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Cave drip water solutes in south-eastern Australia: Constraining sources, sinks and processes

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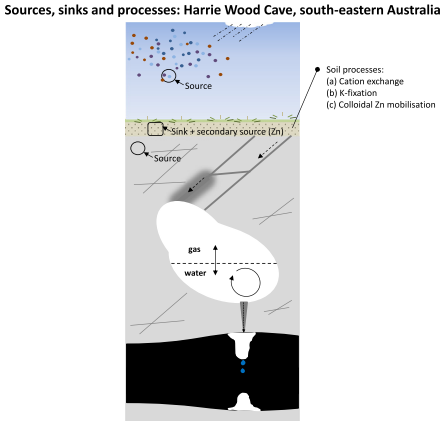
HIGHLIGHTS

- Atmospheric inputs contribute to drip water: Na, K, Zn and other trace elements.
- K-fixation in soils controlled drip water K during the Millennium Drought.
- Na and K respond to soil processes and to higher water flux at drought termination.
- Zn colloidal mobilisation is linked to a decrease in soil pH.
- Na, K and Zn show promise as speleothem palaeo-climate proxies.

GRAPHICAL ABSTRACT



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ABSTRACT

Constraining sources and site-specific processes of trace elements in speleothem geochemical records is key to an informed interpretation. This paper examines a 10-year data set of drip water solutes from Harrie Wood Cave, south-eastern Australia, and identifies the processes that control their response to El Niño-Southern Oscillation events which varies the site water balance. The contributions of aerosol and bedrock end-members are quantified via hydrochemical mass balance modelling. The parent bedrock is the main source for the drip water solutes: Mg, Sr, K and trace elements (Ba, Al, V, Cr, Mn, Ni, Co, Cu, Pb and U), while atmospheric aerosol inputs also contribute significantly to drip water trace elements and Na, K and Zn. A laboratory investigation evaluating water-soluble fractions of metals in soil samples and soil enrichment factors provided a basis for understanding metal retainment and release to solution and transport from the soil zone. These results identified the role of the soil as a sink for: trace metals, Na and K, and a secondary source for Zn. Further, soil processes including: cation exchange, K-fixation, metal adsorption to colloids and the release of Zn associated with organic matter degradation further modify the chemical composition of the resultant drip waters. This research is significant for the south-eastern Australian region, as well as other sites in a karst setting with clay-rich soil. In particular these results reveal that the response of drip water chemistry to hydroclimatic forcing is non-linear, with the greatest response

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observed when the long-term gradient in the cumulative water balance reverses. This longer-term drip water monitoring dataset is significant because it provides the pivotal framework required to reliably identify suitable trace element proxies for interpretation in geochemical speleothem records on multi-decadal timescales.

1. Introduction

In eastern Australia, droughts, floods, bushfires, dust storms and cyclones are natural phenomena associated with El Niño and La Niña events with significant economic, social and environmental ramifications (Au, 2017). ENSO-related rainfall variability in south-east Australia has increased and these extreme weather events have become more frequent since 1950 (Nicholls, 2003). In Australia, ENSO is the main driver for dust events, where high dust activity is correlated with El Niño phases of the Southern Oscillation (Shao et al., 2013). Extended drought reduces vegetation cover and results in aeolian dust being transported from Australia's deserts, as well as from the alluvial and lacustrine environments of the Lake Eyre and Murray-Darling Basins, to Australia's east coast (Greene et al., 2009; Speer, 2013; Tadros et al., 2018). South-east Australia is also one of the most bushfire prone areas in the world. The current severity of bushfire events compared to observations since the 1940s, are related to more frequent hot and dry El Niño conditions (Lucas et al., 2007). Dust storms and bushfire events release significant amounts of aerosols to the atmosphere providing a novel opportunity to investigate in more detail, the potential contribution of dust to the trace element record in speleothems from south-east Australia (Rutlidge et al., 2014).

Aerosols are introduced into the atmosphere from sea spray, volcanic and geothermal activity and from biogenic emissions, as well as from anthropogenic sources such as mining, industry, agricultural and transportation sources (Tomasi et al., 2017). Dredge et al., 2013 presented the first investigation into the potential contribution of in-cave aerosols to speleothem geochemistry, highlighting the important role of aerosols as endmembers in the supply of trace elements (Tooth and Fairchild, 2003; Fairchild and Treble, 2009; Baldini et al., 2012; Tremaine and Froelich, 2013; Rutlidge et al., 2014; Treble et al., 2016). Based on atmospheric aerosol measurements over the years 2013–2017, Tadros et al. (2018) identified the chemical characteristics and sources of atmospheric aerosols in the Snowy Mountains alpine region, Yarrangobilly, SE Australia, postulating that deposited ambient particulate matter may be a significant source of trace metals to the site ecosystem. Trace elements are removed from the atmosphere by wet deposition (dissolved in precipitation) or by dry deposition of particles. Aerosols need to be considered as they may significantly affect the physical and chemical properties of karst soil (Rutlidge et al., 2014).

