Titre du sujet : Variability in stream chemistry from seasonal- to event time scales: water-rock interactions, nutrient cycling, and water transport

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The chemistry of a river reflects the functioning of the critical zone at the scale of its catchment. These geochemical signals thus potentially host a wealth of information on water-rock interactions and ecosystem activity. However, progress in using river chemistry as a tool for catchment-scale understanding and quantification of fundamental processes such as soil formation or nutrient cycling, is still hampered by competing interpretations of the ways these signals vary with time. Such variations are embedded in the relationships between river discharge and solute concentrations (« C- Q relationships »), which display characteristic trends that depend on the solute of interest and the time scale (in particular seasonal *vs.* individual storm event) considered (*e.g.*, Godsey et al., 2019).

In order to bridge this critical gap, this project will combine the following advancements that emerged over the last decade in the field of critical zone science:

#1 We are now able to infer an accurate characterization of the time it takes for water to travel through a catchment from infiltration to discharge, using chronicles of hydrological fluxes (precipitation, discharge, evapotranspiration) and conservative tracers (isotope ratios of the water molecule, chlorine concentration). In particular, the framework offered by « StorAge Selection » functions results in a quantitative characterization of a transit time distributions (TTDs) of water exiting a given catchment (*e.g.*, Benettin et al., 2022).

#2 The isotopes of some of metal(loid) elements (such as silicon, calcium, or potassium) involved in the formation of the fundamental bricks of soil (clays and oxides), as well as in nutrient cycling, are partitionned during these uptake reactions. As a result, any parcel of water affected by such processes leaves the catchment enriched or depleted in a specific isotope. These characteristic river isotope signatures thus offer the possibility to quantify the extent to which clay formation and plant uptake affect solute export (*e.g.*, Bouchez and von Blanckenburg, 2021).

#3 We now possess the ability to quantitatively account for the role of plant demand for water and nutrients on the chemistry of water as it infiltrates into the ground, passes through the rooting zone, reaches groundwater and emerges in streams. This can be accomplished through the mean of 1-D model frameworks recently developed (Druhan and Bouchez, 2024).

#4 Critical Zone Observatories (CZOs) are now in place under the umbrella of (inter)national research infrastructures, fostering inter-disciplinary collaboration around field sites and scientific questions. Within these networks, instrumented catchments offer unique opportunities to use long-term hydrological and geochemical data, and to deploy novel instrumentation (*e.g.*, Gaillardet et al., 2018).

To this date, these major advancements have never really been leveraged together within in a given project. The study of Fernandez et al. (2022) provided the first example of the use of silicon (Si) isotopes as a marker of biogeochemical functioning and solute export across several CZOs (**#2** and **#4**). More recent work by Druhan and Benettin (2023) and Guertin et al. (2024) develop and use a framework combining TTD estimates and Si isotopes (**#1** and **#2**). Through an on-going collaboration between IPGP, the University of Illinois Urbana-Champaign (UIUC) and the University of Lausanne (UNIL), theoretical work is in place to include the effect of ecosystem water and nutrient demand in SAS-type models, including metal(loid) isotope fractionation (**#1**, **#2**, and **#3**). *The objective of the present PhD project is to bridge all these advancements through model development and application at a pair of CZOs with contrasted lithological and land cover characteristics.*

The specific research objectives of this PhD project are :

(a) Collect new datasets for isotope ratios of the water molecule (δ^{18}O and δD ; to « feed » the SAS modeling) and of the nutrient and clay-forming metalloid element silicon (δ^{30}Sil ; as a proxy for how rock-derived elements are cycled through soils and ecosystems) in rivers, sampled both at baseflow and during meteorological events such as storms and droughts.

(b) Generate TTD estimates for the instrumented catchhments located in two CZOs in France (Mt-Lozère, Cévennes ; *e.g.*, Aranda Reina et al., 2025) and the USA (Eel River, California ; *e.g.*, Golla et al., 2022). Across these two CZOs, five catchments will be studied, offering contrasted rock types (granite *vs*. shale) and land cover (forest *vs*. grassland).

(c) Leverage existing and new datasets on subsurface water chemistry (*e.g.*, Golla et al., 2021), including major and trace element concentrations, and isotope ratios of the water molecule and of rock-derived solutes, to constrain the relationships between water age, and plant uptake and clay formation.

