RT-Flux-PIHM (Bao et al. 2017, Li et al. 2017a). The *Dhara* model includes explicit treatment of energy, moisture, carbon and nitrogen dynamics (Fig. 12A), and has been used to characterize both nutrient age (Woo and Kumar 2016), and fluid flow and transport through tile drainage networks (Woo and Kumar 2017). The RT-Flux-PIHM model integrates the Noah LSM, PIHM, and RT (Fig 12B). The Noah LSM (Flux) is the land-surface module that solves surface energy balance (Chen and Dudhia 2001, Shi et al. 2013); PIHM calculates surface and groundwater interactions (surface runoff, infiltration, recharge, subsurface lateral flow, channel routing); while the RT component uses calculated water distribution and flow rates from Flux-PIHM to solve Advection-Dispersion-Reaction (ADR) equations for the spatio-temporal evolution of aqueous and solid phase composition. The alteration in aqueous and mineralogical composition is assumed to have negligible impacts on hydrological processes at the time scale of months to years. In essence, this model enables conversation between meteorologists, hydrologists, and biogeochemists. Similarly, the terrestrial integrated modeling system (TIMS) of Niu et al. (2014) uses a set of existing models that describe land-atmosphere exchange of water and energy, catchment hydrologic flows, vegetation dynamics and biogeochemical reactions for the purpose of exploring mechanisms and the coupling of process.

The type of cross-disciplinary, multi-scale integration represented by these two CZ-based models enables an array of new hypotheses to be uniquely tested for the first time. For example, how do land-surface interactions influence surface and subsurface water chemistry? As shown in Fig 13, the RT-Flux-PIHM model allows examination of spatial patterns of local mineral (chlorite) dissolution rates (Fig. 13A), Mg concentration on soil exchange sites (Fig. 13B), as well as quantification of watershed rates and fluxes (Fig. 13C).

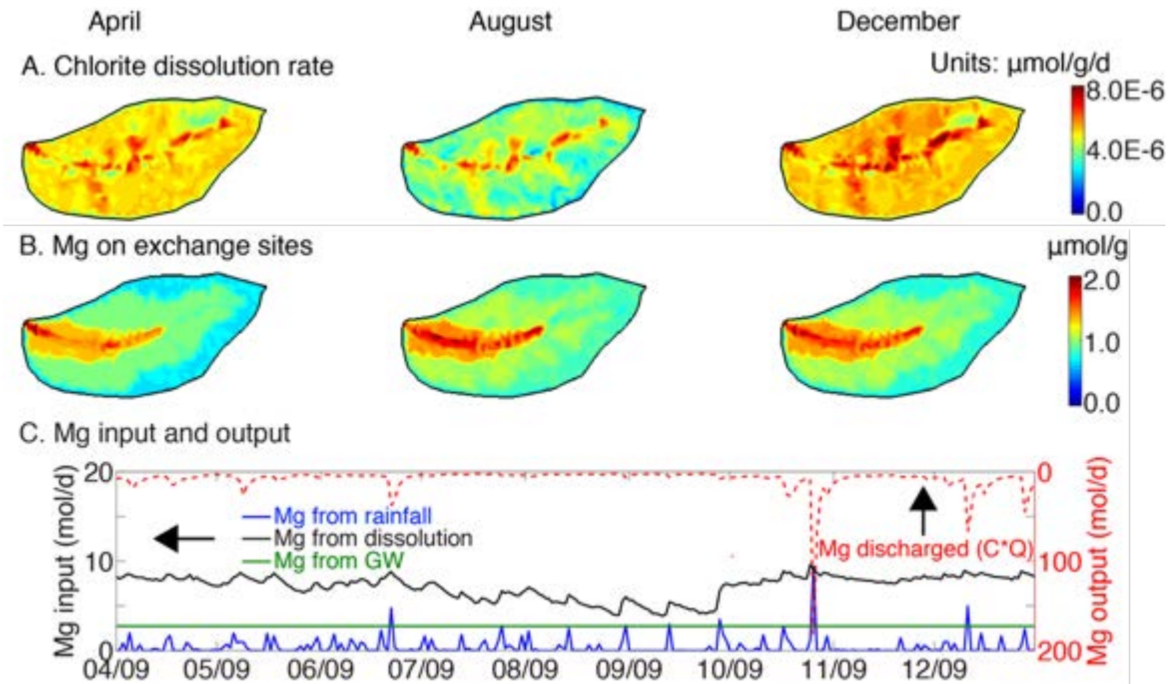


Fig. 13 A: Predicted spatial distribution of chlorite dissolution rate (source of Mg) on in April, August, and December, 2009; **B**: Predicted patterns of Mg concentration on solid surface through ion exchange at these times; **C**: Temporal evolution of watershed-scale Mg input (dissolution, GW, and rainfall) and Mg export through discharge in SSHCZO.

Another model under development and used at more than one CZO is the effective energy and mass transfer (EEMT) model. Ecosystem production and soil development in the southwestern U.S. are limited by water availability. Research in the Catalina-Jemez CZO has shown that climate (varying as a function of elevation) exerts strong control over mineral transformation, carbon storage and soil depth (Lybrand and Rasmussen 2015). Studies have also shown, however, that the specifics of landscape position (i.e., aspect, convergent versus divergent flow positions) and its impact on micro-climate and lateral subsidies of water and carbon, also strongly influence regolith depth and patterns in element depletion/enrichment (Holleran et al. 2015, Lybrand and Rasmussen 2015, Vazquez-Ortega 2016). Such observations are quantitatively consistent with EEMT model predictions that include consideration of aspect controls over radiation and evapotranspiration, and topographic controls over lateral hydrologic flux (Fig. 14; Rasmussen et al. 2015).

The importance of linking models directly to processes, as opposed to surrogates for those processes, is becoming more evident as measuring and monitoring is intensifying. For example, aspect related microclimate differences at several watersheds are likely sufficient enough to affect carbon cycling as well as regolith mineral composition. At RCCZO, extensive soil temperature data demonstrating approximately a 5°C mean annual soil temperature difference between adjacent slopes on contrasting aspects are driven the interactions between the land surface cover (e.g., snow cover, vegetation), within soil processes (heat transport and freezing) and incoming solar radiation govern carbon and mineral weathering dynamics. These are all processes that can be effectively and simultaneous simulated with the SHAW model (i.e., heat and water transport in freezing, vegetated soils). In the temperate forest of the northeastern U.S., variations in microclimate associated with aspect are also associated with strong changes in mineral weathering. On south-facing hillslopes weathering rates are faster, but on north-facing hillslopes the soils are more weathered (Ma et al. 2011). Linking of the hydrologic model Flux-PIHM and the geochemical box model WITCH to Earthcast — forward projections of the Earth's surface — shale weathering fluxes demonstrated that in this same catchment, an 0.45°C increase in temperature and its resultant effect on evapotranspiration will lead to a 4-13% increase in weathering fluxes from the shale. Earthcasting also demonstrated that soils with a low clay content were more sensitive to climate warming and that nutrient cycling by vegetation slows the rate of weathering fluxes in shale landscapes (Sullivan et al. in review).

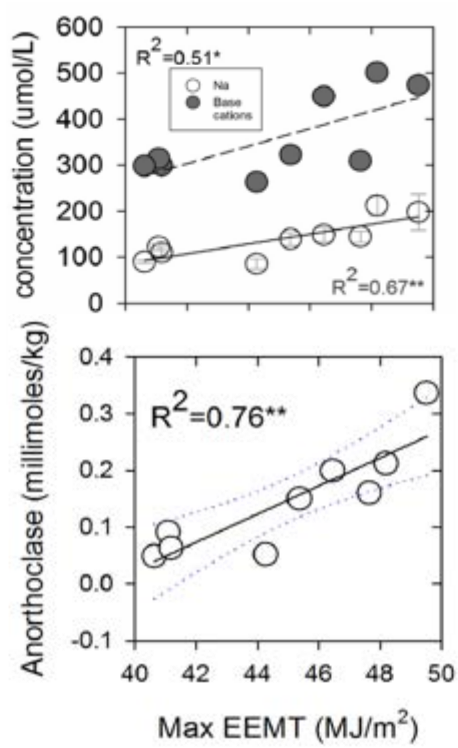


Fig.14: Effective energy and mass transfer (EEMT) – an integrated measure of climatic forcing developed by the Catalina-Jemez CZO – is an effective predictor of geochemical weathering in catchments subjected to variation in micro-climate as a result of differences in aspect (Zapata-Rios et al. 2015).

1.10 The structure of regolith is a function of the distribution of microorganisms in the subsurface — "the weathering microbiome" —; the co-evolution of CZ structure and geo-microbiologic function is just beginning to be deciphered.

CZ scientists are participating in the huge explosion in use of molecular biological tools to explore the variety of micro-organisms in the environment. As different disciplines explore the "microbiome" in different organisms and environments, CZ scientists are exploring the "weathering microbiome". In particular, CZ scientists are investigating how microbiota vary with depth and landscape position and how soil-forming factors such as lithology and climate affect the distribution of microbiota (Eilser et al. 2012, Minyard et al. 2012, Yesavage et al. 2012, Gabor et al. 2014, Liermann et al. 2015).

This exploration is mapping patterns in microbiota identity and distribution in the subsurface and is leading to understanding of the controls on these distributions (Fig. 15). CZO researchers have also emphasized that microbiota affect mineral composition and distribution, leading to the growing idea that mineral composition and distribution may be used to understand microbial processes at depth.

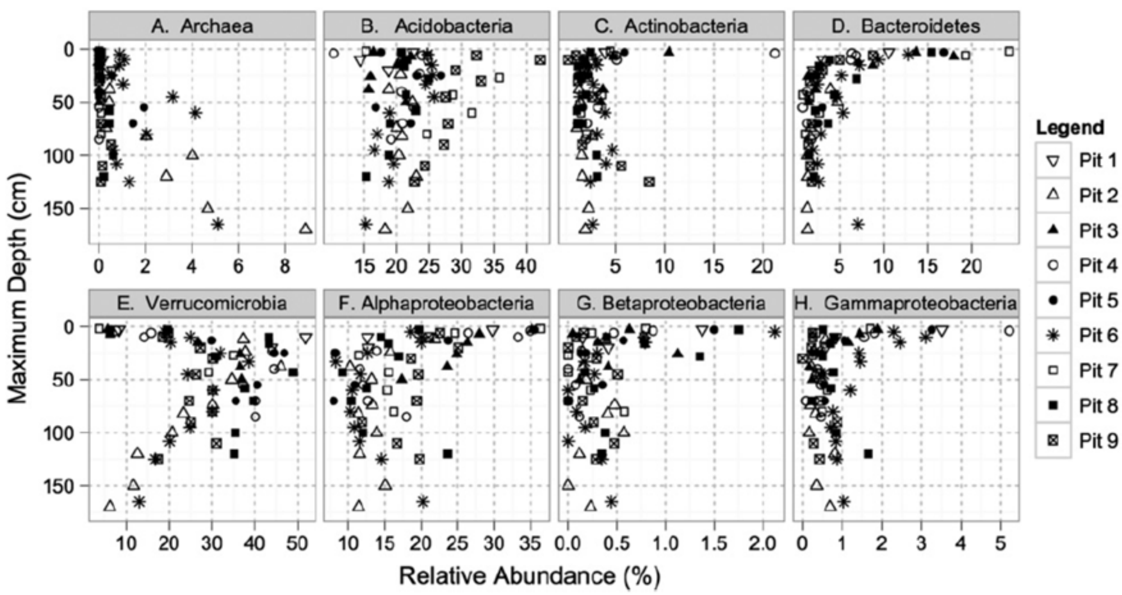


Fig. 15: Geomicrobiome (archaea and bacterial taxa) versus depth for 9 soil pits in a forested montane watershed in the Boulder Creek CZO. The authors discovered that there was as much variation within individual soil pits as across the surface soils from different biomes. This study emphasizes the need for greater investigation of the deep weathering microbiome (Eilers et al. 2012).

2 Compelling CZ Science Questions for the Coming Decade

We describe ten compelling questions that arose at the Arlington meeting or other discussions of CZ scientists based on the transformative findings summarized above. These questions should drive the CZ science and network of the future.

2.1 As energy propagates through the CZ, how does it drive the emergence of patterns in porosity, fracturing, permeability, grain size, mineralogy, and micro-organisms and how are these patterns distributed at depth and across landscapes?

