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In situ high-frequency UV-Vis spectrometer probes for investigating runoff processes and end member stability.

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In recent years, several limitations as to the application of end member mixing analysis with isotope and geochemical tracers have been revealed: unstable end member solutions, inputs varying in space and time, and unrealistic mixing assumptions. In addition, the necessary high-frequency sampling using conventional methods is time and resources consuming, and hence most sampling rates are not suitable for capturing the response times of the majority of observed headwater catchments. However, high-frequency observations are considered fundamental for gaining new insights into hydrological systems.

In our study, we have used two portable, *in situ*, high-frequency UV-Vis spectrometers (spectro::lyser; scan Messtechnik GmbH) to investigate the variability of several signatures in streamflow and end member stability. The spectro::lyser measures TOC, DOC, nitrate and the light absorption spectrum from 220 to 720 nm with 2.5 nm increment. The Weierbach catchment (0.45 km^2) in the Attert basin (297 km^2) in Luxemburg is a small headwater research catchment (operated by the CRP Gabriel Lippmann), which is completely forested and underlain by schist bedrock. The catchment is equipped with a dense network of hydrological instruments and for this study, the outlet of the Weierbach catchment was equipped with one spectro::lyser, permanently sensing stream water at a 15 minutes time step over several months. Hydrometric and meteorologic data was compared with the high-frequency spectro::lyser time series of TOC, DOC, nitrate and the light absorption spectrum, to get a first insight into the behaviour of the catchment under different environmental conditions. As a preliminary step for a successful end member mixing analysis, the stability of rainfall, soil water, and groundwater was tested with one spectro::lyser, both temporally and spatially. Thereby, we focused on the investigation of changes and patterns of the light absorption spectrum of the different end members and the stream water. Besides using DOC and nitrate for characterizing the end members, our idea is to use the light absorption spectrum as a fingerprint of various constituents of the water. To get a better understanding on how to handle the *in situ* spectro::lyser, the instrument was compared to conventionally analysed water samples with a special focus on fundamental technical issues: Is there a general difference between *in situ* and lab measurements and does it make a difference whether the samples are analysed immediately in the field or after days and weeks in the lab and/or again with the spectro::lyser? First results indicate the value of using *in situ* spectrometers to capture high-frequency variations of hydro-chemistry and end member mixing during runoff events in a small headwater catchment.