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Seasonal and spatial variations in rare earth elements to identify inter-aquifer linkages and recharge processes in an Australian catchment

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ABSTRACT

With the aim of elucidating the seasonal behaviour of rare earth elements (REEs), surface and groundwaters were collected under dry and wet conditions in different hydrological units of the Teviot Brook catchment (Southeast Queensland, Australia). Sampled waters showed a large degree of variability in both REE abundance and normalised patterns. Overall REE abundance ranged over nearly three orders of magnitude, and was consistently lower in the sedimentary bedrock aquifer (18 ppt $< \sum$ REE $<$ 477 ppt) than in the other hydrological systems studied. Abundance was greater in springs draining rhyolitic rocks ($\sum$ REE $=$ 300 and 2054 ppt) than in springs draining basalt ranges ($\sum$ REE $=$ 25 and 83 ppt), yet was highly variable in the shallow alluvial groundwater (16 ppt $< \sum$ REE $<$ 5294 ppt) and, to a lesser extent, in streamwater (85 ppt $< \sum$ REE $<$ 2198 ppt). Generally, waters that interacted with different rock types had different REE patterns. In order to obtain an unbiased characterisation of REE patterns, the ratios between light and middle REEs ($R_{(M/L)}$) and the ratios between middle and heavy REEs ($R_{(H/M)}$) were calculated for each sample. The sedimentary bedrock aquifer waters had highly evolved patterns depleted in light REEs and enriched in middle and heavy REEs ($0.17 < R_{(M/L)} < 1.00$ and $-0.16 < R_{(H/M)} < 0.93$), whereas the springs draining intrusive and extrusive rocks had relatively flat patterns ($0.20 < R_{(M/L)} < 0.38$ and $-0.16 < R_{(H/M)} < 0.09$). Surface waters were generally enriched in middle REEs (median $R_{(M/L)} = 0.35$ and median $R_{(H/M)} = -0.04$), and waters from the shallow alluvial aquifer had very diverse patterns with important spatial variations. Samples collected from the alluvium exhibited an increasing influence of the sedimentary bedrock from upgradient to downgradient; typically they showed flat patterns in the upstream section of the alluvium (median $R_{(M/L)} = 0.21$ and median $R_{(H/M)} = -0.06$) gradually evolving towards patterns depleted in light REEs and enriched in middle and heavy REEs downgradient (median $R_{(M/L)} = 0.48$ and median $R_{(H/M)} = 0.38$). To document the seasonal variations in REE patterns, the difference in ratios between dry and wet sampling campaigns was determined for each repeated sampling location. Contributions from the sedimentary bedrock water to the alluvium during the wet season were identified at two locations (increase from $R_{(H/M)} = 0.03$ and 0.35 to $R_{(H/M)} = 0.62$ and 0.89). The effect of recharge through fractured igneous rocks was also observed in two boreholes intercepting the sedimentary bedrock, where the freshly recharged waters likely contributed to the deeper groundwater flow during the wet season (decrease from $R_{(M/L)} = 0.81$ and 0.56 to $R_{(M/L)} = 0.46$ and 0.17). Results from this study suggest that REEs may be usefully applied as indicators of recharge processes and inter-aquifer mixing. They also underline the importance of conducting seasonal sampling campaigns to capture possible short-term variations in REE patterns and abundance, which is essential to enable a better understanding of hydrological and hydrochemical processes in complex geological settings.

