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Assessment of Hydrochemistry for Use as Groundwater Age Proxy

Monique Beyer (1,2), Chris Daughney (2), Bethanna Jackson (1), and Uwe Morgenstern (2)
(1) Victoria University of Wellington, New Zealand, (2) GNS Science, Lower Hutt, New Zealand

Groundwater dating can aid groundwater management by providing information on groundwater flow, mixing and residence-, storage- and exposure-time of groundwater in the subsurface. Groundwater age can be inferred from environmental tracers, such as tritium, SF6 and CFCs (CFC-12, -11 and -113). These tracers often need to be applied complementarily, since they have a restricted application range and ambiguous age interpretations can be obtained. Some tracers, such as the CFCs, will become of limited use in near future, due their fading out atmospheric concentration. As a consequence of these limitations, there is a need for additional, complementary tracers to ensure groundwater dating in future. Hydrochemistry parameters, such as the concentrations and ratios of major ions, appear to be promising candidates. Hydro-chemistry data at various spatial and temporal scales are widely available through local, regional and national groundwater monitoring programmes. Promising relationships between hydrochemistry parameters and groundwater residence time or aquifer depth have been found in near piston flow environments. However, most groundwater samples contain proportions of different aged water, due to mixing of water emerging from different flow lines during sampling or discharge, which complicates the establishment of hydrochemistry-time relationships in these environments.

In this study, we establish a framework to infer hydrochemistry – (residence) time relationships in non-piston flow environments by using age information inferred from environmental tracer data and lumped parameter models (LPMs). The approach involves the generation of major element concentrations by 'classic' Monte Carlo simulation and subsequent comparison of simulated and observed element concentrations by means of an objective function to establish hydrochemistry-time relationships. The framework also allows for assessment of the hydrochemistry-time relationships with regards to their potential to further constrain the (often ambiguous) age interpretation inferred from environmental tracers.

We apply the framework to age information (inferred from SF6 and tritium) and hydrochemistry observations from a groundwater system in the Wellington Region, New Zealand. We found that the strongest hydrochemistry-time relationships can be established for the concentration of silica, calcium, sodium and total dissolved solids. Mineral weathering kinetics inferred from these relationships agree with mineral weathering kinetics found in other groundwater environments. For 4 out of 9 sites, with previously ambiguous age interpretation, ambiguity can be resolved by using the established hydrochemistry-time relationships. There does not appear to be one hydrochemistry parameter which can constrain age information at all sites, but different parameters work at different sites. Further study is vital to better understand under what conditions hydrochemistry can be used as a complementary or alternative groundwater age tracer in various groundwater environments.

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