Energy propagates through the CZ to form the structure that controls gas, fluid, solute and sediment fluxes. At the base of the CZ, tectonic energy sets the initial fracture density and dip angle, and at the top of the CZ plants and climate variability (freeze-thaw, shrink-swell) impart gradients in chemical and thermal energy, which drive fractures into the subsurface. Together these processes shape the distribution and connectedness of pore space and the mineral surface area on which reactions can take place. To be able to predict CZ structure and evolution into the future, we must be able to reconcile how this energy, which is transported and stored through the CZ, governs the properties that control its gas, water, solute and sediment fluxes.

Numerous models have been published that describe how trees, frost, tectonics, and chemical processes drive fracturing in the CZ; however, few studies have linked theoretical models to in situ observations of the CZ. Our primary focus in the coming decade will be to develop and test models of the dynamics of CZ architecture with field measurements. These measurements should be used to link the disparate thermal, tectonic, biological, and chemically-based process models that describe evolution of CZ architecture. From the last decade of research, CZ scientists have only very recently identified the unifying emergent property of all of these processes as porosity development. Numerous upcoming conference sessions are planned to bring together scientists from a variety of disciplines to integrate our knowledge of porosity development under a CZ reference frame (AGU 2017 session EP053 Where things aren't: Understanding the role of porosity in the Critical Zone; Chapman conference, in prep). As a result, the key scientific question moving forward with respect to how energy storage and transport drives the evolution of porosity include the following: What primes the onset of porosity development or fracturing in the critical zone and how are these processes affected by stresses across spatial and temporal scales? What are the relative contributions from chemical, physical, and biological mechanisms toward porosity development in the CZ? Where are these individual mechanisms most important within the CZ? Where does the interplay between mechanisms happen? How do we measure the relative contributions of these processes and how do we tease them apart? How do we connect process-based models to reflect the complex feedbacks in the CZ, and how do we generalize these processes to make these models transportable? Can we generalize these processes to predict how they may control CZ emergent properties near the surface?

2.2 What role does the deep CZ play in regulating terrestrial carbon dynamics?

Much of our knowledge about soil carbon transformation processes are based on soils examined ≤ 30 cm deep (Richter and Billings 2015), rendering key knowledge gaps in carbon formation, transformation, and fate at depth. Given this lack of knowledge it remains elusive as to how deep carbon dynamics will evolve over time, as ecosystems and reaction kinetics respond to changing climatic conditions. Globally our best estimates are that ~36% of the total SOC pool resides between 1-3 m deep (Jobbágy and Jackson 2000); limited data from deeper soil limits our ability to estimate very deep (> 3m) carbon pools. Recently models have incorporated multi-layer soil carbon processes, which has helped reduce the apparently over-estimated effects of a warming Earth on soil decomposition rates (Jenkinson and Coleman 2008). However, current models of soil organic carbon frequently invoke unrealistic microbial physiology (Ballantyne and Billings in revision), and the modeling of deep soil behavior is still based on topsoil carbon cycling processes with slightly different parameterization (Salome et al. 2010).

Recent work suggests that changes in land cover/land use may drive both structural and chemical changes that alter CZ carbon dynamics at depth. Specifically, where land cover changes alter deep root densities (Billings et al. in review), the organic acid production by mycorrhizal fungi that accelerates mineral dissolution reactions proximal to plant roots, effectively increases porosity, and alters permeability. Similarly, plant roots can open fractured rock, exposing fresh rock surfaces to weathering solvents (e.g., water, acid). Plant roots may also contribute to surface erosion processes via tree-throw and root growth and heave, sending soil incrementally down hillslopes (e.g., Gabet and Mudd 2010, Roering et al. 2010, Hoffman and Anderson 2014). Finally, after plant death, plant roots may leave behind macropores through which meteoric fluids and gases can reach previously unweathered minerals, driving CZ evolution deeper into the subsurface. Evidence suggests changes in CZ subsurface carbon budgets may already be detectable, given that DIC fluxes in larger river systems (Raymond and Cole 2003; Raymond et al. 2008) and groundwater concentrations (Macpherson et al. 2008 [USA]; Liu and Zhou 2000 [China]) have been increasing in over the last few decades.

These phenomena prompt important questions: Do changes in land cover/ land use drive changes in the CZ subsurface structure that significantly alter carbon dynamic? What surface and subsurface conditions promote: a) SOC retention by the whole soil profile, b) release via carbon decomposition and subsequent mineralization, or c) DOC export via leaching? To what extent are these dynamics driven by the structure of the soil profile as compared to depth-dependent biological substrate demand and organic carbon inputs?

2.3 How do CZ services evolve in response to anthropogenic and natural disturbance?

Critical Zone services include storage and transport of clean water, maintenance of regolith suitable for growing vegetation and crops, and mitigation of climate change through drawdown of atmospheric CO2. These services are perturbed (and perhaps threatened) by both gradual (e.g., climate change, erosion, contaminant accumulation, land use change) and episodic (e.g., hurricanes, wildfires, spills) disturbances that result from both natural and human activities. To project the response of CZ services to disturbance requires that we continue to open the "black box" that is the CZ and address fundamental processes underlying the transport of water, solute and sediment through the CZ and the transformation of solutes, especially nutrients, within the CZ. We must be able to quantify, for example, where water is stored and for how long, where plants access nutrients, how vegetation is distributed across the landscape, and how deep and at what rate carbon can be moved through the subsurface. We must understand how plant communities are distributed across watersheds, and their respective contributions to soil organic carbon, and overall carbon loss from disturbances such as fire (Li et al. 2015, Poley et al. in preparation, Will et al. 2017). Widespread, large scale highly destructive wildfire has become commonplace in the western US, costing lives, money, and extensive loss of critical zone services. One way of minimizing the threat of such fires is to intentionally light smaller, controlled fires that reduce the fuel and hence risk of catastrophic fire. This carries with it obvious risks and leads to questions regarding how rapidly the system recovers. Work at RCCZO has shown that, under some conditions, the hydrologic recovery is rapid (Flerchinger et al., 2016), plant productivity resumes rapidly (Fellows et al., 2017 in review) and soil OM properties are not greatly affected (Chandler et al., 2017 in review) even while the above ground biomass is much less, thus reducing the fire hazard for some time. We must directly investigate how CZ processes respond to natural and human-induced perturbation across short and long timescales. Such quantification is necessary to determine CZ resilience, or how long a system can sustain disturbances, before the function of the systems is permanently altered. For example, cultivated systems may be unable to sustain the intensive management required to provide food and fiber resources, jeopardizing our ability to plan future resource and land use.

To predict the effects of disturbances to the CZ typically requires development of conceptual and quantitative models using knowledge gleaned from US and International CZOs. For example, there is a great opportunity for growth in geomorphic models of the CZ. The fields of bio- and eco-geomorphology, which emphasize the connections between organisms, geomorphic processes, and physical evolution of the landscape, provide novel targets for both conceptual and numerical models of geomorphology from a CZ perspective (see Corenblit et al. 2011 for a review). Humans as drivers of geomorphic and ecological change and intentional managers of the CZ is an area ripe for development of new models (e.g. Richter 2007, Tarolli and Sofia 2016). Finally, there is a great need to develop geomorphic models of the CZ that consider temporal variability in climate, vegetation/land use, and landscape relief. Conceptual and numerical geomorphic models that couple temporally-varying geomorphic processes with vegetation, climate, soil production, chemical weathering, sea level change and isostatic loading and unloading by glaciers are d are vital for understanding the form and function of the CZ in the context of the dynamic Quaternary (and Anthropocene) history of Earth.

2.3.1 As the CZO network grows and integrates models and data, where should new observatories be located?

One of the intents of the CZO program is to understand the form, function and dynamics of the critical zone. Clearly, we cannot investigate the CZ everywhere, and we should be able to extrapolate from one site to another once our models are robust enough. However, it is also clear that some geological locations may be so unusual or some land use impacts may be so intense that extrapolation from the current CZO network will not be possible. A thrust over the next ten years should be to investigate four under represented CZs: urban systems, carbonate terrains, arctic regions and coastal margins.

1. *Urban system's* CZ structure and function is poorly understood even though 54% of humans globally, and 77% of the population in more developed countries, live in urban areas (UN, 2014). While a growing number of geochemical and ecological studies are focused on urban areas (Chambers et al. 2016, Kaushal et al. 2014, Tanner et al. 2014), scientific research on urban areas would benefit greatly from the application of CZ science. The geologic framework and history (topography and glaciation) underlying urban watersheds produce different streamflow characteristics such as flashiness and high flows in response to urbanization (Fletcher et al. 2013, Hopkins et al. 2015) despite apparent homogenization in surface land use and ecology (Groffman et al. 2014). An overarching question about the urban CZ is: does the urban CZ function in a different way than the CZ in forested or, even more, agricultural areas? Or does the urban CZ function similarly, albeit at different rates? This overarching question can be answered by 1–2 urban US CZOs, along with leveraging urban CZOs abroad (e.g., Peri-Urban and Ningbo CZOs in China) or addition of an urban component to largely rural sites. Broadening our understanding of more specific questions about the urban CZ can be addressed through campaign approaches with synchronous sampling of multiple urban areas or satellite approaches (e.g., building on LTERs that exist within, or at an interface with, urban environments such as the Baltimore, Phoenix and Plum Island LTERs). Key research questions to be answered through an urban CZO include: How does landscape disturbance and the addition of engineered surface and subsurface infrastructure affect water movement through, and storage in, the urban CZ; and how does altered water movement change elemental cycling and fluxes, including subsurface weathering? Does urbanization cause increased weathering of regolith and bedrock minerals through addition of anthropogenic acids (nitric and sulfuric) and movement of unweathered material from the subsurface to the surface? Or does urbanization reduce weathering through decreased flow of water into the subsurface? How does urban water supply, wastewater, and stormwater infrastructure affect CZ water storage, chemical composition, and weathering rates? Does urbanization shift the location of CZ "hotspots", e.g., N cycling shifting from vadose zone and shallow groundwater to stream channels and engineered structure? How do high solute concentrations originating from the urban CZ influence C export and cycling in coastal ecosystems and globally? How do different geological and climatic settings affect the import and export of water and solutes from urban areas? Some of these questions may be best answered by collaborating with social scientists (economists, anthropologists, sociologists, political scientists) to help quantify the broader inputs/outputs from urban centers and there influence on hydrological/elemental cycling.

2. *Carbonate terrains* cover 20% of the ice-free terrestrial land (Hartmann and Moosdorf 2012), supply 20–25% of the world's population with potable water (Ford and Williams 2007), and via their relatively rapid dissolution rates, act as a disproportionately dominant source of dissolved weathering fluxes to the ocean (Gaillardet et al. 1999). The relatively fast dissolution rates of carbonate minerals also support the development of vuggy porosity and conduits that lead to rapid hydrologic fluxes. These fluxes are sufficiently fast that we can observe CZ responses to stochastic events, such as individual storms, as well as seasonal and yearly fluctuations in environmental conditions that generate observable responses in the

CZ. The rapidity of mineral dissolution and water/gas/solute fluxes leads to a central question: Can carbonate terrains be leveraged as bellwethers for how Earth's CZ will respond to future climatic and human perturbations? Moreover, given the significant consumption of CO_2 associated with rapid carbonate dissolution rates (Liu et al. 2011), what role will carbonate terrains play in controlling atmospheric CO_2 dynamics over short time scales in the Anthropocene? In comparison to CZs developed on other lithologies, it is likely that the greater hydrologic flashiness and heterogeneity in conduit development exhibited by carbonate systems drives distinct patterns of vegetation water use and productivity, top-down (e.g. biological processes) and bottom-up (e.g. regolith-bedrock interface characteristics, bedrock topography) drivers of soil development, and surface-groundwater interactions. However, these ideas are rarely examined in detail. Illuminating these and related phenomena in carbonate terrains is likely to shed light on other, non-carbonate CZs by revealing how plant and microbial communities, soil fabrics, and hydraulic properties evolve over the relatively short time periods required for detectable change to occur. Carbonate-based observations can be used to formulate hypotheses addressing questions of system evolution in non-carbonate terrain, to be tested at existing CZOs and in a myriad of future studies. Carbonate-based observations will also be critical for understanding systems influenced by the eolian, pedogenic, or groundwater inputs, or the precipitation and dissolution of carbonate minerals. Examples of these CZs include calcareous loess-mantled landscapes of the Midwestern US and alluvial landscapes in the arid southwest that contain various stages of calcic soil horizons and indurated pedogenic calcretes. Key research questions that can be addressed through a carbonate terrain CZO include: What are the interactions and feedbacks among biological CO_2 production, transport, and carbonate weathering, and how do they vary across carbonate terrains and along climatic gradients? Does carbonate dissolution by sulfuric (produced by sulfide minerals) and nitric acid (enhanced by inputs of anthropogenic reactive nitrogen) act as an important source of atmospheric CO_2, given the CO_2 released with marine carbonate mineral precipitation is not compensated through these dissolution reactions?, How does the regolith-bedrock interface—including its depth and topography, the density and orientation of bedrock fractures and conduits, and morphological and chemical properties of the regolith—drive changes in soil-water potential energy gradients that affect the distribution of soil moisture, water flux and roots? Can we leverage the rapid dissolution of carbonates to elucidate how acid production (e.g., malic, citric, oxalic) by roots and associated microbes influences the relative abundance of soil minerals? How does this weathering vary with ecosystem productivity, plant community, and ecosystem development? What role does this play in epikarst development? Does the rate of nutrient recycling by vegetation differ in carbonate terrains compared to non-carbonate terrains given the affinity of carbonate minerals for P and Fe, and does this recycling rates increase over time at the same rate as mineral depletion? How do erosion signals propagate through landscapes developed on layered rocks (carbonate or carbonate/non-carbonate) and how does this process differ under conditions of progressive karstification? Are there key carbonate CZ processes and functions (some listed above) that are essential to include for more accurate Earth system model predictions?

