

Exploring Multiscale Variation in Concentration-Discharge Patterns

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Concentration (c) -discharge (Q) analyses allow inference of catchment-scale processes that combine aspects of streamflow generation and water quality genesis, including solute source areas, flowpaths, and biogeochemical processing. Here, we explore differences in c-Q patterns at long-term watersheds thru time and at nested spatial scales. Watersheds span agricultural, forest, and urban land uses, including Mahantango Creek and Conewago Creek, Long-Term Agroecosystem Research (LTAR) watersheds, the Penn State Leading Ridge Experimental Watersheds, and the Baltimore Ecosystem Study watersheds. C-Q patterns reveal changes thru time and across spatial scales. Additionally, we find differences in c-Q slopes between composite analysis and individual events in sites with high-frequency water quality data. Multi-decadal grab sampling at Mahantango Creek's WE-38 subwatershed, conducted three times per week, reveal a clear enrichment pattern over a 36-year record (1983-2019). The long-term composite data show a decrease in peak concentrations over recent decades and that slopes across all time periods are impacted by both low and high flow conditions in wetter vs. drier years. We also analyze dissolved inorganic nitrogen c-Q patterns at Conewago Creek, a larger, mostly agricultural watershed. Conewago Creek has two gaging stations that have been less intensively sampled between (2012-2022). Temporal trends in c-Q patterns diverge between upper and lower stations. Baltimore Ecosystem Study watersheds were sampled weekly (1998-2018) and span an urban gradient. Seasonal patterns of c-Q patterns change with increasing scale. While land use change has been minimal in these urbanized watersheds, sewer infrastructure and stormwater controls have increasingly been implemented. Leading Ridge, PA is a forested watershed that has been sampled approximately weekly from 1972-2007 and from 2018-current. In the forested watersheds, including Pond Branch, MD and Leading Ridge, PA, changes in c-Q patterns are notable thru time and are poorly correlated with reductions in atmospheric deposition. In sum, these results suggest other controls beyond hydroclimatic variability on the temporal dynamics of c-Q relationships, including watershed management effects. Changing cQ patterns thru time and across spatial scales have implications for process level inference and future water quality sampling design.