

Disentangling concentration-discharge relationships during a flood event using a multi-isotope approach

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Concentration-discharge (C-Q) variations have been widely used as indicators of hydrologic and biogeochemical reactions. However, elemental concentrations must be representative of most compartments contributing to C-Q variations to identify processes driving changes in chemical fluxes produced by hydrologic forcing. Isotopic ratios (R) are helpful tracers providing complementary fingerprints about flow path, mixing or reactivity in catchments. Here, we analyze C-Q-R dynamics during a flood in the headwater experimental catchment of the Weierbach in Luxembourg by the combined use of silicon ($\delta^{30}\text{Si}$), hydrogen (δD) and oxygen ($\delta^{18}\text{O}$) isotopes. For one 28-day storm event, rain, soil pore water, groundwater and stream water were sampled at high frequency (1h) to determine $\delta^{30}\text{Si}$, δD , $\delta^{18}\text{O}$ as well as major cations and anions, metals, and DOC. The rain produced a double peak hydrograph response in the stream; the first is likely an immediate response to precipitation, meanwhile the second is delayed from the rain event by 2 days and presents higher discharge. Isotopic ratios and elemental concentrations exhibit different behavior for both peaks. During the first peak, Si shows a dilution pattern while $\delta^{30}\text{Si}$ decrease on the rising limb and reverse in the falling limb. For the second peak, Si concentration shows no dilution with respect to base flow but a similar shift to lighter $\delta^{30}\text{Si}$ values during the rising limb and then reverse during the descending limb, reaching heavier values than baseflow. Water isotopes point to a higher contribution of “new” water (~20%) during the first peak, whereas the second peak is mainly composed of pre-event water (> 95%). In the first peak, the decrease of $\delta^{30}\text{Si}$ during the rising limb, younger water fraction, and the flushing behavior of metals and DOC suggest an increase of water flowing through superficial layers promoting dissolution of clays and/or phyloliths. The shift of $\delta^{30}\text{Si}$ to a lighter signature during the second peak can be explained by the rise of the water level, allowing the reaction of groundwater with new materials and enhancing soil and saprolite weathering. Our results indicate that C-Q variations are related to changes in water flow path and contribution of “new” biogeochemical reactions.