

## **New insights for Concentration-Discharge relationships : High frequency of stream water chemistry**

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Concentration–discharge relationships (C-Q) of river water is a powerful tool to track the coupling between water flow and chemical reactions in the Critical Zone. C-Q have been extensively studied the last two decades. However, it is likely that C-Q will depend on the time resolution (sampling frequency) and span (e.g. flood vs. drought) over which data are acquired.

We present a new C-Q data series recorded at very high frequency by a prototype called River Lab (RL) [1]. Confined in a bungalow next to the river, the RL performs an analysis at a 40-minutes frequency of all major dissolved species ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ) using ion chromatographs, through continuous sampling and filtration of the river water. The RL allows us to revisit the C-Q at the highest time resolution ever reported.

The RL was deployed between 2015 and 2017 in the Orgeval hydrological Observatory (OZCAR Research Infrastructure), an agricultural watershed underlain by carbonates, France. The year 2016 was exceptional by the number of flood events and their intensity. Five major floods have been recorded including 1 at 1/(20y) frequency of occurrence and 2 at 1/(5y). We present the C-Q recorded for each of the flood events. We observe i) element-specific C-Q ii) C-Q loops, the size and the excentricity of which decrease with the intensity of the flood. The most reproducible C-Q patterns are observed for  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , whereas  $\text{K}^+$  and  $\text{NO}_3^-$  present a more erratic behaviour.

We focus our interpretations on the recession of each flood event, where precipitation and evapotranspiration can be considered as negligible. We examine several ways of interpretation such as a basic “double-bucket mixing” model as well as a “grey box” model such as already developed from stream flow [2] but here extended to solute fluxes.

[1] Floury et al. Hydrol. Earth Syst. Sci. Discuss., doi:10.5194/hess-2017-12, 2017.

[2] James W. Kirchner. Water Resources Research, VOL. 45, W02429, doi:10.1029/2008WR006912, 2009.