



### INTRODUCTION TO A SPECIAL SECTION

10.1002/2017WR021111

#### Special Section:

Concentration-discharge Relations in the Critical Zone

#### Key Points:

- Interdisciplinary critical zone science can provide transformative insights into controls on concentration-discharge relations observed in streams and rivers
- Critical zone scientists and observatories are making hydrologic and hydrochemical measurements using common approaches that enable comparison across sites
- This special section contains a set of papers wherein insights into critical zone structure and function are applied to interpret catchment concentration-discharge relations

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#### Citation:

Chorover, J., Derry, L. A., & McDowell, W. H. (2017). Concentration-discharge relations in the critical zone: Implications for resolving critical zone structure, function, and evolution. *Water Resources Research*, 53, 8654–8659. <https://doi.org/10.1002/2017WR021111>

Received 12 MAY 2017

Accepted 25 JUN 2017

Accepted article online 12 SEP 2017

Published online 10 NOV 2017

## Concentration-Discharge Relations in the Critical Zone: Implications for Resolving Critical Zone Structure, Function, and Evolution

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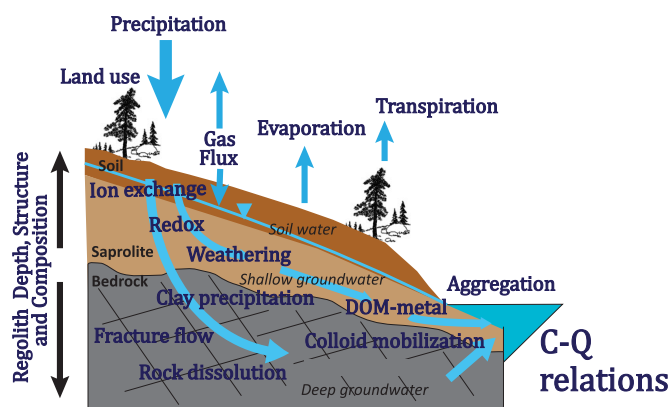
**Abstract** Critical zone science seeks to develop mechanistic theories that describe critical zone structure, function, and long-term evolution. One postulate is that hydrogeochemical controls on critical zone evolution can be inferred from solute discharges measured down-gradient of reactive flow paths. These flow paths have variable lengths, interfacial compositions, and residence times, and their mixing is reflected in concentration-discharge (C-Q) relations. Motivation for this special section originates from a U.S. Critical Zone Observatories workshop that was held at the University of New Hampshire, 20–22 July 2015. The workshop focused on resolving mechanistic CZ controls over surface water chemical dynamics across the full range of lithogenic (e.g., nonhydrolyzing and hydrolyzing cations and oxyanions) and bioactive solutes (e.g., organic and inorganic forms of C, N, P, and S), including dissolved and colloidal species that may cooccur for a given element. Papers submitted to this special section on “concentration-discharge relations in the critical zone” include those from authors who attended the workshop, as well as others who responded to the open solicitation. Submissions were invited that utilized information pertaining to internal, integrated catchment function (relations between hydrology, biogeochemistry, and landscape structure) to help illuminate controls on observed C-Q relations.

**Plain Language Summary** This article introduces the special section of *Water Resources Research* entitled “Concentration-Discharge Relations in the Critical Zone”.

### 1. Introduction

The critical zone (CZ) is that portion of the Earth’s land surface that is permeated by the hydrologic cycle. It extends vertically from its upper boundary, the outer-periphery of the vegetation canopy, down through the plant rooting zone, the vadose and saturated zones, and porous bedrock, to the lower boundary, which is denoted by bedrock with negligible permeability (and hence the lower limit of freely circulating groundwater) (National Research Council, 2001). As water flows through the CZ, it interacts with a wide variety of solid-liquid and gas-liquid interfaces whose compositions and reactivities alter aqueous geochemistry (Figure 1). Variations in contact times (i.e., residence times) affect the extent to which kinetically limited processes—such as weathering and microbial transformation of nutrients—generate a chemical signal in the water moving through the CZ, whereas variations in hydrologic flow paths and their connectivity control the mixing of waters from distinct CZ locations, and their relative contributions to the chemical load in receiving stream water. Interactions among these processes are expected to vary across hydrologic events, such as rainfall or snowmelt, thereby producing a range of potential correlations between chemical composition and flux of receiving waters, i.e., concentration-discharge (C-Q) relations.

