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Use of trace and rare earth elements to quantify autogenic and allogenic inputs within a lowland karst network

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ABSTRACT

Trace element geochemistry of natural waters has emerged as an important strategy for tracing anthropogenic sources, water mixing, and physicochemical parameters such as redox conditions. In this study, ultra-trace element water geochemistry, with emphasis on the rare earth elements and yttrium (REY), was tested as a tool to fingerprint groundwater origin and pathways within a lowland karst aquifer network. The study area is well-defined from a hydrological perspective and provides an excellent natural system to investigate geochemical characteristics of allogenic and autogenic water mixing within a karst network. The new geochemical data have yielded refined insight into the temporal fluxes of water at different hydrological times of the year and, in particular, proved important for quantifying contributions of autogenic and allogenic runoff to the ephemeral karst lakes (known as turloughs) which emerge after surcharge of the karst conduit network following periods of high flows. Endmember definitions of the allogenic waters derived from rivers draining a catchment of predominantly Devonian Old Red sandstone vs. autogenic waters derived from limestone in contact within the karst network were established from REY pattern slope (Pr/Yb), Y/Ho ratio, and a number of other ratios generated from contrasting enrichments of high-solubility/low-particle reactivity elements that exhibited conservative or near-conservative behaviour (e.g,. Sr, Ba, Li, U, Mo). Under high-flow conditions, waters within the surcharged conduit network fall on mixing lines between the endmembers, and these relationships can be used to quantify the relative contribution of each water source in the conduit network. In contrast, under low-flow conditions the endmembers could still be defined but the geochemical mixing relationships in the aquifer network appear to have been complicated by enhanced particle reactivity in soil reservoirs