Above the cave, soil represents the major sink for trace metals released from the atmosphere and plays an important role in the retention and release processes (Kabata-Pendias, 2010). Generally, trace elements in the soil solution phase are affected by adsorption onto mineral surfaces or present as aqueous ions or solutes where they are mobilised through the soil profile. In solution they exist as: free trace metal ions (hydrated cations or oxyanions), as stable complexes with inorganic compounds or as organic compounds bound to suspended colloids including clay, organic matter and sesquioxides (Hartland et al., 2012). Trace elements in soil solution are biotransformed by microorganisms and also readily interact with biomass (Adriano, 2001; Hooda, 2010). Chemical weathering of bedrock through partial or complete dissolution, also releases rock-derived trace elements.

In karst environments, trace elements in soil solution may be leached and transported through the unsaturated zone, where further transformations occur. Between the soil zone and the cave ceiling, multiple hydrological flow pathways through the host rock and the capacity of storage, mixing and open system conditions can produce variations in the drip water trace element composition through dissolution-precipitation processes. Within the cave, increased ventilation and CO_2 degassing from drip waters or prior calcite precipitation (PCP), causes the removal of Ca through calcite precipitation along the flow path prior to reaching the stalagmite. Thus trace elements incorporated into speleothems have potential atmospheric, soil and bedrock sources. Dust transport, bushfires, weathering, and infiltration of meteoric water are often strongly influenced by climate. These events determine the supply of trace elements to the surface soil and bedrock, hence the drip-water thereby provides a potentially rich archive of palaeo-climate and palaeo-environmental information that is recorded in the geochemistry of stalagmites (Johnson et al., 2006; Siklosy et al., 2009; Sundqvist et al., 2013). Therefore, the motivation for the current research is to constrain sources and sinks and to differentiate between climate and karst processes impacting the drip water trace element composition in Harrie Wood Cave, Yarrangobilly, south-east Australia. This will build further validation on the potential use of trace elements as proxies for palaeo-environments.

In recent decades south-east Australia has experienced ENSO-related rainfall variability that has led to multi-year trends in the site water balance, including the Millennium drought from 1997 to 2009 that was followed by a short relatively wet phase during July 2010 to March 2011, and a dry episode in 2015 (BoM, 2017). A previous cave monitoring study from a different karst region in south-east Australia; Wombeyan Caves, located approximately 85 km from Harrie Wood Cave, demonstrated a relationship between PCP and climate (McDonald et al., 2004). McDonald et al. (2004) proposed that reduced recharge during the 2002–03 El Niño event resulted in more open system conditions, driving PCP and consequently raising drip water Mg/Ca and Sr/Ca ratios. At the current study site, Tadros et al. (2016) confirmed an enhanced PCP response to the 2006–07 and 2009–10 El Niño events. This longer study (2007–2013) also captured the opposite hydroclimate phase, the 2010–12 La Niña event that followed. Dilution dominated at the onset of the La Niña phase and a period of reduced PCP ensued in response to wetter conditions. Additional processes were also found to be linked to the extreme climate phases e.g. hydrological routing, and enhanced limestone dissolution mediated by microbial respiration in warmer soils was identified.

This research reports 10 years of cave drip water data (2007–2016) collected from three drip sites in Harrie Wood Cave, thus extending the dataset presented in Tadros et al. (2016) by a further three years. The objective is to firstly quantify the source(s) and sink(s) of solutes from Harrie Wood Cave. Secondly, to investigate the mobility of metals through the soil and assess processes which modulate the trace element concentrations in cave drip-water. This research is required for full characterisation of the source contributions and processes which have not yet been investigated for south-east Australia. Lastly, the implications of these findings for interpreting trace elements in stalagmite records for south-east Australia are also discussed.

2. Study area

2.1.1. Region and climate

The study site is located in the Snowy Mountains alpine region of south-eastern Australia along the Great Dividing Range. This region is the highest part of Australia and provides the headwaters to major river systems in the Murray Darling Basin, one of Australia's most important drainage basins (Fig. 1a). Situated in a temperate climate