(d) Contribute to model development aiming to merge the SAS and ecological frameworks described above, in particular using (c).

(e) Use the newly developed frameworks to produce river C-Q relationships (including isotope ratios of metal(loid) elements) that can be tested against observations (a) at the instrumented catchments (b).

The proposed work includes hydrological modeling, laboratory work (analyses of major anion and cation concentrations by ion chromatography, water isotope measurements by laser spectrometry, measurements of trace element concentrations and silicon isotopes by plasma-source mass spectrometry) and field work at the two field sites. Access to field sites is guaranteed through research infrastructures (OZCAR-eLTER, CZnet). The project will also involve instrument deployment (sap flow sensors, dendrometers, soil moisture probes) and regular operation of the equipment already present on site, as well as *in situ* measurements (groundwater dating and geochemical characterization) during targeted sampling campaigns. The projet also offers the possibility for the candidate to be involved in the design and construction of automated, low-volume, high-frequency water samplers dedicated to the measurement of water isotopes in precipitation and streams.

The PhD project will benefit from technical and logistical support by staff at IPGP (PARI platform) and UMR ESPACE (St-Christol-les-Alès), as well as from the financial support the national projects TerraForma and Carbonium (PEPR FairCarboN). A vibrant scientific environment will be provided through the participation of one alreday-present post-doctoral researcher (IPGP) and two already-present PhD students (IPGP and UIUC, USA) working on the same field sites. The project involves the participation of two foreign research groups (UIUC and UNIL) and four research units in France (IPGP, ESPACE, METIS-Sorbonne U, Géosciences Rennes), and benefits from funding from the USA-NSF and from the ANR project NutriBor (coordinated at IPGP-G2E). The capacity for international mobility is expected from the candidate, in particular in the frame of a collaboration with the USA partner, in order to participate in field work at the site in California. The trips will be financed through bilateral funding opportunities and the ED STEP'UP mobility programme.

References

Aranda Reina C., Bouchez J. and Druhan J.L. Quantifying the impacts of exogenous dust inputs to the critical zone using reactive transport modeling, *Geochimica et Cosmochimica Acta* **393**:254-267 (2025) ; Benettin P., Rodriguez N.B., Sprenger M. *et al.* Transit time estimation in catchments: Recent developments and future directions. *Water Resources Research* **58**(11) (2022) ; Bouchez J. and von Blanckenburg F. The role of vegetation in setting strontium stable isotope ratios in the critical zone. *American Journal of Science* **321**:1246-1283 (2021) ; Druhan J.L. and Benettin P. Isotope ratio – discharge relationships of solutes derived from weathering reactions. *American Journal of Science* **323**(5) (2023) ; Druhan J.L. and Bouchez J. Ecological regulation of chemical weathering recorded in rivers. *Earth and Planetary Science Letters* **641**:118800 (2024) ; Fernandez N.M., Bouchez J., Derry L.A. *et al*. Resiliency of silica export signatures when low order streams are subject to storm events. *Journal of Geophysical Research: Biogeosciences* **127**:e2021JG006660 (2022) ; Gaillardet J., Braud I., Hankard F. *et al*. OZCAR: the French Network of Critical Zone Observatories. *Vadose Zone Journal* **17**:1–24 (2018) ; Godsey S.E., Hartmann J. and Kirchner J.W. Catchment chemostasis revisited: Water quality responds differently to variations in weather and climate. *Hydrological Processes* **33**:3056–3069 (2019) ; Golla J. K., Kuessner M.L., Henehan M.J. *et al*. The evolution of lithium isotope signatures in fluids draining actively weathering hillslopes. *Earth and Planetary Science Letters* **567**:116988 (2021) ; Golla J.K., Bouchez J., Kuessner M.L. *et al.* Subsurface weathering signatures in stream chemistry during an intense storm. *Earth and Planetary Science Letters* **595**:117773 (2022) ; Guertin A., Cunningham C., Bouchez J. *et al.* Stable silicon isotope fractionation reflects the routing of water through a mesoscale hillslope, *Earth and Planetary Science Letters* **648**:119098 (2024).