3. *Arctic Regions* should be an important geographic focus for CZ science. Although substantial research has focused on ecological processes in arctic regions, CZ science is uniquely poised to evaluate ongoing changes in CZ structure due to subsurface permafrost thaw and associated impacts on hydrology (e.g. thermokarst processes), ecology, and biogeochemistry that are occurring on relatively short timescales. Changes in the Arctic are likely to have disproportionate effects on the biosphere, especially given that they are extremely large carbon stores. Studies of permafrost-affected systems would benefit from collaboration between CZ scientists and the current network of Arctic observatories (e.g. Bonanza and Toolik Lake Long Term Ecological Research sites) where research is actively conducted in this challenging and dynamic environment. In addition, the climate is changing most rapidly at northern high latitudes where extensive permafrost degradation due to increasing temperatures is driving changes in hydrology, ecology, and biogeochemistry (Hinzman et al. 2013, Bring et al. 2016, Wrona et al. 2016). Of major consequence is the potential for soils in these regions to become a source for atmospheric carbon (CO_2 and CH_4) and accelerate climate change (Schuur et al. 2008, Schuur et al. 2013).

4. *Coastal margins* are a broad zone where land meets sea that hosts over 600 million people (McGranahan et al. 2007)– characterized by complex biophysical interactions, productive and dynamic ecosystems, ongoing environmental change, and maintains significant value to society. With climate change, the coastal zone will be rapidly altered due to impacts such as sea levels rise, and shifts in the extent of seawater intrusion into groundwater, or changes in submarine groundwater discharge. The critical zone is connected to the coastal ocean in interesting and potentially important ways that remain poorly explored in many regions of the world. In this light, the critical zone observatory (CZO) framework has the potential to reorganize the way we think about coastal margins. For example, freshwater runoff and terrestrial nutrients have long been recognized as important contributors to coastal ocean dynamics; yet, watersheds are often treated as simplistic (e.g., 2D) sources of flux to the ocean. The CZO concept emphasizes integrated analysis of the vertical column "where rock meets life", prompting deeper investigation of the factors driving dynamic stream exports and submarine groundwater discharge to the coastal ocean (e.g., Hakai Institute, Canada; the Florida Coastal Everglades LTER, USA). Conversely, coastal ocean research questions can provide a strong driving purpose for CZOs as oceans can influence critical zone evolution through processes such as the atmospheric deposition of marine salts.

2.3.2 How will climate change alter the CZ and how will CZ services respond to extremes in weather?

The fact that landscapes change through time means that the CZ will dynamically respond to climate change and extreme variability in weather (e.g., Anderson et al. 2012). In addition, climate variability at glacial-interglacial timescales (and shorter) drives variability in moisture and vegetation and creates important temporal variability in CZ processes that are integrated into CZ structure (e.g., Pelletier et al. 2013, Kumar et al. in review). Today's models still do not incorporate such variability or the effects of climate and weather variability on CZ form, function, and process.

Despite our lack of modelling capability, extreme weather events driven by climate change are pushing the boundaries of CZ function and potentially leading to irreversible changes to CZ services. Increasing global temperatures are causing regional changes in hydrologic forcings, including increases in heavy precipitation events, increases in drought duration and extent, decreases in snowpack, and early snowmelt (Karl and Trenberth 2003, Trenberth 2011). Severe drought and floods directly impact water storage, vegetation growth and resilience, sediment transport, and solute export from watersheds (e.g., Bearup et al. 2014a, Borsa et al. 2014, Rue et al. 2017, Wicherski et al. 2017). For example, the comparisons across all mountainous, snow-driven CZOs provide important insights into possible ranges of snowpack sensitivity to climate variability across the western US, with elevation driving snowpack thickness in forested and shrubland systems and aspect mainly driving snowpack thickness at alpine sites (Tennant et al. 2017). In addition, the rain-snow transition and rain-on-snow events in these regions (e.g., RCCZO; Godsey et al. in review) shows the partitioning of precipitation phase drives differences in timing and amount of soil moisture storage and snowpack storage, while modeling results show strongly heterogeneous spatial distribution of contributions to stream flow at the watershed-scale (Enslin 2016). These impacts have cascading effects on regolith evolution, plant-mediated weathering, and drawdown of atmospheric carbon (Bearup et al. 2014b, Anderson et al. 2015). In order to better predict CZ function in a rapidly changing climate, it is essential to understand how the CZ currently responds to these weather extremes, and over what timescales these events cause temporary or irreversible change.

2.4 How can observatory measurements and models be extrapolated to explain global feedbacks in climate, weathering, and tectonics?

One of the strengths of the CZ framework is the focus on the coupling between physical, chemical, and biological processes both at surface and at depth. Just as it is well known that feedbacks govern the CO_2 in the atmosphere at the global scale, similar feedbacks must also govern soil development and energy, matter and water fluxes, at smaller scales. Another well-known feedback is that weathering is thought to balance volcanic degassing over long timescales, which leads us to think erosion must balance weathering advance at depth in order for much of Earth's landscapes to remain soil- and regolith-mantled.

2.4.1 *CAN WE CLASSIFY THE TYPES OF CRITICAL ZONES AND QUANTIFY THEM WITH APPROPRIATE DIMENSIONLESS NUMBERS THAT DESCRIBE THE FORM, FUNCTION, AND DYNAMICS?*

To what extent do climatic, pedologic and ecologic classifications fall short of capturing the process interactions that determine the fluxes of energy and mass through the critical zone, and the physical, chemical and biological structures that modulate them? Can a classification of CZ not only capture the distinct 'phenotypes' of CZs that we observe today, but also explicitly distinct 'genotypes' of dominant contemporary and historical drivers that determined the co-evolution of these distinctions over time (Harman and Troch 2014)?

Within many distinct domains contributing to CZ science dimensionless numbers have had a tremendous impact in helping us understand first-order controls on landscape functions and ecosystem processes: the aridity index and Budyko Curve in hydrology (Budyko 1974), the geomorphic Peclet number (Perron et al. 2008), elemental stoichiometry in ecology (e.g. Taylor and Townsend 2010; Wymore et al. 2016), and so on. Can other dimensionless numbers be developed that link across CZ process domains, including the influence of human activities? Or can a 'tree' of dimensionless numbers be constructed to help develop the classification scheme described above?

2.4.2 *HOW CAN METHODS OF DATA ASSIMILATION BE USED IN CRITICAL ZONE SCIENCE TO CREATE FORWARD-PREDICTIVE MODELS?*

Process-based integration models can be used to tease apart the importance of individual processes, to test nonlinear coupling, and to identify controlling processes or parameters that need to be further constrained. Such predictive forward model frameworks offer a pathway toward developing new conceptual frameworks for simple models (Li et al. 2017b, Druhan and Maher 2017). However, models commonly function over one of two characteristic time scales. At the scale of hydrologic cycling (hours to years), the principal interests addressed by modeling studies are oriented toward the functioning of the CZ (Meixner et al. 2000), whereas at the geological time scale (10^4 – 10^6 years), the primary focus is on the formation and evolution of the CZ (Lebedeva et al. 2015, Murray et al. 2009, Pandey and Rajaram, 2016, Zhang et al. 2016). Duffy et al. (2014) argued that to span the entire CZ from the scale of the meteorologist to that of the geologist requires multiple models written for simulations at different timescales. Several CZOs are working with such different models. What remains to be accomplished, however, is using such different models in cascades so that long timescale models are used to inform short timescale processes. For example, the weathering of primary minerals and ingrowth of secondary phases occurs over geologic timescales. These minerals in turn contribute to the geomorphic and hydrologic characteristics of the landscape including the short-term solute-discharge relationship.

To inform such models requires data. Despite the large datasets collected at CZOs, new methods of infilling data gaps and extrapolating data are needed for CZ science. Data assimilation originated from numerical weather prediction (Daley 1991) and has been extensively used in atmospheric, geographic, oceanic, and hydrologic sciences (Rabier 2005, Navon 2009). In contrast, such approaches in soil modelling, reactive transport and biogeochemistry have been comparatively limited and only a few papers have been written for CZO research using these techniques (Shi et al. 2013). Data assimilation techniques, such as the extensively used ensemble Kalman filter (EnKF) (Evensen 1994), offer a potentially powerful means of identifying key parameters and processes in highly nonlinear biogeochemical reaction networks. More importantly, data assimilation experiments can also be used to guide where and what to measure, therefore facilitating observation system design. Such work will foster connections between the DOE Scientific Focus Area (SFA) and NSF CZO funded research.

2.5 How do we integrate CZ science into educational efforts at all levels and promote the CZ approach among scientists, managers, and policy makers?

The grand challenges facing society are inherently complex and cross multiple scientific disciplines. The CZ approach is ideal to both understand the problems and identify solutions. Training the next generation of scientists, managers, and policy makers begins through education, both formal and informal, where a fundamental understanding of scientific concepts and geoscientific habits of mind are developed. A CZ approach can enhance student learning and science competency by providing both context and relevance to the science. The current generation of scientists, managers, and policy makers are in need of science they can translate to solve problems and make decisions on behalf of stakeholders and constituents. A CZ approach to science and decision making would enhance our ability to consider the many complexities inherent in such problems and decisions and provide the foundational science that can be translated to applied problems.

Traditionally, science is taught as disciplinary subjects (e.g. biology, chemistry, physics), especially at the elementary and secondary levels (K-12), or as semi-integrative (e.g. ecology, environmental science) more commonly at the post-secondary level. A CZ approach, however, fosters systems thinking, whereby a more holistic vision of Earth and hydrological processes and how they integrate with ecological and anthropogenic processes is considered and could help develop more scientifically literate students that ultimately may become scientists, managers and policy makers. Education also occurs informally outside the classroom, through civic engagement and politics, providing another important avenue through which a CZ approach should be broadly disseminated to engage and inform all citizens.

CZ science must be disseminated to help the current generation of scientists, managers and policy makers solve problems and make decisions that take into account both environmental and societal needs. A CZ approach can account for the complexity of such problems by involving multiple components, feedbacks and thresholds in thinking about earth systems. Collaboration among current CZ scientists and other groups is needed to foster and expand a CZ approach to problem solving and decision making. Continued opportunities to collaborate and expand the network of CZO sites will facilitate dissemination and application of CZ science and this uniquely trans-disciplinary approach to a wide variety of geographic settings.

3 CZ Approach for the Future:

Resonating across the CZ community is the need to support observatory science, because "doing" CZ science—deriving mechanistic theories and models of CZ processes and functions— requires diverse measurements (hydrologic, biogeochemical, structural) that are often taken over long-time periods and multiple spatial scales and are frequently well beyond the capabilities of any single investigator. The CZ community is calling for four primary expansions of the CZ approach over the next decade, beyond maintenance of a core set of ongoing observatories: (i) adoption of new observatories with characteristics beyond those represented in the current observatory network, and especially in areas undergoing rapid CZ change; (ii) establishment of satellite sites that leverage existing infrastructure (e.g., NEON and LTERs) to address specific questions; (iii) development of national campaigns to test CZ hypotheses across a larger domain; (iv) support for synthesis efforts to foster the cross pollination of ideas and disciplines. Below we synthesize the support of CZ scientists to support four facets of CZ science.

