Estimating endmember chemistry of contributing sources to low flows in Alpine headwater catchments

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After extended dry periods, streamflow is fed by groundwater to a large fraction. In high elevation, Alpine catchments these low flow periods occur typically in winter, when there is minor contribution to streamflow and catchment storage from liquid precipitation and snowmelt. Snapshot sampling campaigns in headwater streams during these low flow periods reveal the chemical fingerprint of the contributing groundwater sources. The chemical composition of these sources is largely influenced by the input precipitation (liquid and solid), weathering products (depended on the lithology) and contaminants (from agriculture and other sources). We analyzed water samples from snapshot campaigns in three Alpine creeks – mixed samples, along the stream network - during low flow for their ion composition. Using maximum likelihood calculations, we define the composition of the selected conservative ions of the major endmembers (up to three), based on the mixed samples along the main stem. In addition, we reproduce the endmember chemistry from the different lithologies by dissolution experiments, and use them as benchmark. The proposed methodology allows to i) reduce uncertainty of the endmembers and ii) quantify the relative contribution of each lithology to streamflow. The latter allows to infer how the contribution of different endmembers varies spatially throughout Alpine headwater catchments.