Plate 1: The automatic discharge monitoring apparatus set up in Kooringa Cave (K1 and K2). The apparatus is described schematically in Figure 3. Photo: J. McDonald.

A MODERN CAVE DRIP WATER STUDY: SE AUSTRALIA

– Janece McDonald *

In the previous ACKMA Journal (No 62: March 2006), Chris Sharples stressed the inextricable relationship between karst and water and the likelihood of changing rainfall patterns impacting on karst physical and biogenic systems. Here we consider the "other side of the coin" where cave deposits, specifically stalagmites, have acted as natural archives of palaeoenvironmental history for millennia. These climate proxies have the potential to provide longer-time series beyond the instrumental record and may help determine the linkages between rainfall and possible causal factors associated with regional ocean-atmospheric circulation. The existing instrumental record may then be placed into a longer-term hydroclimatic perspective.

SPELEOTHEMS AS NATURAL PALAEOENVIRONMENTAL ARCHIVES

For natural proxies to be suitable for palaeoclimate reconstruction, the proxy should fulfil certain criteria, namely: be sensitive to climate change; able to be accurately dated; possess high preservation-potential, with no post-depositional alteration; formation processes should be well understood and importantly there must be the availability of modern material for calibration. Speleothems fulfil all these criteria, but their strength lies in their sensitivity to climate change and their ability to be dated accurately by U/Th decay series. In addition, the closed-crystalline nature of their deposits and their position in a protected cave environment potentially make them more robust encoders of geochemical information (Lauritzen and Lundberg 1999).

However, while the calcite precipitation process are understood, the relationships between the drip geochemistry, hydrology (and hence climate) and geochemical variability in speleothem calcite are less well-understood. This study explores the climate-drip water-calcite system, by taking a "total system" approach where the evolution of meteoric waters is traced from the atmosphere to the speleothem (Figure 1).

The speleothem is considered not in isolation, but as the end-product of a series of complex and inter-connected inputs and processes. Consideration is given to both the atmosphere and lithosphere, and to trace element supply and processes along the hydrological route of each drip. This coupled modern drip water/calcite study is carried out at two karst systems, where drip water sites were chosen for their variability in discharge, depth below the surface and spatial distribution.

THE STUDY SITES

The study sites, Wombeyan Caves (34°19'S, 149°59'E) and Cliefden Caves (32°34'S 148°50'E), are karst areas 240 km apart, located in SE mainland Australia. Wombeyan Caves are located on a dissected plateau east of the Great Dividing Range, whilst Cliefden Caves are located on the western slopes of New South Wales (NSW) and in the rain shadow of the Great Dividing Range (Figure 2). The Wombeyan Caves karst drains eastward into the Tasman Sea, whilst the Cliefden Caves karst drains westwards, and is part of the Murray-Darling Basin.