1. Nourishing the CZ Observatory Network — The NSF Earth Sciences Program (NSF EAR) has shown leadership in nucleating, growing, and nourishing the network of nine observatories. In turn, the community has used these observatories and developed datasets that are driving new understanding; models that are elucidating the function and dynamics of pedons, hillslopes, and catchments; and theories that are being tested worldwide beyond the observatories themselves and that should be helpful to decision makers. These observatories are cost effective resources for the broader scientific community, supplying the "scientific infrastructure" of a data collection network, historic data and results, background information and facilities. The existence of these observatories allows us to understand how the CZ responds to both slow climatic changes and extreme events, something rarely observed at such intensities. In the last five years, the US CZOs have afforded us the opportunity to examine a 1000-year flood in Boulder Creek (CO), the biggest hurricane in 90 years (1928) to hit Puerto Rico, intense fires in the Jemez Mountains (NM), and massive swing in snow pack/ extreme drought in the Southern Sierra (CA). The 2013 Las Conchas wildfire (Fig. 16) for example, which was the largest New Mexico wildfire to date and burned through the Jemez CZO,

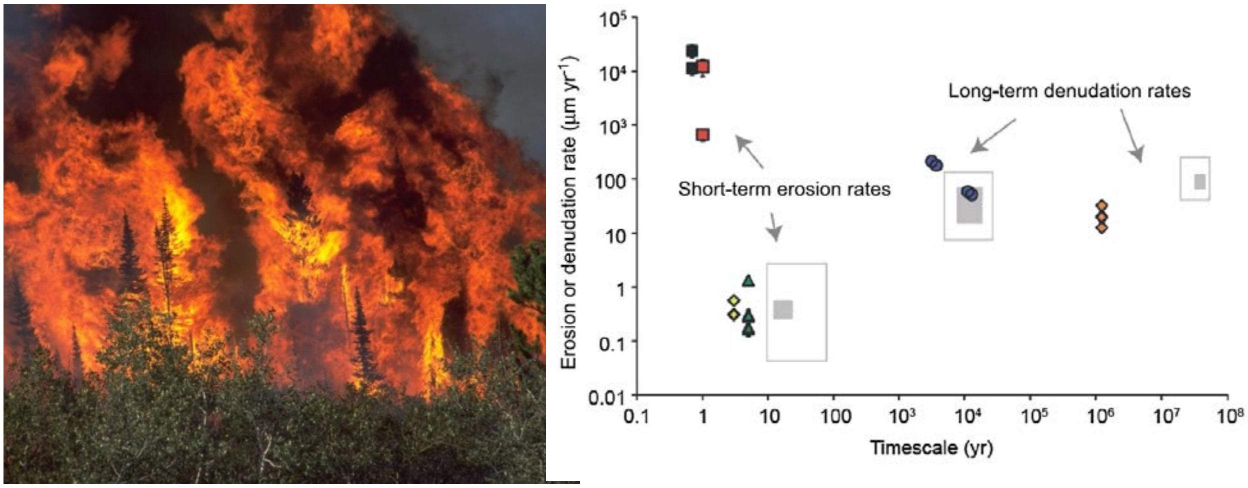


Fig. 16: Plot of the erosion or denudation rate for several watersheds in the Jemez CZO using different methods versus the time scale of measurement. Short-term wildfire-affected derived erosion rates (red and black squares), non-wildfire-affected derived erosion rates (green triangles), chemical flux-derived erosion rates (yellow diamonds), and long-term 10Be-derived denudation rates (blue circles), and denudation rates derived from incision into a paleosurface (orange diamonds) are shown. Data from Kirchner et al. (2001) are also shown in gray (middle 50% of data) and rectangles (full range of data) for comparison.

provided unique opportunities to document the CZ response to disturbance. LiDAR data collected shortly before and one year after the Las Conchas wildfire of 2013 revealed that post-fire erosion is responsible for > 95% of long-term erosion in upper elevations of the Jemez Mountains (Orem and Pelletier, 2016). The discovery was enabled by ongoing CZO measurements including multi-temporal airborne and ground LiDAR, sediment loads, cosmogenic isotopes and modeling. The results highlight the importance of observatories for capturing the effects of extreme events on long-term processes. *The ten scientific advances articulated in this report would not be possible without observatories, where datasets on deep Earth surface processes can be integrated with overlying ecosystem processes across multiple lithologies and climatic conditions—generating integrative theories that move science forward and motivate rising scientists to work together*. Perhaps most importantly, the observatories have helped train the scientists of the future who can see the CZ as a single entity and can understand the inter-relationships of its component parts (Wymore et al. 2017a, b). While the observatory network provides nine functions that have recently been summarized (Brantley et al. 2017), one of the most important reasons for continuing the network is that it draws scientists together from disparate fields to make measurements, develop models and test theories on the same locations. RCCZO, for example, has recently "hosted" research on bed load transport (Olinde and Johnson 2015), soil water repellency (Chandler et al. in review), remote sensing technology (Olsoy et al. 2016, Anderson et al. 2017), and downscaling regional forecast data (Cowley et al. 2017). This did not happen before the CZO program and it is truly a paradigm shift in earth surface science. This achievement by the NSF EAR program cannot be understated and should not be underestimated by the program officers themselves. For the next ten years, the National Science Foundation has the opportunity to make similarly game-changing investments to push CZ science forward by maintaining or growing a CZO network and by implementing ideas from the following list of initiatives.

2. Adoption of New CZ Observatories— To project CZ structure, function and evolution into the future, there is a need to expand the current CZO network to include systems that are undergoing rapid change. Highlighted among the CZ community were needs for Urban, Polar/Arctic, Carbonate, and Coastal CZOs. Beyond the fact that these are not included in the current USA CZO network configuration, each of these landscapes acts as a fast-responding end member to perturbations of the earth system (e.g. urbanization, climate change, sea level rise) or represents an end member that cannot simply be understood from extrapolation from other observatories (e.g. urban sites, carbonates).

3. CZ Satellite Sites and Leveraging Existing Environmental Networks (e.g., LTER, LTAR and NEON) — Nationally and internationally a variety of environmental observatories already exists, from large entities like ILTER to individual university field stations (Brantley et al. 2017). This was one of the resounding themes at the 2017 Arlington meeting, where participants resoundingly supported greater (and continued) interaction between/among programs especially LTER but also NEON and LTAR. These types of sites are rich in data, well characterized for many important attributes, and offer a platform upon which specific hypotheses can be tested. However, observatories by definition are expensive to maintain: while essential to the CZ science endeavor, the program must also be augmented with short-term initiatives that address individual research questions. One mechanism is the establishment of temporary sites of intense measurement activities – satellite sites. Such sites might be located along a gradient in environmental variables as discussed in one of the founding documents of the CZO network (Brantley et al. 2006) or exemplified by CZO activities (Dere et al. 2013). Alternately, sites could be located between CZOs or between a CZO and an LTER/NEON/LTAR, etc. The salient feature of satellite sites would be that they would be shorter timescale than observatories, they would be less resource-intensive, and they could target a single research question of importance.

The US CZOs were all developed around pre-existing observational infrastructure, albeit of varying types and extent. Cost-effective expansion of the CZO network into some of the kinds of settings identified above can, in part, be facilitated by making additional focused investments in existing LTER and other observing sites. By no means should development of new CZOs be arbitrarily limited to pre-existing sites of a particular type, but in a number of cases an expansion of observing capabilities and most importantly conceptual models at existing sites could open up new research avenues while taking advantage of the existing infrastructure and long-term data sets. This combination can bring new investigators with new ideas and tools and interdisciplinary insight into critical environments in a cost-efficient way. Investigation of the deep sub-surface (including water and biota), a physical approach to landscape evolution, and coupled hydrological-reactive transport models are just a few examples of how extension of the measurements and concepts at traditionally ecologically or agriculturally oriented observatories might create new hybrid CZOs

4. National CZ Research Campaigns— One of the big successes within the CZO program of the last decade was the geophysics campaign led by S. Holbrook of the University of Wyoming. This extremely well-funded effort benefitted from NSF EPSCOR resources which support use of geophysical techniques to understand hydrologic and other questions. The Wyoming group visited almost every CZO and produced geophysical measurements that complemented CZO efforts. The Wyoming team was highly successful in making broad ranging observations that synthesized ideas across CZOs and developed new theories and models. The salient feature of this effort was that it highlighted the use of a set of techniques to address important CZ questions, it was led by excellent scientists, it was well funded, it targeted multiple CZOs, and it was collaborative. Such a national campaign could be repeated to implement cross-CZO microbiological approaches, remote sensing approaches, modelling approaches, or other ideas. For example, a campaign to examine the role of fungus in governing weathering across the CZ has been highlighted in a recent synthesis effort examining the role of trees as plumbers of the CZ. Such an approach encourages CZ specialists to expand the scope of their work, to test the boundaries at which hypotheses and models begin to fail. Such endeavors could easily be led by junior researchers who already have expertise in one or more CZOs. These campaigns could focus on characterizing patterns over large spatial scales.

5. *CZ Synthesis Programs and CZ Postdoctoral Scholars* — Workshops have been very successful in moving CZ science forward over the past decade leading to multiple special issues (e.g., C-Q relationships in Water Resources Research; Isotopes in the CZ in Chemical Geology, Landscape Evolution from a CZ perspective in ESPL). In the past, such efforts have been funded by small grants or subgrants (e.g., $25k or less from individual CZOs or the NSF supported SAVI program) and have relied upon enthusiasm more than funded effort. We seek mechanisms that can promote such integrative efforts more systemically. One challenge as we move into the future, is to foster an environment where CZ data are integrated with data collected across other networks. One mechanism to accomplish this goal would be to support small competitive grants, similar to those of the USGS Powell Center program, which would fund diverse teams of researchers to work together over a relatively short period of time (1-2 y). Another idea that could promote synthesis would be a postdoctoral research program for junior researchers to address CZ questions that span the national scale and that necessarily incorporate data from multiple CZOs. A good example of the latter such effort is the ongoing research spearheaded by Ciaran Harman, Noah Molotch and Adam Wlostowski who are seeking to understand how CZ structure affects hydrologic partitioning.

6. CZ *Data Management Initiatives*. One of the most difficult aspects of CZ science is finding ways to publish data online in well documented formats chosen by scientists from each discipline. Publishing specific datasets with associated doi's has proven to be an effective way of conveying data to the scientific public, effectively archiving, and allowing the scientists who generate these datasets a means of obtaining credit. To push CZ science into the larger scientific community and heighten cross site comparisons we need to enhance and support these data sharing capabilities. In the first ten years of the program, NSF mostly funded a central group to provide data management. We discovered, however, that the large variety of CZ data required a more distributed approach. Currently, each CZO is pushing an effort to format and systematize key data sets from all CZOs that will prove valuable for individual disciplines. Some success has been observed from this grassroots approach. In the next ten years, we have the opportunity to push forward on this growth in data management capability by explicitly funding these distinct efforts. At the same time, we also argue there is a need to expand transdisciplinary CZ science to include computer science, and revolutionize the integration of earth science data both in terms of data retrieval, visualization and predictive capabilities that advance science, bring about necessary societal changes (e.g., reduction is CO_2 emissions) and help to sustain natural resources. Data management should be augmented in the next five years by promoting grassroots efforts to systematize data streams from disciplinary initiatives as well as to promote new cyber-enabled efforts in data mining, machine learning, visualization, and data assimilation.

4 CZ Educational Initiatives for the Future:

Given CZ science is a burgeoning field, there is a need to integrate into K-16 Ed and incorporate the story of place in a natural history context. We can use CZ science to help address the failures of systems teaching that have been identified by Don Duggan-Haas. An outreach component of the new proposals should yield materials that describe CZ concepts at each grade level. These can be delivered to teachers to use in classrooms. Additionally, we can expand RET programs to expose K-16 educators to CZ concepts in the field, that they can take back to the classroom. The relatively new Next Generation Science Standards (NGSS)—a multi-state effort, representing 35% of students in the USA, to provide students an internationally benchmarked science education— propose using environmental contexts to teach basic science concepts and systems thinking. An effort to incorporate CZ science in implementing the NGSS would help instill a CZ approach in the rising generation of both citizens and scientists alike. At the post-secondary level, CZ science could be incorporated into existing science courses through the use of InTeGrate teaching materials (available through the Science Education Resources Center at Carleton College; e.g. White et al. 2017), which use data collected from CZOs to teach about CZ form and function, especially as it relates to human activities and decision-making.

In the coming decade, there is a key need to develop a CZ public and policy maker communication plan that helps to package information gleaned from CZ science and demonstrates how this knowledge informs key CZ services. One mechanism to facilitate this plan would be to create a CZ-centric version of the Leopold Fellowships, which train ecological scientists to engage more effectively in the public arena.

Finally, CZ science needs to reach the broader public through entities like PBS Media Learning Center and the CZO Youtube channel. Opportunities like these let us bring CZ science into everyone's home and provide a platform to train the public in transdisciplinary CZ thinking.

