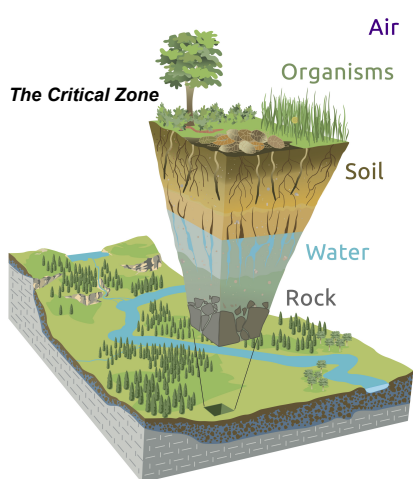


## CZ-TOP: The Critical Zone as a Non-Steady State Biogeochemical Reactor

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The Critical Zone is where much of the world's surface water is generated, and processes within the CZ play a large role in determining the flux and composition of stream waters, including "water quality." The flow of water through the landscape and its chemistry are intimately related, as water takes multiple pathways depending on the structure of the Critical Zone, in turn influencing the type and extent of reaction experienced along the path. New data now available with Critical Zone observing networks represent an opportunity to "look inside" hydrobiogeochemical systems and gain insight into water pathways, transit time scales and reactions that control biogeochemical fluxes.

Relationships between variations in stream discharge and solute concentrations (C-Q relations) contain information about multiple Critical Zone processes, from hydrologic flow paths to weathering reactions to transport and reaction time scales (e.g. Hornberger et al., 2001; Godsey et al. 2009; Chorover et al., 2017). Variations in stream export are a dynamic integrator of Critical Zone processes. A typical stream system may show large variations in discharge with only modest variations in the concentration of solutes, with interesting implications for solute fluxes. As an example, a system that shows factor of ten variation in discharge (Q) but only factor of two variation in concentration of a given solute (C) has a factor of five variation in solute flux, and this can occur over short time scales. *Where does this five-fold increase in solute flux "come from", and what does that tell us about the fluid flow and geochemical reactions that take place within the Critical Zone, and how they vary with time?* If we are to understand the function of the CZ now, and predict how it will respond to variable forcing under a changing climate, we need to be able to answer this question.

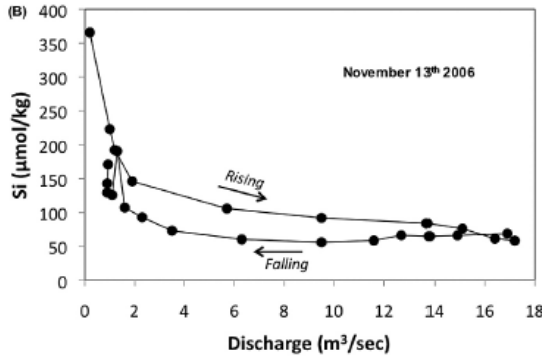
*The Big Question, put as simply as possible – what controls C-Q patterns in catchments?*

This question has a long history, but is still with us. In part, at least, it's because it is neither a hydrological or geochemical question, but some combination of both. The idea here is that a combination of new infrastructure (Critical Zone Observatories), new measurements (high frequency time series of reactive and non-reactive tracers), and new models (isotope-enabled reactive transport and non-steady state hydrologic models) can be used together to make significant new advances on this old issue.

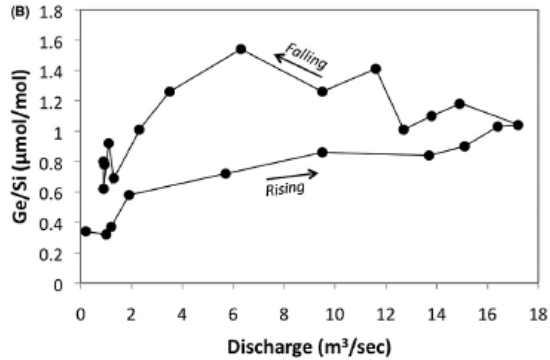
A project along these lines was recently funded under the *Make Our Planet Great Again* program of the Agence Nationale de la Recherche, France. We will focus on predominantly weathering-derived solutes, although there are rich questions about the C-Q behavior of DOC, nitrate, and others. The "home" of this project will be the Institut de Physique du Globe de Paris (IPGP). But like any good idea, this one has many roots and many branches, and we hope it will involve a number of colleagues from France, the U.S. and elsewhere.

The figure below illustrates a system in which both concentration of dissolved silica and the "pseudo-isotope" tracer Ge/Si vary throughout a hydrologic event in a granitoid watershed from Luquillo, Puerto Rico (Kurtz et al. 2011). The stream here samples a deep regolith with a

weathering front as much as 8 m below the surface. The mineralogy of the system is roughly vertically stratified, with kaolinite, gibbsite and quartz in the upper part; feldspar, quartz, hornblende and biotite in the bedrock; and a transitional zone in between. Ge/Si varies among mineral phases, and in pore waters as a function of depth. Water that has reacted with different parts of this system contributes variably to stream flow under different hydrologic conditions.