Early models used to characterize episodic variation in dissolved solutes and their correlation (or lack thereof) with discharge focused on time-variant mixing of chemically distinct source waters (e.g., “precipitation,” “soil water,” and “groundwater”) whose compositions were considered constant (e.g., Evans & Davies, 1997). Although an improved understanding of chemical reactions occurring along hydrologic flow paths enables the development of mechanistic reactive transport models of hydrochemical response (Steeffel



**Figure 1.** An array of coupled hydrologic and biogeochemical processes superimposed on a complex critical zone structure give rise to concentration-discharge relations observed in surface waters.

et al., 2005), such efforts are often hindered by the poorly known complexity of CZ structure (Orlando et al., 2016), an incomplete understanding of transit time distributions, including how flow paths change in response to catchment wetness (Heidbuchel et al., 2012) and a lack of information on the composition and spatial distribution of water-wetted interfaces (Chorover et al., 2007).

Critical zone science seeks to develop a mechanistic-predictive understanding of critical zone structure, function, and long-term evolution (Brantley et al., 2007; Rasmussen et al., 2011). One emerging postulate is that hydrochemical controls on all three can be related quantitatively to solute releases measured down-gradient of reactive flow paths of variable length and residence time, whose mixing is reflected in concentration-discharge (C-Q) relations. Although C-Q relations have been studied for decades, an improved understanding of the underlying mechanisms depends on “opening the black box” of upgradient watersheds, to more accurately assess the behavior, dynamics and distribution of flow paths. Specifically, we ask *how does*

*CZ structure (e.g., distribution of topography, vegetation and microbiota, subsurface porosity, biogeochemical composition of solid-fluid interfaces) affect C-Q relations of receiving surface waters?* Such a question is perhaps best answerable by a CZ science approach—i.e., one that integrates ecohydrologic, geomorphic, and biogeochemical information across a single three-dimensional CZ domain.

C-Q relations may manifest as dilution, chemostasis, or enrichment with increasing discharge, depending on chemical species, catchment climate and lithology, and CZ evolution. Prior work has taken advantage of large U.S. Geological Survey and other databases of catchment chemistry and discharge. For example, Godsey et al. (2009) studied 59 hydrologic benchmark sites with diverse physical characteristics distributed across the U.S. The analysis revealed remarkably consistent chemostatic to slight dilution response for major lithogenic elements (Si, Ca, Mg, Na, and K), suggesting undefined stores of labile species poised for release in CZ weathering compartments. The authors presented a continuum of hydrologic modeling approaches to reproduce C-Q relations that ranged from simple bucket models to porosity-permeability-aperture models.

Controls on C-Q relations in streams result from complex linkages between geochemical and hydrologic processes and, in this regard, the ratio of time scales for chemical reaction to fluid transit time provides a useful parameterization. Chemostasis is favored when heterogeneous reactions are fast relative to water transit times, and dilution occurs when the reverse is true. The dimensionless Damköhler number ( $Da$ ), which has been used extensively in the chemical engineering discipline to classify a system according to the balance between transport and reaction, has also proven useful for classifying material processing in the context of hydrologic systems (Oldham et al., 2013; Wagner & Harvey, 1997). For example, Maher (2010) has shown that for systems with large Damköhler number ( $Da > 1$ ), the characteristic time for reaction rates is small relative to that for advective transport, which implies that local geochemical equilibria and chemostatic conditions prevail. Conversely, for  $Da < 1$ , reaction rates are slow relative to water transit times, and dilution effects are observed in C-Q data sets.

## 2. Special Section on Concentration-Discharge Relations in the Critical Zone

The idea for a special section of *Water Resources Research* originated with a workshop held in July 2015 at University of New Hampshire that focused on the challenge of developing mechanistic interpretations of C-Q relations through an improved understanding of critical zone (CZ) structure and function, such as is underway at critical zone observatories worldwide. The “*C/Q relations in the Critical Zone*” workshop, funded by the National Science Foundation through the Critical Zone Observatories (CZO) National Office, brought together scientists working in a variety of CZ sites to present their approaches to resolving mechanistic controls over discharge-induced variation in hydrochemistry. Several of the papers initially presented at the workshop, as well as others that were subsequently submitted, are included in this special section.

