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Seasonal variability of geochemical signatures of streamflow: potential implications for end-member characterizations

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Until recently, the vast majority of investigations on water source and flowpaths have been focusing on small catchments with homogenous landuse and geology. While these studies have brought new knowledge on how these individual hydrological systems behave, we still face uncertainties inherent to basic assumptions related to end-member stability and degree of mixing.

We rely on hydroclimatological and hydrogeochemical datasets collected in three small experimental catchments with contrasting lithology in the Attert river basin (Luxembourg, Europe): the Weierbach (schists), the Huewelerbach (sandstone) and the Wollefsbach (marls). Investigations based on oxygen and hydrogen stable isotope signatures in streamwater show the dominant influence of geology on catchment storage and mixing potential (Pfister et al., in preparation). Catchments dominated by permeable substrate exhibit stable isotopic signatures through the entire range of the flow duration curve, consistent with large storage volumes and mixing potential. On impermeable substrate, storage volumes are smaller and reduced mixing potential exists; isotopic signatures of streamflow are much more variable.

Here, our objective is to determine whether (i) geochemical signatures along the individual flow duration curves of catchments exhibit similar patterns to those of stable isotopes and (ii) what potential implications those patterns have on mixing assumptions and end-member stability/identification.

Our findings show two distinct patterns along the flow duration curves for cations, silica, EC and Abs254: during low flow conditions (i.e. restricted to groundwater contributions), concentrations of these parameters tend to increase as discharge values decrease, whereas during high flows, concentrations are more or less stable. For anions, no distinct patterns could be determined. Nitrates exhibit a special behaviour, in that their concentrations gradually increase with rising discharge values along the entire flow duration curve.

Our observations document a significant variability of all investigated geochemical parameters during low flow conditions – a flow condition were only one well-mixed component is supposed to be hydrologically active. These findings give new insights to the use of streamwater sampled during low flow conditions for characterizing groundwater as a potential end-member.