1. Introduction

Rare earth elements (REEs) form a group of 14 trace metals with gradually increasing atomic number that behave coherently and predictably (Henderson, 1984). Because of their potential use as tracers of groundwater origin and mixing processes, these elements have received much attention over the last several decades (Smedley, 1991; Johannesson et al., 1997; Dia et al., 2000; Gruau et al., 2004; Willis and Johannesson, 2011; Noack et al., 2014). REEs have been successful in describing processes that are not revealed when using conventional hydrochemical methods such as major ions and stable isotopes (Tweed et al., 2006). Where there is contrasting geology, and so contrasting mineralogy, REEs can be useful fingerprints of host aquifers or catchment geology

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(Playà et al., 2007). However, there is still some debate as to whether REE concentrations and their shale-normalised patterns represent the water–rock interactions occurring at a recent stage, i.e., reflecting host rock conditions (Johannesson et al., 1997; Tang and Johannesson, 2006; Göb et al., 2013), or at an earlier stage, i.e., reflecting recharge conditions (Möller et al., 2006; Tweed et al., 2006; Willis and Johannesson, 2011). This controversy stems from the considerable number of factors controlling REE concentrations and patterns in groundwater. Processes such as sorption, colloidal organic matter-mediated complexation and co-precipitation have been shown to occur after the dissolution of REEs from rocks following changes in pH and/or redox conditions (Johannesson et al., 1997, 2000; Biddau et al., 2002; Pourret et al., 2007). Preferential adsorption of light REEs relative to heavy REEs has also been observed (e.g., Johannesson et al., 2000; Leybourne et al., 2000; Tweed et al., 2006). Overall, the factors influencing geochemical reactions and thus REE fractionation patterns in aquifers are still not fully understood.

While spatial variations of REEs have been studied extensively and in a variety of aquifer systems (e.g., Biddau et al., 2009; Guo et al., 2010; Hagedorn et al., 2011; Siebert et al., 2012; Göb et al., 2013), the assessment of seasonal variations of REEs in groundwater systems is still lacking in the literature. Acquisition of temporally discretised data is important because single samples may not reflect the usual state of a system due to temporarily unusual conditions (e.g., Shiller, 1997). More importantly, capturing seasonal variations in REEs appears essential to appreciate the possible linkages between different aquifers as well as possible variations in driving mechanisms. Due to the ease of surface water sampling, several authors have reported on the temporal variability of REEs in rivers (Ingri et al., 2000; Shiller, 2002; Bagard et al., 2011; Möller et al., 2014). All such studies showed that fluctuations in REE concentrations and patterns could be substantial over time. In groundwater studies, however, temporal variability has been poorly examined so far: Olivié-Lauquet et al. (2001), followed by Gruau et al. (2004) and Pourret et al. (2010), investigated the temporal evolution of REE concentrations and patterns in the shallow groundwaters of wetland areas in Brittany, France. Pourret et al. (2010) showed that patterns were remarkably stable over their 7-year sampling record, whereas Gruau et al. (2004) described pronounced seasonal variations in absolute REE concentrations. Similarly, Poh and Gasparon (2011) found that REEs responded rapidly to recharge in boreholes intercepting a wetland aquifer of Southeast Queensland, Australia. In a deeper aquifer setting, Möller et al. (2006) reported substantial seasonal variations in the REE patterns from two bores drilled in a limestone aquifer system in Jordan; the authors concluded on inter-aquifer linkages with an underlying sandstone unit. Overall, little is known about the temporal variability of REEs in groundwater, and this particularly applies to mountainous areas where systems can be highly responsive to seasonal changes. There is, therefore, a need not only to document the spatiotemporal variability of REEs in groundwater bodies, but also to test their effectiveness as an indicator of inter-aquifer linkages as well as recharge processes. No such research has been undertaken to assess the impact of recharge on groundwater REE patterns.

In this study, we investigate the geochemical behaviour of REEs within a catchment located in Southeast Queensland, Australia (Fig. 1). The Teviot Brook catchment has been selected because it comprises a number of aquifers from a range of geological formations, which provide an ideal setting in which to explore inter-aquifer interactions. A Jurassic sedimentary formation forms the bedrock underlying much of the Quaternary alluvium, and recharge is expected to occur mainly through numerous Cenozoic intrusive and extrusive rocks scattered throughout the catchment. In some parts of the catchment, the sedimentary bedrock is in direct contact with the drainage network, and linkages between different aquifers and the river system can be anticipated. Here we test the hypothesis that REEs can be a valuable tracer of the spatial and temporal changes taking place within hydrological units and, consequently, of the linkages between streams and shallow and deeper aquifers. The detailed objectives of this study are (i) to define the REE concentrations and patterns for each hydrological unit (i.e., drainage system, igneous 'recharge' water, shallow alluvial groundwater, and deeper sedimentary bedrock aquifer), (ii) to explore the spatial and seasonal variability of REE signatures, and (iii) to use our findings to assess the usefulness of REEs as tracers of the linkages between aquifers and recharge processes.