The common focus of the special section is on resolving mechanistic CZ controls over surface water chemical dynamics across the full range of lithogenic (e.g., nonhydrolyzing and hydrolyzing cations and oxyanions) and bioactive (e.g., organic and inorganic forms of C, N, P, and S) constituents in water samples, including dissolved, macromolecular and colloidal species that may cooccur for a given element. The question of why some catchments are chemostatic (small variations in C across large variation in Q), whereas others show strong dilution or enrichment, is a common focal point in many of the papers, as discussed below.

### 2.1. Impacts of Spatial Variation

There are multiple potential reasons for discharge-related variations in surface water chemistry, including spatial variation in CZ composition and structure, and aggregation of waters from several pathways. Three of the papers in the special issue test such effects in the Amazon basin, which is the world's largest river system. In part 1 of a two-part series of papers, Torres et al. (2017) develop a conceptual framework of how variation in lithology, erosion rate, and climate across a river's catchment area, superimposed with temporal variations in the contributions of tributary subcatchments can modulate observed variation in solute chemistry driven by hillslope processes. In part 2, the same team uses C-Q data for a wide range of solutes across a nested series of catchments in the Amazon to show that observed main stem dynamics are influenced by variable mixing of waters from upgradient tributaries with distinct C-Q relationships (Baronas et al., 2017). The impacts of tributary mixing in the Amazon basin are explored further by Bouchez et al. (2017), who test a model of C-Q relations wherein solute-rich upland waters derived from actively weathering mountain systems are mixed with dilute waters from low-relief areas as downstream aggregation of tributaries progresses. They observed both stronger hysteresis loops and a trend from largely chemostatic to dilutional C-Q behavior with down-gradient migration from mountains to mouth.

### 2.2. Power Law Equations and Hysteresis

Power law equations of the form  $C = aQ^{-k}$  enable synoptic comparisons of C-Q relations across multiple systems where the slope  $k$  can be related to potential CZ structural controls. For example, Wymore et al. (2017) used 10–30 years of weekly stream chemistry and discharge data across 10 watersheds in Luquillo CZO (Puerto Rico, USA) to show that vegetation, lithology and basin order exert strong controls over the power law exponent for both weathering products (Si, Ca, Mg, Na, and  $\text{SO}_4$ ) and biologically controlled solutes (DOC,  $\text{PO}_4$ , and inorganic N). In a study of C-Q relations in headwater streams of the Sierra Nevada, Hunsaker and Johnson (2017) observed chemostatic behavior for bedrock-derived solutes and nonchemostatic behavior for biologically active solutes, with the former showing slight dilution and the latter, deriving from soil solutions, showing increased concentration during storm events. Through end member mixing analysis, Liu et al. (2017) proposed that C-Q hysteresis (manifest as a difference in power law exponent between the ascending and descending limbs of the snowmelt hydrographs for Sierra Nevada streams) are attributable to larger deep groundwater contributions on the ascending limb.

Some authors have argued that power law relations may not be the most useful descriptors for comparison across catchments, as reproducible nonlinearities (Ibarra et al., 2016) and slope breaks are frequently observed, and these must have process-relevant underpinnings. For example, based on an analysis of 40 years of C-Q data from 293 monitoring stations covering catchments draining nearly half of France, Moatar et al. (2017) found that ~60% showed nonlinear C-Q relations, and they observed significantly different C-Q behaviors above and below the median discharge.

### 2.3. Information Afforded by High Frequency Data Streams

High frequency in situ sensor data were found to shed light on C-Q relations that are typically unresolved with traditional grab or automated sampling methods. For example, correlation of in situ electrical conductivity (EC) measurements with discharge enabled Singley et al. (2017) to identify hydrologic mechanisms governing hysteretic behavior across the hydrograph in the McMurdo Dry Valleys of Antarctica. Using in-stream sensors (combined with stable isotopes) for hydrograph separation enabled Clark et al. (2017) to show that new water, transmitted laterally downslope in the near subsurface, dominated storm hydrographs in events following extreme drought in the Rio Icos watershed of the Luquillo CZO.

