Water Flowpath and Source Chemistry Control C-Q Relationships Across Spatial Scales

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Hydrologists are learning to predict concentration-discharge (C-Q) behaviors for solutes in streams. This is essential because we need to understand how streams will respond to climatic, hydrologic, and anthropogenic changes in the future. The C-Q behavior of sulfate is complex because different subsurface flowpaths transport sulfate from different sources. For example, pyrite oxidation typically releases sulfate deep in the subsurface; therefore, deeper flowpaths tend to transport this sulfate to streams. Additionally, acid rain and fertilizers can release solute that is transported to streams via shallow flowpaths or surface runoff. We hypothesize that the dominant flowpath and sulfate source control C-Q behavior across spatial scales. Here, we investigate this hypothesis in four nested watersheds in the northeastern United States: Shale Hills (0.08 km²), 3 sites in Shavers Creek watershed (165 km²), 2 sites in Juniata River watershed (1,960 km²), and 9 sites in the Susquehanna River watershed (71,250 km²). Using the major ion chemistry and an unsupervised machine learning model, we separate the sources of sulfate in each sample. Additionally, we quantify the ratio of baseflow to streamflow (baseflow index; BFI) as a proxy for groundwater inputs into the stream using discharge data. We found that in both Shavers Creek and the Susquehanna River, sulfate in the headwaters was predominantly derived from acid rain, and that contributions of pyrite-derived sulfate increased downstream. Sites with low pyrite-derived sulfate and low BFI tended to show slopes on plots of C vs. Q that are close to zero (chemostatic) and sites with high pyrite-derived sulfate and high BFI tended to show steeper negative slopes (dilution C-Q behavior). Based on our finding, we predict steeper C-Q slopes in the future as watersheds recover from the impacts of acid rain and as agricultural best management practices reduce fertilizer runoff. Using machine learning techniques with C-Q data will help predict river chemistry into the future.