**Figure 4.** Si concentration-discharge curve for (a) the 24 June 2006 storm event and (b) the 13 November 2006 storm event (secondary discharge peak excluded for clarity).



**Figure 5.** Ge/Si ratio-discharge curve for (a) the 24 June 2006 storm event and (b) the 13 November 2006 storm event (secondary discharge peak excluded for clarity).

Figure 1. High  $[Si] \approx 370 \mu M$  and low  $Ge/Si \approx 0.3$  at baseflow samples plagioclase dissolution near the bedrock –saprolite interface (plag  $\rightarrow$  kaol, yielding  $(Ge/Si)_{soln} = 0.3$ ). At higher Q, Ge/Si increases but Si decreases, reflecting kaolinite and quartz dissolution taking place higher in the regolith. High Ge/Si results from kaolinite- $\rightarrow$ gibbsite reaction ( $Ge/Si_{soln} \approx 5$  to 6). The high Ge/Si component is diluted by low Ge/Si coming from qtz dissolution ( $Ge/Si \approx 0.5$ ). This example shows how tracers identify time-varying reactions that reflect changing flow paths at different hydrologic states (Kurtz et al., 2011).

#### Concentration-discharge-ratio (C-Q-R) relations

C-Q-R relations (where “R” are elemental or isotope ratios) arise from interactions between water transport fluxes and pathways and solute sources. Solutes that are largely generated within a catchment such as rock weathering products carry information about water flow paths and transit times, and mineral source distributions. Because water-mineral reactions are not instantaneous both the transit time of a parcel of water and the reaction time constants effective along a flow path will influence the solute concentration (Maher, 2010). Further, the outflow values ( $C_Q$ ) at some time  $t$  are the result of a convolution of multiple individual transit pathways or times (Harman 2015):

$$C_Q(t) = \int_{-\infty}^t C_j(t_i) P_Q(t - t_i, t) dt_i$$

where  $C_j$  is the tracer value at the time of solute injection,  $t_i$  is the time a water parcel enters the system, and  $P_Q$  is the transit time distribution for parcels leaving the system (equivalent to the “age at death” of a population).  $P_Q$  need not be fixed, i.e. the transit time distribution can be non-steady state, and this must be the case in order to produce the temporally varying C-Q-R relations

observed in some systems. Thus models for  $C$  and  $R$  as  $f(Q)$  must consider non-steady state transit time distributions (Heidbuchel et al 2012; Harman 2015; Rinaldo et al, 2015).

Figure 2 is a conceptual illustration of the impact of “sampling distribution” on stream composition, and this concept can be generalized to account for time-varying distributions. In other words, under different hydrologic conditions (precipitation inputs, antecedent storage, etc.), the contributions from the range of possible pathways will vary. When that happens, water that has reacted with different mineral assemblages and for different amounts of time will emerge to contribute to stream flow, thus impacting  $C$  and  $R$  as a function of  $Q$ . Variations in  $C$  cannot usually provide unique constraints on the solute source (or reaction time scale), but the addition of  $R$ , especially for multiple tracers, creates the potential for substantially improved constraints. If the regolith column schematically illustrated in Figure 2 is stratified with respect to mineralogy and isotopic composition (because of the progression of a weathering front, for example), appropriate  $R$  data could immediately identify which of the three proposed distribution function was most appropriate, in a way that  $C$  alone could not

