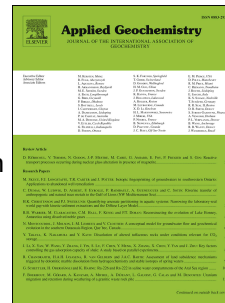


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Use of trace and rare earth elements to quantify autogenic and allogenic inputs within a lowland karst network

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

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11
12 **ABSTRACT**

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

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