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Diurnal variation of dominant nitrate retention processes in an agricultural headwater stream

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Nitrate and ammonium are introduced by agricultural practice into the environment and are transformed and retained on their pathway through aquatic environments. In particular, biological transformation processes (i.e. microbial denitrification or ammonium oxidation and assimilation) are responsible for the largest part of nitrate removal, which are also crucial processes in headwater streams. It is well known, that most of the biological processes are influenced by available (solar) energy fluxes, temperatures and dissolved oxygen concentrations, which vary with time and space. However, looking at biogeochemical hot spots in the landscapes‘ hydrological interface, the stream and river network (e.g. stream sections with a high biological activity), the temporal variability of biological processes can be an important control on total nitrate export. In this study, we therefore identified most important diurnal time periods for nitrate retention in a 75 m impervious section of an agricultural headwater stream using oxygen saturation dynamics and nitrate isotopes.
We regularly measured discharge, hydro-geochemical and climate parameters, as well as nitrate and water isotopes in grab samples at three locations along the reach. On average, we observed a decrease of 10% in nitrate concentration from up- to downstream, which was only caused by biological processes and not by dilution. Nitrate isotope analysis indicated distinct trends along the reach and with time of the day. Both nitrate assimilation and nitrification caused significant changes in nitrate isotope distribution in the early day. To explain the distinct observed process dynamics from the morning to the afternoon, we simulated net primary production (NEP) and respiration using the river metabolism model RIVERMETC with observed oxygen concentrations and water temperatures. Comparing the results with the observed nitrate dynamics, the short time period when NEP occurs ($\sim$10:30 -12:30) seems to be crucial for nitrate assimilation processes. These results indicate that diurnal variation of the nitrogen cycle at biogeochemical hot spots can partly control the spatial nitrate-retention function of headwater stream networks. This needs to be considered in ecological stream management, especially when setting up water quality monitoring networks.