Goldschmidt 2021 Abstract
https://doi.org/10.7185/gold2021.6832

Overcoming the EMMA dilemma: on the potential for PHREEQC's Inverse modelling functionality to decouple chemical processes from conservative mixing processes and reducing variability in end member mixing analysis

KARL NICOLAUS VAN ZWEEL[1], LAURENT GOURDOL[1], CHRISTOPHE HISSLER[1], LAURENT PFISTER[1] AND ERWIN ZEHE[2]

[1]Luxembourg Institute of Science and Technology
[2]Karlsruhe Institute of Technology
Presenting Author: nicolaus.vanzweel@list.lu

The common conceptualisation that surface waters more closely resemble soil- or ground water than precipitation, has led many researchers to theorize that the magnitude and mobility of stored subsurface water can be inferred from stream chemistry. Many studies have attempted to link the hydrological- and biogeochemical functioning of the Critical Zone to concentration-discharge patterns observed at catchment scale. This is usually achieved through End Member Mixing Analysis (EMMA). However, one major limitation of this technique is the variability in end-member hydro-chemical signatures caused by chemical reactions. A recent study has shown by using a synthetic hydro-chemical dataset, that the variance caused by chemical reactions in a mixing model can be accounted for by decoupling the chemical component for a mixing ratio calculation. If done by hand, this process can be tedious and cumbersome. In this study we show that this process can eventually be streamlined by using the PHREEQC's inverse modelling capabilities in conjunction with principle component analysis. This allows for identifying the minimum number of endmembers that explain the observed variability within a dataset – thereby addressing the non-conservative nature of chemical species when applying multi-variate methods on groundwater datasets.

The methodology proposed here is first applied on a synthetic dataset, where the chemical reactions are known, before being applied to an extensive hydro-chemical database spanning over 10 years that include surface, soil, and groundwater monitoring data. Our analysis sheds new light on the potential chemical reactions governing chemical change during mixing and the relative contributions of the identified endmembers to streamflow generation.