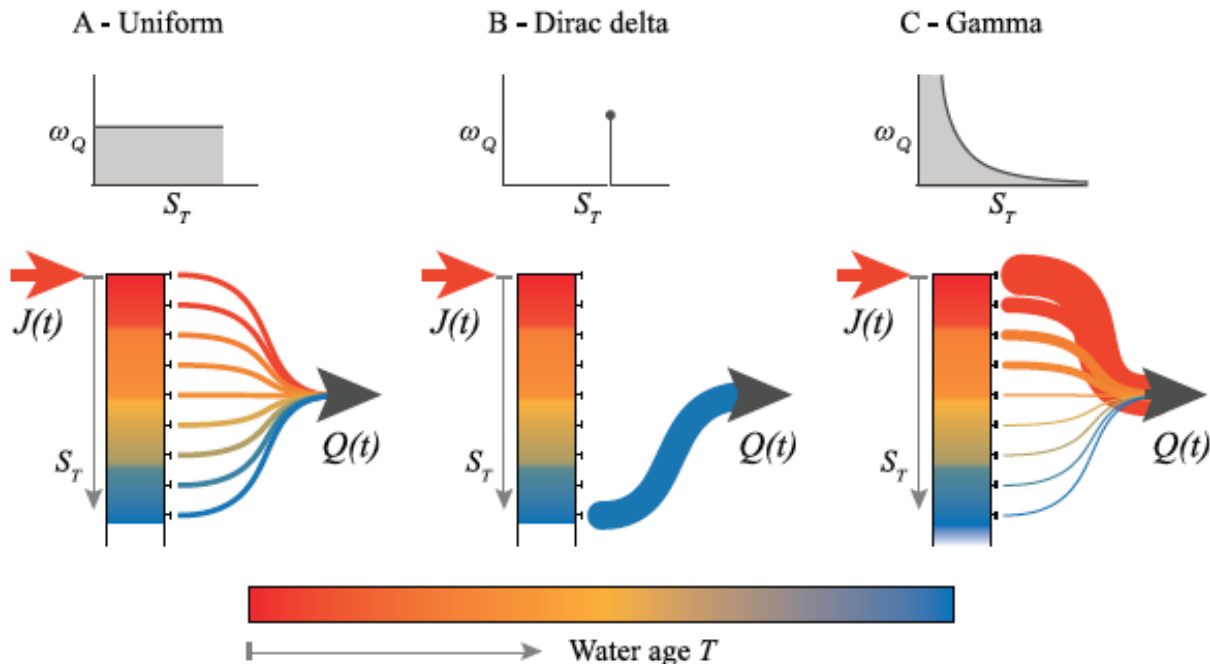


Figure 2 A schematic “transport” column where water is added to the top and “ages” downward (shamelessly lifted from Harman, 2015). If this same column is compositionally and isotopically stratified, water of different “age” will also contain different concentrations ( $C$ ) and tracer values ( $R$ ) for reactive solutes. Then, not only is water of different “ages” sampled according to any of the three example distribution functions, but  $C$  and  $R$  values will reflect the distribution as well. If the system is kinetically limited,  $C$  and  $R$  may be dynamic functions of age.

As an example we can consider variables that may impact  $C$ - $Q$  relations in a dynamic regolith-bedrock-water system. As the hydrologic state of the system evolves in response to a rainfall event, different flow paths will become active.

- Flow paths can be activated by precipitation inputs, thus different regions and mineralogy of the CZ are sampled under different forcings (Kurtz et al. 2011).
- The characteristic hydrologic transit time for these flow paths will differ, impacting time scales available for water-rock interaction (Heidbuchel et al., 2012).
- Kinetic constants for chemical and isotopic interaction vary with changes in mineral assemblage (Maher, 2010).
- Differences in time available for water rock interaction (transit time) will impact the expression of kinetic versus equilibrium controls on reactive chemistry (Druhan and Maher 2017).

Tracers for weathering reactions such as Ge/Si (Kurtz et al., 2002),  $\delta^{30}\text{Si}$  (Ziegler et al., 2005), and  $\delta^{44}\text{Ca}$  (Cenki-Tok et al., 2009) reflect both their mineral sources and equilibrium and kinetic fractionations along their transport path (Lugolobi et al., 2010; Druhan and Maher 2017), potentially providing unique constraints on flow path. Further, kinetically limited systems embed information on transport time scales. Reactive transport models with kinetic and equilibrium reactions can be combined with tracer data to constrain flow paths and reaction time scales. As data from accumulating parts of the system (e.g. streams) will integrate multiple paths and transit times such data need to be interpreted in terms of transit time distributions. Fractionation factors can be explicitly included in the RTM framework to compute stable isotope distributions dynamically (Rolle et al., 2010; Druhan et al., 2014). Stream water reflects the integrated output of the system, and solutions for output values can be obtained for different TTDs, thus providing a test of applicability.

Our working hypothesis is that an improved understanding of CZ dynamics and C-Q-R relations can come from a combined approach:

- High resolution time series of C and R over varying Q in well-constrained systems.
- Including isotope fractionation in reactive transport models, to gain additional insight into reaction mechanisms and time scales.
- Interpreting these results in terms of non-steady transit time distributions, i.e. variations in the types of flow paths and transit times sampled in stream output as a function of hydrologic state.

The growing international CZO network provides opportunities to test these hypotheses in new ways. We can include both well-studied CZOs and analog experimental systems, and also take advantage of new systems for making very high resolution measurements available for a number of solutes and stable water isotopes (e.g. Floury et al., 2017; von Freyberg et al, 2017) that can provide additional constraints. While progress has been made on the different legs of this project, work on all three is needed: analytical geochemistry to collect appropriate data sets, RT modeling, and non-steady state hydrologic modeling.

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