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Does topography explain the spatial variability in shallow groundwater chemistry in a small pre-alpine catchment?

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Landscape characteristics influence the storage and release of water and thus groundwater dynamics and chemistry. Even though it is well known that shallow groundwater is not one well-mixed storage and shallow groundwater chemistry varies spatially, often only one or two groundwater samples are used in hydrograph separation studies to determine the contribution of groundwater to streamflow. Quantification of catchment scale variability in groundwater chemistry may help to better understand hydrological flow pathways and allow interpretation of the variations in streamwater chemistry in terms of which parts of the catchment contribute to streamflow.

We present the results from nine snapshot campaigns in a 20-ha steep mountainous catchment in the Swiss pre-Alps during baseflow conditions. During each campaign, shallow groundwater was sampled from 34 - 47 wells and analysed for major ion concentrations and stable isotopes (δ^2H and δ^{18}O). The spatial variability in the isotopic composition of the groundwater and solute concentrations was large for all sampling campaigns and varied seasonally. The lowest measured EC was 68 μS/cm and the highest measured EC was 825 μS/cm. The spatial variability in the isotopic composition of the groundwater was smallest in early summer and autumn (standard deviation: δ^2H 2.3 ‰ and 3.4 ‰ respectively) and largest during the dry conditions in late August (standard deviation: δ^2H 9.5 ‰). Similarly, the standard deviation of the EC was 128 μS/cm, 114 μS/cm, and 118 μS/cm in spring, summer and autumn, respectively. The solute concentrations and isotopic composition of the groundwater were related to landscape characteristics, such as (local) slope and upslope accumulated area, and indices that describe groundwater dynamics, such as the skewness of the frequency distribution of the groundwater levels and the fraction of time that groundwater levels were close to the soil surface (i.e. persistence of near-surface groundwater levels). The concentrations of manganese and iron were highest at sites that had persistent high groundwater levels, while the concentrations of lead and zinc were highest at sites that were predominantly dry. However, all relations were weak (spearman correlation coefficients $<$0.55), indicating that it is difficult to determine the spatial variability in shallow groundwater from a few point measurements.

The temporal variability in the isotopic composition of the groundwater was used as a proxy for shallow groundwater residence time and to distinguish sites with a relatively rapid turnover of the groundwater from sites that are flushed less regularly. The temporal variability of the isotopic composition was largest at sites in the upper part of the catchment, close to the catchment water divide, and at sites near local ridges. The EC at these locations was lower (rs= -0.53) than at sites with a less variable isotopic composition. The observed large spatial variability in groundwater chemistry highlights the need to sample groundwater at more than one location, even in small catchments, but possibly also provides opportunities to distinguish different groundwater source areas based on the temporal variability in streamwater quality.