Conclusion:

With over a decade of CZ science now behind us, we stand poised to predict CZ structure, dynamics and evolution. Integration across broad spatial scales, temporal scales and scientific fields creates an incubator for developing novel approaches and solutions to meet societal needs for potable water, nutritious food and a sustainable environment. We propose that the next step to achieve this outcome requires us to continue opening the "black box" of the CZ. By elucidating linear and non-linear behavior in CZ function and removing the bounds of the steady-state assumption, we will be much better able to anticipate how the CZ will evolve over time. The trajectory of CZ science now focuses on five questions posed by the next generation of CZ science:

(i) As energy propagates through the CZ, how does it drive the emergence of patterns in porosity, fracturing, permeability, grain size, mineralogy, and micro-organisms and how are these patterns distributed at depth and across landscapes?

(ii) What role does the deep CZ play in regulating terrestrial carbon dynamics?

(iii) How do CZ services evolve in response to anthropogenic and natural disturbance?
   a. As the CZO network grows and integrates models and data, where should new observatories be located?
   b. How will climate change alter the CZ and how will CZ services respond to extremes in weather?

(iv) How can observatory measurements and models be extrapolated to explain global feedbacks in climate, weathering, and tectonics?
   a. Can we classify the types of critical zones and quantify them with appropriate dimensionless numbers that describe the form, function, and dynamics?
   b. How can methods of data assimilation be used in critical zone science to create forward-predictive models

(v) How do we integrate CZ science into educational efforts at all levels and also promote the CZ approach among scientists, managers, and policy makers?

References

Abban B, Papanicolaou AN, Cowles MK, Wilson CG, Abaci O, Wacha K, Schilling K, and Schnoebelen D (2016). An enhanced Bayesian fingerprinting framework for studying sediment source dynamics in intensively managed landscapes. Water Resources Research.

Aciego SM, Riebe CS, Hart SC, Blakowski MA, Carey CJ, Aarons SM, Dove NC, Botthoff JK, Sims KWW, Aronson EL. (2017) Dust outpaces bedrock in nutrient supply to montane forest ecosystems. Nature Communications 8, 1–10. doi: 10.1038/ncomms14800

Anderson KE, Glenn NF, Spaete LP, Shinneman DJ, Pilliod DS, Arkle RS, McIlroy SK, Derryberry DWR (2017). Methodological considerations of terrestrial laser scanning for vegetation monitoring in the sagebrush steppe. Environmental Monitoring and Assessment 189. doi: 10.1007/s10661-017-6300-0

Anderson SW, Anderson SP, and Anderson RS (2015). Exhumation by debris flows in the 2013 Colorado Front Range storm. Geology 43(5), 391-394.

Anderson, RS, Anderson, SP, and Tucker, GE (2013). Rock damage and regolith transport by frost: An example of climate modulation of critical zone geomorphology. Earth Surface Processes and Landforms 38, 299-316

Anderson, SP, Dietrich, WE, Montgomery, DR, Torres, R, Conrad, ME, and Loague, K (1997). Subsurface flow paths in a steep, unchanneled catchment. Water Resources Research 33 (12): 2637-2653.

Anderson, SP, and Dietrich, WE (2001). Chemical weathering and runoff chemistry in a steep, headwater catchment. Hydrological Processes 15, 1791-1815.

Anderson SP, Anderson RS, and Tucker GE (2012). Landscape scale linkages in critical zone evolution. Comptes rendus- Geoscience 344, 586-596.

Anderson, SP, Hinckley, E-L, *Kelly, P, *Langston, A (2014). Variation in critical zone processes and architecture across slope aspects, Procedia Earth and Planetary Science 10: 28-33, doi:10.1016/j.proeps.2014.08.006.

Anderson, SP, Wlostowski, A, Murphy, SF, and Rock, N (in prep). Lessons in watershed hydrology from a semi-arid basin with ephemeral snow. For Hydrological Processes.

Aguirre A, Derry LA, Mills TJ, and Anderson S (2017). Colloidal transport in the Gordon Gulch catchment of the Boulder Creek CZO and its effect on C-Q relationships for silicon, germanium, aluminum and iron. Water Resources Research, 53:16, doi: 10.1002/2016WR019730.

Arvin LJ, Riebe CS, Aciego SM, Blakowski M. (in review) Global patterns of dust and bedrock nutrient supply to montane ecosystems. Science Advances

Austin, J.C., Perry, A., deB Richter, D. and Schroeder, P.A. (In Review) Modifications of 2:1 clay minerals in a kaloinite dominated Ultisol under changing land-use regimes. Clays and Clay Minerals.

Bales RC, Hopmans JW, O'Geen AT, Meadows M, Hartsough PC, Kirchner P, Hunsaker CT, and Beaudette D (2011). Soil moisture response to snowmelt and rainfall in a Sierra Nevada mixed-conifer forest. Vadose Zone Journal 10, 786-799.

Ballantyne IV F and Billings SA. (in revision). Model formulation of microbial CO2 production and efficiency can significantly influence short and long term soil C projections. International Society for Microbial Ecology Journal.

Bao C, Li L, Shi Y, and Duffy C. (2017) Understanding watershed hydrogeochemistry: 1. Development of RT-Flux-PIHM. Water Resour. Res. 53, 2328-2345.

Bazilevskaya E, Rother G, Mildner DFR, Pavich M, Cole D, Bhatt MP, Jin L, Steefel CI, Brantley SL (2015). How oxidation and dissolution in diabase and granite control porosity during weathering. Soil Science Society of America Journal 79, 55-73.

Bearup LA, Maxwell RM, Clow DW, and McCray JE (2014a). Hydrological effects of forest transpiration loss in bark beetle-impacted watersheds. Nature Climate Change 4(6), 481-486.

Bearup LA, Mikkelson KM, Wiley JF, Navarre-Sitchler AK, Maxwell RM, Sharp JO, and McCray JE (2014b). Metal fate and partitioning in soils under bark beetle-killed trees. Science of the Total Environment 496, 348-357.

Billings SA, Hirmas D, Sullivan PL, Lehmeier CA, Bagchi S, Min K, Brecheisen Z, Hauser E, Stair R, Flournoy R, Richter D deB (in review). Loss of deep roots limits biogenic agents of soil development only partially restored by 80 y of forest regeneration. Elementa.

Borsa AA, Agnew DC, and Cayan DR (2014). Ongoing drought-induced uplift in the western United States. Science 345(6204), 1587-1590.

Brantley SL, Holleran MW, Jin L, and Basilevskaya E (2013). Probing deep weathering in the Shale Hills Critical Zone Observatory, Pennsylvania (USA): The hypothesis of nested chemical reaction fronts in the subsurface: Earth Surface Processes and Landforms 38 (11), 1280–1298, doi: 10.1002/esp.3415.

Brantley SL, McDowell WH, Dietrich WE, White TS, Kumar P, Anderson S, Chorover J, Loshe KA, Bales RC, Richter D, Grant JG, Gaillardet J (2017). Designing a network of critical zone observatories to explore the living skin of the terrestrial Earth. Earth Surface Dynamics Discussion.

Brantley SL, White TS, White AF, Sparks D, Richter D, Pregitzer K, Derry L, Chorover J, Chadwick O, April R, Anderson S, and Amundson R (2006). Frontiers in Exploration of the Critical Zone: Report of a workshop sponsored by the NSF Newark, DE, p. 30.

Bressan F, Papanicolaou AN, and Abban BK (2014). A model for knickpoint migration in first- and second-order streams. Geophysical Research Letters 41(14), 4987-4996. doi:10.1002/2014GL060823

Bring A, Fedorova I, Dibike Y, Hinzman L, Mård J, Mernild SH, Prowse T, Semenova O, Stuefer SL, and Woo MK (2016). Arctic terrestrial hydrology: A synthesis of processes, regional effects, and research challenges. Journal of Geophysical Research. Biogeosciences 121(3), 621-649

Brocard GY, Willenbring JK, Miller TE, and Scatena FN (2016). Relict landscape resistance to dissection by upstream migrating knickpoints. Journal of Geophysical Research: Earth Surface 121(6), 1182-1203.

Brunke MA, Broxton P, Pelletier J, Gochis D, Hazenberg P, Lawrence DM, Leung LR, Niu GY, Troch PA, and\ Zeng X (2016). Implementing and Evaluating Variable Soil Thickness in the Community Land Model, Version 4.5 (CLM4. 5). Journal of Climate 29, 3441-3461.

Budyko MI. 1947. Climate and Life, Elsevier, New York, p.508.

Chadwick OA, Derry LA, Vitousek PM, Huebert BJ and Hedin LO (1999). Changing sources of nutrients during four million years of ecosystem development. Nature, 397(6719), 491.

Chambers LG, Chin YP, Filippelli GM, Gardner CB, Herndon EM, Long DT, Lyons WB, Macpherson GL, McElmurry SP, McLean CE, Moore J, Moyer RP, Neumann K, Nezat CA, Soderberg K, Teutsch N, and Widom E (2016). Developing the scientific framework for urban geochemistry. Applied Geochemistry 67, 1-20.

Chandler DG, Cheng Y, Seyfried MS, Madsen MD, Johnson CE and Williams JW (in review). Seasonal wetness, soil organic carbon and fire influence soil hydrological properties and water repellency in a sagebrush-steppe ecosystem. Water Resources Research.

Chauvin GM, Flerchinger GN, Link TE, Marks D, Winstral AH, Seyfried MS (2011). Long-term water balance and conceptual model of a semi-arid mountainous catchment. Journal of Hydrology 400, 133-143. doi: 10.1016/j.jhydrol.2011.01.031

Chen F and Dudhia J (2001). Coupling an advanced land surface-hydrology model with the Penn State-NCAR MM5 modeling system. Part I: Model implementation and sensitivity. Monthly Weather Review 129, 569-585.

Cohen S, Willgoose G, Svoray T, Hancock G, and Sela S (2015). The effects of sediment transport, weathering, and Aeolian mechanisms on soil evolution. Journal of Geophysical Research: Earth Surface 120, 260-274.

Comas X, Wright W, Hynek S, Orlando J, Buss H, Brantley SL, and Fletcher RC. (in preparation). Understanding the architecture of the deep critical zone and its relation to knickpoint evolution in the Rio Icacos watershed (Luquillo Critical Zone Observatory, Puerto Rico) using hydrogeophysical methods combined with stress modeling. Earth Surface Processes and Landforms.

Corenblit D, Baas AC, Bornette G, Darrozes J, Delmotte S, Francis RA, Gurnell AM, Julien F, Naiman RJ, and Steiger J (2011). Feedbacks between geomorphology and biota controlling Earth surface processes and landforms: a review of foundation concepts and current understandings. Earth-Science Reviews 106(3), 307-331.

Cowley GS, Niemann JD, Green TR, Seyfried MS, Jones AS, Grazaitis PJ (2017). Impacts of precipitation and potential evapotranspiration patterns on downscaling soil moisture in regions with large topographic relief. Water Resources Research 53, 1553-1574. doi:10.1002/2016WR019907

Daley R (1991). Atmospheric Data Analysis. Cambridge University Press.

Davis CA, Ward AS, Burgin AJ, Loecke TD, Riveros-Iregui DA, Schnoebelen DJ, Just CL, Thomas SA, Weber LJ, and St. Clair MA (2014). Antecedent Moisture Controls on Stream Nitrate Flux in an Agricultural Watershed. Journal of Environmental Quality.

Dere AL, White TS, April RH, Reynolds B, Miller TE, Knapp EP, McKay LD, and Brantley SL (2013). Climate dependence of feldspar weathering in shale soils along a latitudinal gradient. Geochim. Cosmochim. Acta 122, 101-126. doi:110.1016/j.gca.2013.08001.

Druhan JL, Fernandez N, Wang J, Dietrich WE, and Rempe D (2014). Seasonal shifts in the solute ion ratios of vadose zone rock moisture from the Eel River Critical Zone Observatory. Acta Geochimica: 1-4.

Druhan J, Lawrence C, Oster J, Rempe D, and Dietrich W (2017). From the surface to the deep critical zone: Linking soil carbon, fluid saturation and weathering rate. In EGU General Assembly Conference Abstracts 19, 13803.

Druhan JL, Steefel CI, Conrad ME and DePaolo DJ (2014). A large column analog experiment of stable isotope variations during reactive transport: I. A comprehensive model of sulfur cycling and δ34S fractionation. Geochimica Et Cosmochimica Acta 124, 366-393.

Druhan JL and Maher K (2017). The influence of mixing on stable isotope ratios in porous media: A revised Rayleigh model. Water Resources Research 53, 1101-1124.