#### 2.4. Opening the “Black Box”

Several papers highlight the fact that processes controlling solute chemistry are not evident from stream chemistry and runoff analysis alone and that “opening the black box” of catchment internal CZ structure is essential to interpreting such data sets. For example, C-Q data were interpreted in light of CZ weathering profiles to reveal the important role of clay mineral formation along deep subsurface flow paths in controlling catchment Si effluxes from weathering rhyolite (McIntosh et al., 2017). Similarly, time series data on groundwater chemistry showed that cation exchange reactions during water percolation into a deeply weathered argillite was superimposed with long-residence time groundwater gave rise to chemostatic C-Q relations (Kim et al., 2017). To better resolve the distribution of flow paths governing solute transport to the stream, Hoagland et al. (2017) combined tracer injection tests, cation exchange experiments and geochemical methods to map groundwater-surface water interactions along a first-order sandstone stream in the Shale Hills Susquehanna CZO. Their data suggested that cation exchange reactions on organomineral complexes in the hyporheic zone exert strong control on C-Q relations in Garner Run.

When geochemically distinct weathering fronts are nested at different depths in the CZ, their influences on solute-specific C-Q relations depend not only on the extent to which they serve as solute reservoirs but also on the extent to which those reservoirs are intersected by predominant flow paths to the stream. Several papers in the special section indicate that such intersections can change across the hydrograph. For example, lithogenic solute mobilization from stores in the deep CZ and finite DOC depletion in the near-surface was suggested by C-Q data from the massive 1,000 year precipitation event that fell in the Boulder Creek watershed in September 2013 (Rue et al., 2017). Vertically nested weathering fronts are also implicated by Winnick et al. (2017), who observed that carbonic acid weathering from subsurface respiration overlies sulfuric acid weathering from pyrite oxidation in the shale-dominated East River catchment in the Rocky Mountains (CO, USA). As a result of the passage of transmitted water sequentially through the two reaction zones, significant CO<sub>2</sub> outgassing occurred upon reequilibration of discharge water with the atmosphere.

#### 2.5. Nanoparticulate Contributions

Colloids and macromolecules are common products of geochemical weathering and organic matter decomposition, respectively, so it is not surprising that they also figure prominently into C-Q relations; standard filtration includes suspended nanoparticles in what is operationally defined (<0.45 μm filtrate) as “dissolved” loads (Pokrovsky et al., 2006). Using cascade filtration coupled to asymmetric flow field flow fractionation, Trostle et al. (2016) quantified the relative contributions of organic matter and mineral colloids to trace element C-Q relations, and showed that the distribution between these carrier types determined the magnitude of positive slope of C-Q relations. Using Ge/Si ratios, Aguirre et al. (2017) showed that Si chemostasis in Boulder Creek stream waters was sustained by a mixing of groundwaters comprising dissolved Si from feldspar weathering with soil pore waters comprising Si-bearing mineral colloids.

#### 2.6. Modeling Approaches

Several of the papers in the special issue couple hydrologic and geochemical models to develop physically based predictions of C-Q relations. Bao et al. (2017) present coupled, physically based descriptions of reactive geochemical transport (using the CrunchFlow database) with saturated and unsaturated hydrologic flows (using the Penn State Integrated Hydrologic Model, PIHM) and land-atmosphere exchange (Noah Land Surface Model) in developing “RT-flux-PIHM” to model catchment hydrochemical response. The same team then applied the model to explain hysteretic C/Q relations for Mg and Cl observed in the Shale Hills Critical Zone Observatory (Li et al., 2017). Ameli et al. (2017) integrated a flow and particle tracking transport model with mineral dissolution rate laws to show how variations in intrinsic mineral weathering rate controls how C-Q relations in the critical zone respond to the decline in saturated hydraulic conductivity with depth, giving rise to either chemostatic (high intrinsic weathering rate) or dilution (low intrinsic weathering rate) behavior.

#### 2.7. Summary

Overall, the papers in this special section reveal that, although multiple databases exist that can be interrogated for globally distributed watershed C-Q relations (e.g., Hydrologic Benchmark Sites, Long Term Ecological Research Sites), CZ science that rigorously integrates biogeochemical and ecohydrological data sets with an understanding of CZ structure is likely to lead to further breakthroughs in our understanding of hydrochemical fluxes and their controls. The CZO network is well situated to continue to address the



question of mechanistic controls over C-Q because the network measures—in addition to stream water discharges—the internal function and structure of the CZ across multiple sites.

### Acknowledgments

This work was supported by grants through the NSF Critical Zone Observatories program including EAR 13-31408 to J. Chorover, EAR 14-45246 to L. A. Derry, and ICER-13-31841 to W.H. McDowell.

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