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End member mixing analysis (EMMA): Estimating the Value of Large Tracer Sets Versus Small Tracer Sets

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End member mixing analysis (EMMA) is a commonly applied method to identify and quantify the dominant runoff producing sources of water. It employs isotopic and geochemical tracers to determine the dimensionality of the hydrologic system, i.e. the number of end members (EM) or components that are necessary to reproduce runoff in the catchment under investigation. This is typically done by applying Principle Component Analysis (PCA) and the Rule of 1 [Joreskog et al., Geological Factor Analysis: Methods in Geomathematics, 1976] or the diagnostic tools of Hooper [Water Resour. Res., 2003, doi:10.1029/2002WR001528]. Based on this information the contribution of each end member to runoff is quantified by solving a set of mass balance equations. Many studies have been conducted to identify and quantify runoff sources using 2 to 6 tracers, with the main tracers being Ca, K, Mg, Na, Cl-, SO42-, Si, the isotopes δ18O and δD, acid neutralizing capacity (ANC), alkalinity and EC. Only few studies use larger tracer sets including also minor trace elements such as Li, Rb, Sr, Ba etc. None of the studies so far addressed the question of the tracer set size and composition, despite the fact that these determine which and how many end members will be identified.

In this study we examine how tracer set size and composition affects the model concept that results from an EMMA. We developed an automatic procedure that iteratively changes tracer set size and composition and conducts EMMA for each tracer set possibility. We are using a set of 14 tracers and 9 EMs. The validity of resulting model concepts was investigated under the aspects of dimensionality (EMs needed to explain flow in a system), EM combinations and contributions to stream water. From the 16.369 tracer set possibilities only 23 delivered results that were plausible as defined by mixing model theory. This large reduction of plausible results can mainly be attributed to differences in tracer ratios of stream water and EM waters. Hence, the resulting model concepts are highly sensitive to the tracer set size and composition. However, a certain degree of consent exists among dimensionality and selected EM combinations. The moderate reproducibility of EM contributions indicates that more field work is necessary to identify a still missing EM. It also emphasizes that the major elements are not always the most useful tracers and that larger tracer sets that contain also minor trace elements have an enhanced capacity to avoid false conclusions about catchment functioning. The presented iterative EMMA approach is able to produce results that may not be apparent from the traditional approach and we stress the fact that this approach provides a very valuable complement.