Duffy C, Shi Y, Davis K, Slingerland R, Li L, Sullivan PL, Goddéris Y and Brantley SL (2014). Designing a Suite of Models to Explore Critical Zone Function. Procedia Earth and Planetary Science 10, 7-15.

Duggan-Haas D, Ross RM, White T, Moore A, Derry LA (2017). Critical Zone Science is to Science as the Next Generation Science Standards are to Science Education. Geol. Soc. America Abstr. Progs. #183-13.

Duggan-Haas D, White T, Ross RM, and Derry L (2016). Opportunities for Professional Development And Curriculum Support From The Critical Zone Observatory Network, Geol Soc. Amer. Abstr. Progs.. 48:2, 11-4. doi: 10.1130/abs/2016NE-272148.

Duggan-Haas D, White T, Ross R, and Derry L (2015). Critical Zone Observatories, Virtual Fieldwork Experiences, The Next Generation Science Standards, and Teaching In and About Complex Systems. Geol Soc. Amer. Abstr. Progs 46, 242-7.

Dühnforth M, and Anderson RS (2011). Reconstructing the glacial history of green lakes valley, North Boulder Creek, Colorado front range. Arctic, Antarctic, and Alpine Research 43(4), 527-542.

Ebel BA, Loague K, Montgomery DR, and Dietrich WE (2008). Physics-based continuous simulation of long-term near-surface hydrologic response for the Coos Bay experimental catchment. Water Resources Research, 44(7), W07417.

Eilers KG, Debenport S, Anderson S, and Fierer N (2012). Digging deeper to find unique microbial communities: The strong effect of depth on the structure of bacterial and archaeal communities in soil. Soil Biology & Biochemistry 50, 58-65.

Enslin C (2016). Understanding the rain-to-snow transition zone: modeling snowmelt and the spatial distribution of water resources in southwestern Idaho. [M.S. Thesis] Pocatello, Idaho State University, 100 p

Evensen G (1994). Sequential data assimilation with a nonlinear quasi-geostrophic model using Monte Carlo methods to forecast error statistics. Journal of Geophysical Research: Oceans 99, 10143-10162.

Fan Y, and Bras RL (1998). Analytical solutions to hillslope subsurface storm flow and saturation overland flow. Water Resources Research 34, 921-927.

Fellows A, Flerchinger G, Lohse KA, and Seyfried M (in review). Rapid recovery of gross production and respiration in a mesic mountain big sagebrush ecosystem following prescribed fire Ecosystems.

Field JP, Breshears DD, Law DJ, Villegas JC, López-Hoffman L, Brooks PD, ... and Lybrand RA (2015). Critical Zone services: Expanding context, constraints, and currency beyond ecosystem services. Vadose Zone Journal, 14(1).

Flerchinger GN, Seyfried MS, Hardegree SP (2016). Hydrologic response and recovery to prescribed fire and vegetation removal in a small rangeland catchment. Ecohydrology 9,1604-1619. doi: 10.1002/eco.1751

Fletcher TD, Andrieu H, and Hamel P (2013). Understanding, management and modelling of urban hydrology and its consequences for receiving waters: a state of the art. Advances in Water Resources 51, 261–279.

Fletcher RC, Buss HL, and Brantley SL (2006). A spheroidal weathering model coupling porewater chemistry to soil thicknesses during steady-state denudation, Earth and Planetary Science Letters 244, 444-457.

Flinchum B, Holbrook WS, Rempe DM, Moon S, Riebe C, Carr B, Hayes J, St. Clair, and Peters M. (In review) Critical zone structure under a granite ridge inferred from drilling and three-dimensional seismic refraction data. Journal of Geophysical Research Earth Surface.

Ford DC, and Williams P (2007). Karst hydrogeology and geomorphology. Academic Division of Unwin Hyman Ltd, p.601.

Foster, M.A., Anderson, R.S., Gray, H.J., and Mahan, S.A., 2017. Dating of river terraces along Lefthand Creek, western High Plains, Colorado, reveals punctuated incision. Geomorphology 295, 176-190.

Gabet EJ, and Mudd SM (2010). Bedrock erosion by root fracture and tree throw: A coupled biogeomorphic model to explore the humped soil production function and the persistence of hillslope soils. Journal of Geophysical Research: Earth Surface 115, F4.

Gabor RS, Eilers K, McKnight DM, Fierer N, and Anderson SP (2014). From the litter layer to the saprolite: Chemical changes in water-soluble soil organic matter and their correlation to microbial community composition. Soil Biology & Biochemistry 68, 166-176.

Gaillardet J, Dupré B, Louvat P, and Allegre CJ (1999). Global silicate weathering and CO2 consumption rates deduced from the chemistry of large rivers. Chemical Geology 159, 3–30.

Godsey SE, Marks D, Kormos PR, Seyfried MS, Enslin CL, Winstral AH, McNamara JP, Link TE (In review). Eleven years of mountain weather, snow, soil moisture and stream flow data from the rain-snow transition zone - the Johnston Draw catchment, Reynolds Creek Experimental Watershed and Critical Zone Observatory, USA. Earth System Science Data. Discussion-only doi: doi.org/10.5194/essd-2017-112.

Grimley D, Anders A, Bettis EA, Bates B, Wang, Butler S, and Huot S (2017). Using Magnetic Fly Ash to Identify Post-Settlement Alluvium and its Record of Atmospheric Pollution, Central USA. Anthropocene.

Groffman PM, Cavender-Bares J, Bettez ND, Grove JM, Hall SJ, Heffernan JB, Hobbie SE, Larson KL, Morse JL, Neill C, Nelson K, O'Neil-Dunne J, Ogden L, Pataki DE, Polsky C, Roy Chowdhury R, and Steele MK (2014). Ecological homogenization of urban USA. Frontiers in Ecology and the Environment 12, 74-81.

Gu X, Mildner DFR, Cole DR, Rother G, Slingerland R, and Brantley SL (2016). Quantification of Organic Porosity and Water Accessibility in Marcellus Shale Using Neutron Scattering. Energy Fuels 30(6), 4438-4449.

Gu X, Rempe DM, Dietrich WE, West J, Lin TC, Jin L, and Brantley SL (in preparation). Investigating the porosity development during shale weathering on hillslopes with different erosion rates. Earth and Planetary Science Letters.

Hahm WJ, Riebe CS, Lukens CE, and Araki S (2014). Bedrock composition regulates mountain ecosystems. Proceeding of National Academy of Science 111, 3338–3343.

Harpold AA, Guo Q, Molotch N, Brooks PD, Bales R, Fernandez-Diaz RC, Musselman KN, Swetnam TL, Kirchner P, Meadows MW, Flanagan J and Lucas R (2014). LiDAR-derived snowpack data sets from mixed conifer forests across the Western United States. Water Resources Research 50(3), 2749-2755.

Harman C and Troch PA (2014). What makes Darwinian hydrology" Darwinian"? Asking a different kind of question about landscapes. Hydrology and Earth System Sciences, 18(2), 417-433.

Hasenmueller EA, Gu X, Weitzman JN, Adams TS, Stinchcomb GE, Eissenstat DM, Drohan PJ, Brantley SL and Kaye JP (2017). Weathering of rock to regolith: The activity of deep roots in bedrock fractures. Geoderma 300, 11-31.

Hayes JL, Riebe CS, Holbrook WS, Flinchum BA, and Hartsough PC (in review). Porosity production in weathered rock: Where volumetric strain dominates over chemical mass loss. Science Advances.

Heimsath AM, Dietrich WE, Nishiizumi K, and Finkel RC (1997). The soil production function and landscape equilibrium. Nature 388, 358-361.

Herndon EM, Jin L, Andrews DM, Eissenstat DM, and Brantley SL (2015). Importance of vegetation for manganese cycling in temperate forested watersheds. Global Biogeochemical Cycles 29, 160–174.

Herndon EM, Jin L, Brantley SL (2011). Soils reveal widespread manganese enrichment from industrial inputs. Environmental Science Technology 45 (1), 241–247.

Herndon EM, Martínez CE, and Brantley SL (2014). Spectroscopic (XANES/XRF) characterization of contaminant manganese cycling in a temperate watershed. Biogeochemistry 121(3), 505-517.

Hinckley, E-L, Barnes, RT, Anderson, SP, Williams, MW, and Bernasconi, S (2014). Nitrogen retention and transport differ by hillslope aspect at the rain-snow transition of the Colorado Front Range. Journal of Geophysical Research-Biogeosciences 119 (7): 1281-1296, doi:10.1002/2013JG002588.

Hinckley, ES, Ebel, BA, Barnes, RT, Murphy, SF, and Anderson, SP (2017). Critical zone properties control the fate of nitrogen during experimental rainfall in montane forests of the Colorado Front Range. Biogeochemistry 132 (1): 213-231, doi:10.1007/s10533-017-0299-8.

Hinzman LD, Deal CJ, McGuire AD, Mernild SH, Polyakov IV, and Walsh JE (2013). Trajectory of the Arctic as an integrated system. Ecological Applications 23, 1837–68.

Hoffman BS and Anderson RS (2014). Tree root mounds and their role in transporting soil on forested landscapes. Earth Surface Processes and Landforms 39(6), 711-722.

Holbrook WS, Bacon AR, Brantley SL, Carr BJ, Marcon V, and Richter D, (In review). Relating physical and chemical weathering of granite as revealed by borehole geophysical and geochemical data in the critical zone.

Holbrook WS, Riebe CS, Elwaseif ML, Hayes J, Basler-Reed KL, Harry DL, Malazian A, Doesseto A, Hartsough PC, and Hopmans JW (2014). Geophyscial constraints on deep weatheirng and water storage in the Southern Sierra Critical Zone Observatory. Earth Surface Processes and Landforms 39, 366-380.

Holleran M, Levi M, and Rasmussen C (2015). Quantifying soil and critical zone variability in a forested catchment through digital soil mapping. SOIL(1), 47-64

Hopkins K. G., Morse N. B., Bain D. J., Bettez N. D., Grimm N. B., Morse J. L., Palta M. M., Shuster W. D., Bratt A. R., and Suchy A. K. (2015) Assessment of regional variation in streamflow responses to urbanization and the persistence of physiography. Environmental Science & Technology 49, 2724-2732.

Hynek S, Comas X, and Brantley SL (2016). The effect of fractures on weathering of igneous and volcaniclastic sedimentary rocks in the Puerto Rican tropical rain forest. Procedia Earth and Planetary Science.

Jenkinson, D. S., & Coleman, K. (2008). The turnover of organic carbon in subsoils. Part 2. Modelling carbon turnover. European Journal of Soil Science 59(2), 400-413.

Jenny H (1941). Factors of soil formation: A system of quantitative pedology, p.281.

Jin L, Ravella R, Ketchum B, Bierman PR, Heaney P, White T, and Brantley SL (2010). Mineral weathering and elemental transport during hillslope evolution at the Susquehanna/Shale Hills Critical Zone Observatory. Geochimica et Cosmochimica Acta 74, 3669-3691.

Jobbágy EG and Jackson RB (2000). The vertical distribution of soil organic carbon and its relation to climate and vegetation. Ecological applications 10(2), 423-436.

Jobbágy EG, and Jackson RB (2004). The uplift of soil nutrients by plants: biogeochemical consequences across scales. Ecology 85(9), 2380-2389.

Karl TR, and Trenberth KE (2003). Modern global climate change. Science, 302(5651), 1719-1723.

Kaushal SS, McDowell WH, and Wollheim WM (2014). Tracking evolution of urban biogeochemical cycles: past, present, and future. Biogeochemistry 121, 1-21.

Kim H, Dietrich WE, Thurnhoffer BM, Bishop JKB, and Fung IY (2017) Controls on solute concentration-discharge relationships revealed by simultaneous hydrochemistry observations of hillslope runoff and stream flow: The importance of critical zone structure. Water Resources Research 53(2), 1424-1443.

Kraepiel AML, Dere AL, Herndon EM, and Brantley SL (2015). Natural and anthropogenic processes contributing to metal enrichment in surface soils of Central Pennsylvania. Biogeochemistry 123, 265–283.

Kumar P, Le PVV, Papanicolaou AN, Rhoads B L, Anders AM, Stumpf A, Wilson CG, Bettis III EA, Blair N, Ward AS, Filley T, Lin H, Keefer L, Keefer DA, Lin Y, Muste M, Royer TV, Foufoula-Georgiou E, and Belmont P (in review). Critical Transition in Critical Zone of Intensively Managed Landscapes.

Kurtz AC, Lugolobi F, and Salvucci G (2011). Germanium-silicon as a flow path tracer: Application to the Rio Icacos watershed. Water Resources Research, 47, doi: 10.1029/2010wr009853.

