



Scale effects of nitrate sinks and sources in stream networks

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Increasing N-fertilizer applications in agricultural catchments are considered as one of the major sources for dissolved nitrate-nitrogen ($\text{NO}_3\text{-N}$) in surface water. While $\text{NO}_3\text{-N}$ mobilization pathways depend on catchment's pedological and hydrogeological characteristics and its runoff generation processes, in-stream retention and removal processes depend on local/reach-scale conditions such as weather, discharge, channel morphology, vegetation, shading or hyporheic exchange and others. However, knowledge is still limited to scale up locally observable retention and removal processes to larger stream networks to understand the spatial and temporal dynamics of in-stream $\text{NO}_3\text{-N}$ concentrations. Relevant processes to consider explicitly are the effects of "hot spots", dominant $\text{NO}_3\text{-N}$ sources (e.g. sub-catchments, "critical source areas") or specific $\text{NO}_3\text{-N}$ sinks (e.g. riparian wetlands and stream reaches with high biogeochemical activity). We studied these processes in a 1.7 km² agricultural headwater catchment, where distinct locations of groundwater inflow (a dense artificial drainage network) and a predominantly impervious streambed allowed separating mixing and dilution processes as well as in-stream retention and removal processes. During two summer seasons we conducted a set (25) of stream network wide (stream water and drainage water) synoptic sampling campaigns including climate parameters, discharge, channel geomorphology, vegetation, stream water chemistry and physical water parameters (dissolved oxygen concentration, water temperatures, electrical conductivity, pH). Analyzing these data sets we were able to determine a) time variant $\text{NO}_3\text{-N}$ concentrations and loads for all sub-catchments (sources), b) time variant in-stream removal rates for all stream reaches (sinks) and c) the hierarchical order of all contributing $\text{NO}_3\text{-N}$ sinks and sources and their time variant influence on total $\text{NO}_3\text{-N}$ export. Climate parameters, discharge, channel geomorphology, vegetation, stream water chemistry and physical water parameters were then used to identify controls of in-stream removal processes. The strongest correlations with $\text{NO}_3\text{-N}$ in-stream removal rates were found for stream water temperatures, vegetation density and shading. We developed a data-driven mixing-and-removal model to directly quantify the spatial scaling effects on the reproducibility of observed in-stream $\text{NO}_3\text{-N}$ concentration patterns. The position of the largest sinks and sources in the stream network is the major control, due the local impacts on the relationship between discharge, concentration and load. The upstream positions of sources control the efficiency of downstream sinks by regulating in-stream $\text{NO}_3\text{-N}$ availability, while the upstream positions of sinks have an impact on downstream mixing and dilution processes. Understanding the interplay of $\text{NO}_3\text{-N}$ sinks and sources in stream networks will contribute to a better description of $\text{NO}_3\text{-N}$ export and retention processes even for catchments with a more diffuse occurrence of $\text{NO}_3\text{-N}$ sinks and sources.