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How do concentration-discharge relations vary among rainfall-runoff events? An analysis for the Ressi experimental catchment (Italian pre-Alps)

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Understanding discharge and solute responses is pivotal for water resources management and pollution mitigation measures. The few studies that have analysed concentration-discharge relations using high temporal resolution tracer data collected during rainfall-runoff events have shown that these relations may vary for different events and depend on season, event characteristics or antecedent wetness conditions.

In this study, we used hydrometric and tracer data (stable isotopes, major ions and electrical conductivity (EC)) to i) compare the concentration-discharge relations for different tracers, ii) characterize the hysteretic relations between discharge and tracer concentrations at the event timescale, and iii) determine whether the changes in hysteresis can be explained by event characteristics.

Data collection was carried out in the Ressi catchment, a 2-ha forested watershed in the Italian pre-Alps. The catchment is characterized by high seasonality in runoff response, due to the seasonality in rainfall (high in fall) and evapotranspiration (high in summer). Discharge and rainfall have been measured continuously since August 2012. Stream water, precipitation, shallow groundwater and soil water samples were collected for tracer analyses during 20 rainfall-runoff events between September 2015 and August 2018. All samples were analyzed for EC, isotopic composition (^{2}H and ^{18}O) and major ion concentrations. To investigate the possible controls on concentration-discharge relations, we determined the main characteristics (e.g., total event rainfall, rainfall intensities, antecedent soil moisture and depth to water table, runoff coefficient) for each selected rainfall-runoff event.

The EC, calcium, magnesium, sodium and sulfate concentrations in stream water decreased during rainfall events, due to the dilution by rain water. The concentration-discharge relations for these tracers with a dilution behavior were stronger and more significant than for the tracers that were mobilized during the event. Interestingly, nitrate, potassium and chloride, concentrations

sometimes increased at the onset of events, likely due to a rapid flushing of solutes from the dry parts of the stream channel and the riparian area, and then decreased during the event. These temporal dynamics in solute concentrations resulted in different hysteretic relations with discharge. Clockwise loops (i.e., discharge peaked later than the tracer concentrations) were common for the isotopes, chloride and potassium, whereas anti-clockwise hysteresis loops were more typical for EC, magnesium, calcium, sulfate, sodium and nitrate. A preliminary correlation analysis suggests that event characteristics alone cannot explain the changes in hysteresis, except for the hysteresis area for the relations between discharge and calcium concentration that depends on the magnitude of the rainfall event (i.e., the larger the rainfall amount and the runoff coefficient, the smaller the hysteresis loop).

These results highlight the importance of the first flush and indicate that runoff processes and solute sources can change when the catchment becomes wetter and connectivity of the hillslopes to the stream increases.

Keywords: concentration-discharge relation; major ions; electrical conductivity; stable isotopes; hysteresis; forested catchment.