Langston A, Tucker GE, Anderson RS, and Anderson SP (2015). Evidence for climatic and hillslope-aspect controls on vadose zone hydrology and implications for saprolite weathering, Earth Surface Processes and Landforms 40, 1254-1269, doi:10.1002/esp.3718.

Le PVV, Kumar P, Valocchi AJ, and Dang HV (2015). GPU-based high-performance computing for integrated surface-sub-surface flow modeling. Env. Modeling & Software 73, 1-13.

Lebedeva M, Sak P, Ma L and Brantley S (2015). Using a mathematical model of a weathering clast to explore the effects of curvature on weathering. Chem. Geol. 404, 88-99.

Li A, Glenn NF, Olsoy PJ, Mitchell JJ, Shrestha R (2015). Aboveground biomass estimates of sagebrush using terrestrial and airborne LiDAR data in a dryland ecosystem. Ag & Forest Met 213, 138–47. doi:10.1016/j.agrformet.2015.06.005.

Li L, Bao C, Sullivan PL, Brantley S, Shi Y and Duffy C (2017a). Understanding watershed hydrogeochemistry: 2. Synchronized hydrological and geochemical processes drive stream chemostatic behavior. Water Resources Research 53, 2346-2367.

Li L, Maher K, Navarre-Sitchler A, Druhan J, Meile C, Lawrence C, Moore J, Perdrial J, Sullivan PL, Thompson A, Jin L, Bolton EW, Brantley SL, Dietrich WE, Mayer KU, Steefel CI, Valocchi A, Zachara J, Kocar B, McIntosh J, Tutolo BM, Kumar M, Sonnenthal E, Bao C and Beisman J (2017b). Expanding the role of reactive transport models in critical zone processes. Earth-Science Reviews 165, 280-301.

Liermann LJ, Albert I, Buss HL, Minyard M, and Brantley SL (2015). Relating Microbial Community Structure and Geochemistry in Deep Regolith Developed on Volcaniclastic Rock in the Luquillo Mountains, Puerto Rico. Geomicrobiology Journal 32, 494-510.

Lui Z and Zhao J (2000). Contribution of carbonate rock weathering to the atmospheric CO2 sink. Environmental Geology 39, 1052-1058. doi: 10.1007/s002549900072.

Lybrand RA and Rasmussen C (2015). Quantifying Climate and Landscape Position Controls on Soil Development in Semiarid Ecosystems. Soil Science Society of America Journal 79(1), 104-116.

Ma L, Jin L and Brantley, SL (2011). How mineralogy and slope aspect affect REE release and fractionation during shale weathering in the Susquehanna/Shale Hills Critical Zone Observatory. Chemical Geology, 290, 31-49.

Ma L, Konter J, Herndon E, Jin L, Steinhoefel G, Sanchez D, and Brantley SL (2014). Quantifying an early signature of the industrial revolution from lead concentrations and isotopes in soils of Pennsylvania, USA. Antaeus 7, 16–29.

Madole RF (1963). Quaternary geology of St. Vrain Basin, Boulder County, Colorado: PhD Dissertation, p. 289.

Macpherson GL (2008). CO_2 distribution in groundwater and the impact of groundwater extraction on the global C cycle. Chemical Geology 264: 328-336. doi:10.1016/j. chemgeo.2009.03.018.

Manning AH, Verplanck PL, Caine JS, and Todd AS (2013). Links between climate change, water-table depth, and water chemistry in a mineralized mountain watershed. Applied geochemistry, 37, 64-78.

Marshall JA, Anderson RS, Dawson TE, Dietrich WE, Sklar LS (2016). Quantifying the role of trees as Critical Zone architects employing crowbars, wedges and other tools of soil production. Eos: American Geophysical Union Fall Meeting, San Francisco, Abstract EP43C-0968.

Marshall JA, Roering JJ, Bartlein PJ, Gavin DG, Granger DE, Rempel AW, Praskievicz SJ, and Hales TC (2015). Frost for the trees: Did climate increase erosion in unglaciated landscape during the later Pleistocene? Science Advances 1 (10), e1500715.

McClintock MA, Brocard G, Willenbring J, Tamayo C, Porder S, and Pett-Ridge JC (2015). Spatial variability of African dust in soils in a montane tropical landscape in Puerto Rico. Chemical Geology

McGranahan G, Balk D and Anderson B (2007). The rising tide: assessing the risks of climate change and human settlements in low elevation coastal zones. Environment and urbanization 19(1), 17-37.

McIntosh JC, Porter C, Perdrial J, Harpold A, Vázquez-Ortega A, Rasmussen C, Vinson D, Zapata-Rios X, Brooks PD, Meixner T, Pelletier J, Derry L, and Chorover J (2017). Geochemical evolution of the Critical Zone on variable time scales informs concentration-discharge relationships: Jemez River Basin Critical Zone Observatory. Water Resources Research 53, 4169–4196, doi:10.1002/2016WR019712.

Meixner T, Bales RC, Williams MW, Campbell DH and Baron JS (2000). Stream chemistry modeling of two watersheds in the Front Range, Colorado. Water Resour. Res. 36, 77-87.

Minyard ML, Bruns MA, Liermann LJ, Buss HL, and Brantley SL (2012). Bacterial associations with weathering minerals at the regolith-bedrock interface, Luquillo Experimental Forest, Puerto Rico. Geomicrobiology Journal 29, 792-803, doi:710.1080/01490451.01492011.01619640.

Moore A, Duggan-Haas D, Ross RM, and Derry LA (2017). Explore the Critical Zone through the CZO network. Geol. Soc. America Abstr. Progs. #362-2.

Mudd SM, and Furbish DJ (2007). Responses of soil-mantled hillslopes to transient channel incision rates. Journal of Geophysical Research: Earth Surface 112(F3).

Murray AB, Lazarus E, Ashton A, Baas A, Coco G, Coulthard T, Fonstad M, Haff P, McNamara D, Paola C, Pelletier J and Reinhardt L (2009). Geomorphology, complexity, and the emerging science of the Earth's surface. Geomorphology 103, 496-505.

Muhs DR, Bush CA, Stewart KC, Rowland TR, and Crittenden RC. (1990). Geochemical evidence of Saharan dust parent material for soils developed on Quaternary limestones of Caribbean and western Atlantic islands. Quaternary Research 33(2), 157-177.

Navon I (2009). Data assimilation for numerical weather prediction: a review, in: Park, S., L, X. (Eds.), Data assimilation for atmospheric, oceanic, hydrologic applications. Springer, Berlin.

Neff JC, Ballantyne AP, Farmer GL, Mahowald NM, Conroy JL, Landry CC, Overpeck JT, Painter TH, Lawrence CR, and Reynolds RL. (2008). Increasing eolian dust deposition in the western United States linked to human activity. Nature Geoscience 1(3), 189-195.

Niu GY, Paniconi C, Troch PA, Scott RL, Durcik M, Zeng X, Huxman T and Goodrich DC (2014). An integrated modelling framework of catchment-scale ecohydrological processes. Ecohydrol. 7, 427–439.

Olinde L and Johnson JPL (2015). Using RFID and accelerometer-embedded tracers to measure probabilities of bed load transport, step lengths, and rest times in a mountain stream. Water Resources Research 51:7572-7589.10.1002/2014WR016120

Olsoy PJ, Mitchell JJ, Levia DF, Clark PE, Glenn NF (2016). Estimation of big sagebrush leaf area index with terrestrial laser scanning. Ecological Indicators 61:815-821.10.1016/j.ecolind.2015.10.034

Olyphant J, Pelletier JD, and Johnson R (2016). Topographic correlations with soil and regolith thickness from shallow-seismic refraction constraints across upland hillslopes in the Valles Caldera, New Mexico. Earth Surface Processes and Landforms 41, 1684-1696.

Orem CA, and Pelletier JD (2016). The predominance of post-wildfire erosion in the long-term denudation of the Valles Caldera, New Mexico. J. Geophys. Res. Earth Surf. 121, 843–864. doi:10.1002/2015JF003663

Orlando J, Comas X, Hynek SA, Buss HL, and Brantley SL (2016). Architecture of the deep critical zone in the Rio Icacos watershed (Luquillo Critical Zone Observatory, Puerto Rico) inferred from drilling and ground penetrating radar (GPR). Earth Surface Processes and Landforms 41, 1826-1840.

Pandey S, and Rajaram H (2016). Modeling the influence of preferential flow on the spatial variability and time-dependence of mineral weathering rates. Water Resour. Res. 52, 9344-9366.

Papanicolaou AN, Elhakeem M, Wilson CG, Burras CL, West LT, Lin H, Clark B, and Oneal BE (2015b). Spatial variability of saturated hydraulic conductivity at the hillslope scale: Understanding the role of land management and erosional effect. Geoderma.

Papanicolao AN, Thomas JT, Wilson CG, Bettis EA, and Elhakeem M (2017b). Mechanisms of knickpoint migration in a channelized western Iowa stream. Earth Surface Processes and Landforms. In preparation.

Papanicolaou AN, Wacha KM, Abban BK, Wilson CG, Hatfield J, Stanier C, and Filley T (2015a). From soilscapes to landscapes: A landscape-oriented approach to simulate soil organic carbon dynamics in intensively managed landscapes. Journal of Geophysical Research: Biogeosciences.

Papanicolaou AN, Wilson CG, Tsakiris AG, Sutarto TE, Bertrand F, Rinaldi M, Dey S, and Langendoen E (2017a). Understanding mass fluvial erosion along a bank profile: Using PEEP technology for Quantifying Retreat Lengths and Identifying Event Timing. Earth Surface Processes and Landforms.

Parsekian AD, Singha K, Minsley BJ, Holbrook WS, and Slater L (2015). Multiscale geophysical imagine of the critical zone. Reviews of Geophysics 53, 1-26

Patton NR, Lohse KA, Godsey SE, Seyfried MS, Crosby BT (In Review). Predicting soil thickness on soil mantled hillslopes. Nature Communications.

Pelletier JD, Barron-Gafford GA, Breshears DD, Brooks PD, Chorover J, Durcik M, Harman CJ, Huxman TE, Lohse KA, Lybrand R, and Meixner T (2013). Coevolution of nonlinear trends in vegetation, soils, and topography with elevation and slope aspect: A case study in the sky islands of southern Arizona. Journal of Geophysical Research: Earth Surface 118(2), 741-758.

Pelletier JD and Swetnam TL (2017). Asymmetry of weathering-limited hillslopes: the importance of diurnal covariation in solar insolation and temperature. Earth Surface Processes and Landforms.

Perron JT, Dietrich WE, and Kirchner JW (2008). Controls on the spacing of first-order valleys. Journal of Geophysical Research: Earth Surface, 113 (F4).