2. Geologic and geochemical setting

Teviot Brook is a tributary of the Logan River, to the southwest of Brisbane (Australia). Precipitation and discharge data in the catchment indicate a pronounced seasonality. Intense rainfall triggering elevated flows occurs in summer from December through April, and this is followed by a much drier period from May to November. The Teviot Brook catchment forms part of the Clarence–Moreton Basin (CMB), a large sedimentary basin that covers the southeast region of Queensland and northeastern New South Wales (Fig. 1). The CMB contains fluvial sedimentary deposits of Triassic, Jurassic and Cretaceous age, which form interbedded sequences of aquifers and aquitards. In the study catchment, a Jurassic sedimentary sequence named the Walloon Coal Measures (WCM) forms the bedrock for much of the catchment and outcrops largely along its edges. The WCM consist of non-continuous beds of sandstone, siltstone, claystone, carbonaceous shale and coal (Wells and O'Brien, 1994), and have a thickness of around 120–240 m in the Teviot Brook catchment (Rassam et al., 2014). In the catchment headwaters, a Cenozoic lava flow sequence that is part of the Main Range Volcanics (MRV) extends over around 9 km^2. This is an almost exclusively mafic formation dominated by mildly alkaline basalt and hawaiite (Stevens et al., 1989; Cohen, 2012). Associated with this volcanic sequence are several intrusions of predominantly felsic composition (i.e., mainly rhyolite), which produce local plugs and dykes, and in places cap the lateral ranges of the catchment. Lastly, the Quaternary alluvium composed of weathered catchment materials overlies the WCM, which typically contains a basal sandy gravel layer overlain by a thicker layer of firm blue clay. The alluvium has a thickness ranging between 5 m upstream and over 20 m in the central sections and lowlands; there is no significant variability in the alluvium lithology from upstream to downstream.

The alluvial aquifer supports intensive irrigated agriculture. The WCM also provide supplies of groundwater that is commonly brackish, and is typically used for livestock watering. Groundwater of elevated salinity has also been observed in sections of the alluvium as well as in the stream (Li and Cox, 1996), indicating that the different geological layers are likely to be hydraulically connected. It is assumed that most of the recharge of aquifers occurs as mountain front recharge through the highly fractured igneous rocks outcropping in the headwaters and along the lateral ranges. In a recent study, Duvert et al. (in revision) used major ion and isotope hydrochemistry to interpret the hydrochemical processes within each hydrological unit of the Teviot Brook catchment. They demonstrated that alluvial groundwater and streamwater had a Ca–Mg–HCO_3 facies in the upstream section of the catchment, predominantly obtained through the weathering of silicates and carbonates. Silicates were mainly derived from the mafic rocks present in the headwaters, whereas carbonates were available as secondary minerals recrystallised in veins and fissures of the basalts. Weathering mechanisms were followed by gradual salinisation from upstream to downstream as a result of the influence of evapotranspiration in the unsaturated zone prior to recharge. In contrast, waters contained in the WCM were classified as Na–HCO_3–Cl type waters influenced by three concurrent processes, i.e., (i) evapotranspiration, (ii) the leaching from albite and Na-rich clay minerals of the WCM, and (iii) the anaerobic decomposition of organic matter (i.e., methanogenesis). Environmental isotope data showed substantial seasonal variations even in WCM waters, highlighting the significance of temporal changes in the groundwater systems of this area. Due to a comparable signature