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High-frequency DOC and nitrate measurements provide new insights into their export and their relationships to rainfall-runoff processes

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Over the past decades, stream sampling protocols for environmental tracers were often limited by logistical and technological constraints. Long-term sampling programs would typically rely on weekly sampling campaigns, while high-frequency sampling would remain restricted to a few days or hours at best. We stipulate that the currently predominant sampling protocols are too coarse to capture and understand the full amplitude of rainfall-runoff processes and its relation to water quality fluctuations. Weekly sampling protocols are not suited to get insights into the hydrological system during high flow conditions. Likewise, high frequency measurements of a few isolated events do not allow grasping inter-event variability in contributions and processes. Our working hypothesis is based on the potential of a new generation of field-deployable instruments for measuring environmental tracers at high temporal frequencies over an extended period. With this new generation of instruments we expect to gain new insights into rainfall-runoff dynamics, both at intra- and inter-event scales.

Here, we present the results of one year of DOC and nitrate measurements with the field deployable UV-Vis spectrometer spectro::lyser (scan Messtechnik GmbH). The instrument measures the absorption spectrum from 220 to 720 nm *in situ* and at high frequencies and derives DOC and nitrate concentrations. The measurements were carried out at 15 minutes intervals in the Weierbach catchment ($0.47\ km^2$) in Luxemburg. This fully forested catchment is characterized by cambisol soils and fractured schist as underlying bedrock.

The time series of DOC and nitrate give insights into the high frequency dynamics of stream water. Peaks in DOC concentrations are closely linked to discharge peaks that occur during or right after a rainfall event. Those first discharge peaks can be linked to fast near surface runoff processes and are responsible for a remarkable amount of DOC export. A special characterisation of the Weierbach catchment are the delayed second peaks a few days after the rainfall event. Nitrate concentrations are following this second peak. We assume that this delayed response is going back to subsurface or upper groundwater flows, with nitrate enriched water. On an inter-event scale during low flow / base flow conditions, we observe interesting diurnal patterns of both DOC and nitrate concentrations. Overall, the long-term high-frequency measurements of DOC and nitrate provide us the opportunity to separate different rainfall-runoff processes and link the amount of DOC and nitrate export to them to quantify the overall relevance of the different processes.