Pett-Ridge JC (2009). Contributions of dust to phosphorus cycling in tropical forests of the Luquillo Mountains, Puerto Rico. Biogeochemistry 94,63-80.
Pewe TL (1981). Desert dust: an overview. Desert dust: Origin, characteristics, and effect on man 186, 1-10.
Poley A, Glenn N, Spaete L, Mitchell J, Dashti H (In preparation) Hyperspectral derived vegetation species and cover across landscape gradients in semi-arid ecosystems using multiple endmember spectral mixture analysis coupled with optimal endmember bundling.
Prospero JM, Glaccum RA, and Nees RT (1981). Atmospheric transport of soil dust from Africa to South America. Nature 289(5798), 570-572.
Pye K (1995). The nature, origin and accumulation of loess. Quaternary Science Reviews 14(7), 653-667.
Rabier F (2005). Overview of global data assimilation developments in numerical weather-prediction centres. Quarterly Journal of the Royal Meteorological Society 131, 3215-3233.
Rasmussen C, Pelletier JD, Troch PA, Swetnam TL and Chorover J (2015). Quantifying Topographic and Vegetation Effects on the Transfer of Energy and Mass to the Critical Zone. Vadose Zone Journal 14(11), doi 10.2136/vzj2014.07.0102.
Raymond PA and Cole JJ. 2003. Increase in the export of alkalinity of North America's largest river. Science 301, 88-90.
Raymond PA, Oh NH, Eugene Turner R and Broussard. Anthropogenically enhances fluxes of water and carbon from the Mississippi River. Nature 451, 449-452. doi:10.1038/nature06505.
Rech JA, Reeves RW, and Hendricks DM (2001). The influence of slope aspect on soil weathering processes in the Springerville volcanic field, Arizona. Cantena 43, 49-62.
Rempe DM (2016). Controls on critical zone thickness and hydrologic dynamics at the hillslope scale. PhD diss., University of California, Berkeley.
Rempe DM and Dietrich WE (2014). A bottom-up control on fresh-bedrock topography under landscapes. Proceedings of the National Academy of Sciences 111, 6576-6581.
Rempel AW, Marshall JA and Roering JJ (2016). Modeling relative frost weathering rates at geomorphic scales. Earth and Planetary Science Letters 453, 87-95.
Rhoads BL, Lewis QW, and Andresen W. (2015). Historical changes in channel network extent and channel planform in an intensively managed landscape: Natural versus human-induced effects. Geomorphology.
Richter DD (2007). Humanity's transformation of Earth's soil: Pedology's new frontier. Soil Science.
Richter DD and Billings SA (2015). 'One physical system': Tansley's ecosystem as Earth's critical zone. New Phytologist 206(3), 900-912.
Riebe CS, Hahm WJ, and Brantley SL (2017). Controls on deep critical zone architecture: a historical review and four testable hypotheses. Earth Surface Processes and Landforms 42(1), 128-156.
Roering JJ, Marshall J, Booth AM, Mort M, and Jin Q (2010). Evidence for biotic controls on topography and soil production, Earth and Planetary Science Letters 298, 183-190.
Rue GP, Rock ND, Gabor RS, Pitlick J, Tfaily M, and McKnight DM (2017). Concentration-discharge relationships during an extreme event: Contrasting behavior of solutes and changes to chemical quality of dissolved organic material in the Boulder Creek Watershed during the September 2013 flood. Water Resour. Res. 53, doi:10.1002/2016WR019708.
Salome C, Nunan N, Pouteau V, Lerch TZ, and Chenu C (2010). Carbon dynamics in topsoil and in subsoil may be controlled by different regulatory mechanisms. Global Change Biology 16(1), 416-426.
Salve R, Rempe DM, and Dietrich WE (2012). Rain, rock moisture dynamics, and the rapid response of perched groundwater in weathered, fractured argillite underlying a steep hillslope. Water Resources Research 48(11).
Schwinning S (2010). The ecohydrology of roots in rocks. Ecohydrology 3, 238-245.
Schuur EAG, Abbott BW, Bowden WB, Brovkin V, Camill P, Canadell JG, Chanton JP, Chapin FS, Christensen TR, Ciais P and Crosby BT (2013). Expert assessment of vulnerability of permafrost carbon to climate change. Climatic Change 119(2), 359-374.
Schuur EAG, Bockheim J, Canadell JG, Euskirchen E, Field CB, Goryachkin SV, Hagemann S, Kuhry P, Lafleur PM, Lee H, Mazhitova G, Nelson FE, Rinke A, Romanovsky VE, Shiklomanov N, Tarnocai C, Venevsky S, Vogel JG, and Zimov SA (2008). Vulnerability of Permafrost Carbon to Climate Change: Implications for the Global Carbon Cycle. BioScience 58, 701.
Seyfried MS, Grant LE, Marks D, Winstral A, McNamara J. (2009). Simulated soil water storage effects on streamflow generation in a mountainous snowmelt environment, Idaho, USA. Hydrological Processes 23, 858-873. doi: 10.1002/hyp.7211
Shi Y, Davis KJ, Duffy CJ, and Yu X (2013). Development of a Coupled Land Surface Hydrologic Model and Evaluation at a Critical Zone Observatory. Journal of Hydrometeorology 14, 1401-1420.

Shi Y, Davis KJ, Zhang F, Duffy CJ, and Yu X (2015). Parameter estimation of a physically-based land surface hydrologic model using an ensemble Kalman filter: A multivariate real-data experiment. Advances in Water Resources, doi: 10.1016/j.advwatres.2015.1006.1009.

St. Clair J, Moon S, Holbrook S, Perron JT, Riebe CS, Martel S, Carr B, Harman C, Singha K, Richter D (2015). Geophysical imaging reveals topographic stress control of bedrock weathering. Science 350, 534-538, doi: 510.1126/science.aab2210.

Sullivan PL, Ma L, West N, Jin L, Karwan DL, Noireaux J, Steinhoefel G, Gaines KP, Eissenstat DM, Gaillardet J, Derry LA, Meek K, Hynek S, and Brantley SL (2016). CZ-tope at Susquehanna Shale Hills CZO: Synthesizing multiple isotope proxies to elucidate Critical Zone processes across timescales in a temperate forested landscape. Chemical Geology, 445, pp.103-119.

Sullivan PL, Goddéris Y, Gu X, Schott J, Hasenmueller EA, Kaye J, Duffy C, Jin L, Brantley SL (in review). Earthcasting reveals weathering fluxes increase with warming temperature but decrease with nutrient cycling. J. Geophys. Res. Earth Surf.

Sutarto TE, Papanicolaou AN, Wilson CG, and Langendoen E (2013).A stability analysis of semi-cohesive streambanks with CONCEPTS: Couple field and laboratory investigations to quantify the onset of fluvial erosion and mass failure. Journal of Hydraulic Engineering-ASCE.

Tanner CJ, Adler FR, Grimm NB, Groffman PM, Levin SA, Munshi-South J, Pataki DE, Pavao-Zuckerman M, and Wilson WG (2014). Urban ecology: advancing science and society. Frontiers in Ecology and the Environment 12, 574-581.

Tarolli P, and Sofia G (2016). Human topographic signatures and derived geomorphic processes across landscapes. Geomorphology 255, 140-161.

Taylor, PG, and Townsend AR (2010). Stoichiometric control of organic carbon-nitrate relationships from soils to the sea. Nature 464 (7292), 1178.

Tennant CJ, Harpold A.A, Lohse KA, Godsey SE, Crosby BT, Larsen LG, Brooks PD, Van Kirk RW and Glenn NF (2017). Regional sensitivities of seasonal snowpack to elevation, aspect, and vegetation cover in western North America, Water Resour. Res., 53, doi:10.1002/2016WR019374.

Trenberth KE (2011). Changes in precipitation with climate change. Climate Research 47(1/2), 123-138.

Troch PA, Paniconi C, and Emiel van Loon E (2003). Hillslope-storage Boussinesq model for subsurface flow and variable source areas along complex hillslopes: 1. Formulation and characteristic response. Water Resources Research 11.

Trostle KD, Runyon JR, Pohlmann MA, Redfield SE, Pelletier J, McIntosh J and Chorover J (2016). Colloids and organic matter complexation control trace metal concentration-discharge relationships in Marshall Gulch stream waters, Water Resour. Res. 52, 7931–7944, doi:10.1002/2016WR019072.

Van Dam L (2012). Landform characterization using geophysics-Recent advances, applications, and emerging tools. Geomorphology 57, 57-73

Van Meter KJ, Basu NB, Veenstra JJ, and Burras CL (2016). The nitrogen legacy: emerging evidence of nitrogen accumulation in anthropogenic landscapes. Environmental Research Letters 11(3), 035014. doi:10.1088/1748-9326/11/3/035014

Vazquez-Ortega A, Huckle D, Perdrial J, Amistadi MK, Durcik M, Rasmussen C, McIntosh J, Chorover J (2016). Solid-phase redistribution of rare earch elemetns in hillslope pedons subjected to different hydrologic fluxes. Chemical Geology 426, 1-18.

Vazquez-Ortega A, Perdrial J, Harpold A, Zapata-Rios X, Rasmussen C, McIntosh J, Schaap M, Pelletier JD, Brooks PD, Amistadi MK, and Chorover J (2015). Rare earth elements as reactive tracers of biogeochemical weathering in forested rhyolitic terrain. Chemical Geology 391, 19-32.

Vrettas MD and Fung IY (2015). Toward a new parameterization of hydraulic conductivity in climate models: Simulation of rapid groundwater fluctuations in Northern California." Journal of Advances in Modeling Earth Systems 7 (4), 2105-2135.

Ward AS, Schmadel NM, Wondzell SM, Harman C, Gooseff MN, and Singha K (2016). Hydrogeomorphic controls on hyporheic and riparian transport in two headwater mountain streams during base flow recession. Water Resources Research, 52: 1479-1497.

West N, Kirby E, Bierman P, and Clarke BA (2014). Aspect-dependent variations in regolith creep revealed by meteoric 10Be. Geology 43, 83–86.

White T, Brantley SL, Banwart S, Chorover J, Dietrich W, Derry L, Lohse K, Anderson S, Aufdendkampe A, Bales R, Kumar P, Richter D, and McDowell B (2015). The role of critical zone observatories in critical zone science, in Principles and Dynamics of the Critical Zone, (eds. R. Giardino and C. Hauser), Elsevier. Chapter 2, Developments in Earth Surface Processes 19, 15–78.

White TS, Wymore AS, Dere A, Hoffman A, Washburne J, and Conklin M (2017). Integrated interdisciplinary science of the Critical Zone as a foundational curriculum for addressing issues of sustainability. Journal of Geoscience Education 65, 136-145.

Wicherski W, Dethier DP and Ouimet WB (2017). Erosion and channel changes due to extreme flooding in the Fourmile Creek catchment, Colorado. Geomorphology.

Will RM, Benner S, Glenn NF, Pierce J, Lohse KA, Patton N, Spaete LP, and Stanbery C (2017). Mapping SOC Distribution in Semi-arid Mountainous Regions Using Variables From Hyperspectral, Lidar and Traditional Datasets [Data set]. https://doi.org/10.18122/B2Q598

Wilson CG, Wacha KM, Papanicolaou AN, Sander HA, Freudenberg VB, Abban BK, and Zhao C (2016). Dynamic Assessment of Current Management in an Intensively Managed Agroecosystem. Journal of Contemporary Water Research & Education.

Winnick MJ, Carroll RWH, Williams KH, Maxwell RM, Dong W, and Maher K (2017). Snowmelt controls on concentration-discharge relationships and the balance of oxidative and acid-base weathering fluxes in an alpine catchment, East River, Colorado. Water Resources Research.

Woo DK and Kumar P (2016). Mean age distribution of inorganic soil-nitrogen. Water Resources Research, 52.

Woo DK and Kumar P (2017). Role of micro-topographic variability on age of soil nitrogen in intensively managed lanscapes. in review.

Woo DK, Quijano JC, Kumar P, Chaoka S, and Bernacchi CJ (2014). Threshold Dynamics in Soil Carbon Storage for Bioenergy Crops. Environmental Science & Technology.

Wrona FJ, Johansson M, Culp JM, Jenkin A, Mård J, Myers-Smith IH, Prowse TD, Vincent WF and Wookey PA (2016). Transitions in Arctic ecosystems: Ecological implications of a changing hydrological regime. Journal of Geophysical Research: Biogeosciences 121(3), 650-674.

Wymore AS, Coble AA, Rodríguez-Cardona B, and McDowell WH (2016). Nitrate uptake across biomes and the influence of elemental stoichiometry: A new look at LINX II. Global Biogeochemical Cycles, 30: doi: 10.1002/2016GB005468

Wymore AS, West N, Maher K, Sullivan PL, Harpold A, Karwan DL, Marshall JA, Perdrial J, Rempe D, and Ma L (2017a). Growing new generations of critical zone scientists. Earth Surface Processes and Landforms. doi: 10.1002/esp.4196

Wymore AS, Brereton RL, Ibarra D, Maher K, and McDowell WH (2017b). Critical zone structure controls concentration-runoff relationships in watersheds draining a tropical montane forest. Water Resources Research. 53. doi: 10.1002/2016WR020016

Yesavage, T.A., Fantle, M.S., Vervoort, J., Mathur, R., Jin, L., Liermann, L.J., Brantley, S.L., 2012. Fe cycling in the Shale Hills Critical Zone Observatory, Pennsylvania: An analysis of biogeochemical weathering and Fe isotope fractionation. Geochimica et Cosmochimica Acta 99, 18-38, doi.org/10.1016/j.gca.2012.1009.1029.

Yoo K, Amundson R, Heimsath AM, and Dietrich WE (2005). Erosion of upland hillslope soil organic carbon: Coupling field measurements with a sediment transport model. Global biogeochemical cycles 19(3).

Zapata-Rios X, Brooks PD, Troch PA, McIntosh J, and Guo Q (2016). Influence of terrain aspect on water partitioning, vegetation structure, and vegetation greening in high elevation catchments in norhter New Mexico. Ecohydrology 9, 782-795.

Zapata-Rios X, McIntosh J, Rademacher L, Troch PA, Brooks PD, Rasmussen C and Chorover J (2015). Climatic and landscape controls on water transit times and silicate mineral weathering in the critical zone. Water Resources Research 51(8), 6036-6051.

Zhang Y, Slingerland R, and Duffy C (2016). Fully-coupled hydrologic processes for modeling landscape evolution. Environmental Modelling & Software 82, 89-107.