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Using concentration-discharge relationships to identify solute and sediment sources and transport pathways at event and longer time scales

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Concentration-discharge (C-Q) relationships reflect the sources, flowpaths, and transformations of solutes and sediments in catchments. Spatial and temporal variations in flow paths and connectivity influence the C-Q patterns observed at the catchment outlet. We examined the C-Q relationships of multiple solutes and sediments at event and inter-annual time scales over 11 years in a mid-Atlantic (USA) catchment. Our results revealed systematic and consistent differences in the C-Q behavior of geogenic/exogenous solutes (e.g., calcium, nitrate), biogenic solutes (e.g., dissolved organic carbon), and particulate materials (e.g., total suspended sediment, total phosphorus). At both event and inter-annual time scales, the C-Q patterns of solutes were linked to the spatial distribution of hydro-biogeochemical sources throughout the catchment, and the timing and sequence of these source contributions to the stream. Geogenic solutes exhibited clockwise hysteresis during individual storm events and negative log(C)-log(Q) regression slopes (indicating dilution) on inter-annual time scales. In contrast, biogenic solutes were generally characterized by anti-clockwise hysteresis during events and positive log(C)-log(Q) slopes (indicating accretion) on longer time scales. These patterns in solute concentrations demonstrate that groundwater is the primary source of stormflow during the earliest and latest stages of storm events, while soil water and direct precipitation inputs increase near the time of peakflow as hillslopes become hydrologically connected to the stream. However, a notable deviation from these consistent patterns occurred during Hurricane Irene, when calcium, magnesium, and sodium demonstrated anti-clockwise hysteresis. Isotope hydrograph separation during this extreme event indicated that stormflow was dominated by direct precipitation inputs rather than groundwater and soil water during this storm. For particulate materials, clockwise hysteresis and longer-term C-Q patterns of accretion were predominant, and the factors responsible for generating these relationships differed from those of solutes. Particulate C-Q relationships are regulated by the spatio-temporal expansion of hydrologic connectivity between the stream channel and near-stream areas, whereas variations in hydrologic source inputs regulate solute C-Q patterns. We will discuss the hydro-biogeochemical source dynamics responsible for the characteristic solute and sediment C-Q patterns observed across temporal scales. In addition, we will describe the calculation and application of hysteresis, flushing, and C-Q indices to characterize catchment-scale biogeochemical export dynamics.