

Understanding the relationship between DOC and nitrate export and dominant rainfall-runoff processes through long-term high frequency measurements

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Over the past decades, stream sampling protocols for hydro-geochemical parameters were often limited by logistical and technological constraints. While long-term monitoring protocols were typically based on weekly sampling intervals, high frequency sampling was commonly limited to a few single events. In our study, we combined high frequency and long-term measurements to understand the DOC and nitrate behaviour and dynamics for different runoff events and seasons.

Our study area is the forested Weierbach catchment (0.47 km²) in Luxembourg. The fractured schist bedrock is covered by cambisol soils. The runoff response of the catchment is characterized by a double peak behaviour. A first discharge peak occurs during or right after a rainfall event (triggered by fast near surface runoff generation processes), while a second delayed peak lasts several days (generated by subsurface flow/ shallow groundwater flow). Peaks in DOC concentrations are closely linked to the first discharge peak, whereas nitrate concentrations follow the second peak. Our observations were carried out with the field deployable instrument spectro::lyser (scan Messtechnik GmbH). This instrument relies on the principles of UV-Vis spectrometry and measures DOC and nitrate concentrations. The measurements were carried out at a high frequency of 15 minutes in situ in the Weierbach creek for more than two years. In addition, a long-term validation was carried out with data obtained from the analysis of water collected with automatic samplers.

The long-term, high-frequency measurements allowed us to calculate a complete and detailed balance of DOC and nitrate export over two years. Transport behaviour of the DOC and nitrate showed different dynamics between the first and second hydrograph peaks. DOC is mainly exported during first peaks, while nitrate is mostly exported during the delayed second peaks. In combination with other measurements in the catchment, the long and detailed observations have enabled us to derive relationships between DOC and nitrate export and different catchment states: soil wetness and groundwater levels, precipitation and seasonality. Altogether, the long-term and high-frequency time series provides the opportunity to study DOC and nitrate export without having to just rely only on either a few single event measurements or coarse measurement protocols.