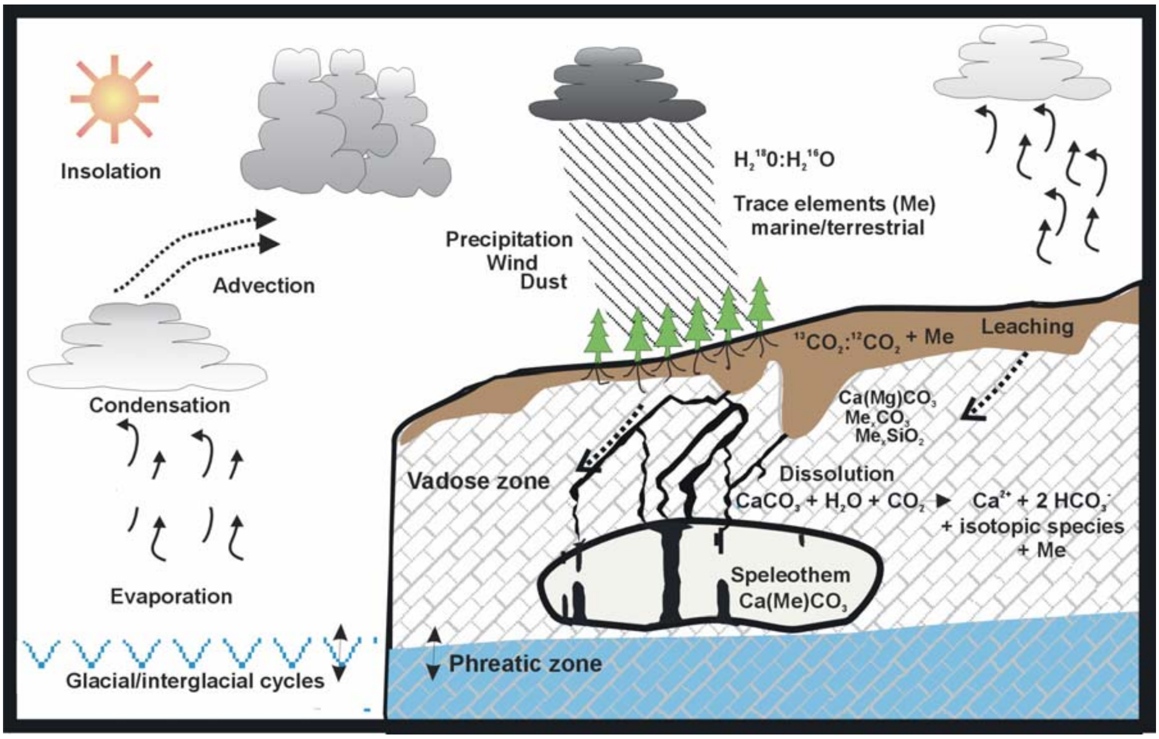

Figure 1: Schematic of the incorporation of geochemical species into speleothem calcite. Meteoric waters contain intrinsic geochemical information (e.g. trace elements and $\delta^{18}O$) and are modified by interaction between vegetation and soils. In a karst environment, their geochemistry is modified further by interaction with the bedrock (e.g. dissolution and re-precipitation) ultimately producing drip waters with a distinct signal, capable of preservation in speleothems (Fairchild *et al.* 2000; Baker *et al.* 2000; Baker and Brunsdon, 2003). Diagram after Lauritzen and Lundberg (1999).

Figure 2: Location map for Wombeyan and Cliefden Caves. Cartography: L. J. Henderson

Both sites are sensitive to inter-annual climate change, specifically to changes in rainfall patterns (e.g. drought periods) which may be recorded by geochemical variations in drip water and, therefore, via speleothem geochemistry (Fairchild *et al.* 2000; Baker *et al.* 2000).

Wombeyan Caves Reserve: Two caves were chosen at this site: Kooringa and Wollondilly. The sites in Kooringa were under the shallowest bedrock depth (12-14 m). In Wollondilly Cave sites were chosen on two levels: Upper Wollondilly (known as Chalker's Retreat in Mulwaree Cave) under 22 m of bedrock and Lower Wollondilly (at the junction to Coronation Cave) under 45 m of bedrock (Wombeyan Marble).

Cliefden Caves: At this site drip water sites were selected in Murder Cave which has approximately 250 m of passage and is well decorated with flowstone, stalagmites, stalactites, straws, helictites and columns. However, present day speleothem deposition is not widespread. The sites were at bedrock (Belubula Limestone) thicknesses of 21 -30 m.

METHODOLOGY

At each site, a pluviometer and dust collection apparatus were set up. Detailed records of rainfall, evaporation and temperature were complied from the Australian Bureau of Meteorology records. Site hydrological water balances were calculated. At selected sites within each cave (chosen to cover a range in discharge and bedrock depths), apparatus was set up to measure discharge and to collect water and calcite samples.

Six sites were continuously monitored for discharge using an IR sensor (Figure 3: Plate 1). Soil and bedrock samples were collected for geochemical analyses and leaching experiments. Frequency of sampling was monthly at Wombeyan and bi-monthly at Cliefden. The lower frequency sampling at Cliefden resulted in a much less rigorous data set since discharge minima and maxima were not recorded, hence the drip chemistry data are limited. The majority of the results and discussion are based on the Wombeyan sites.

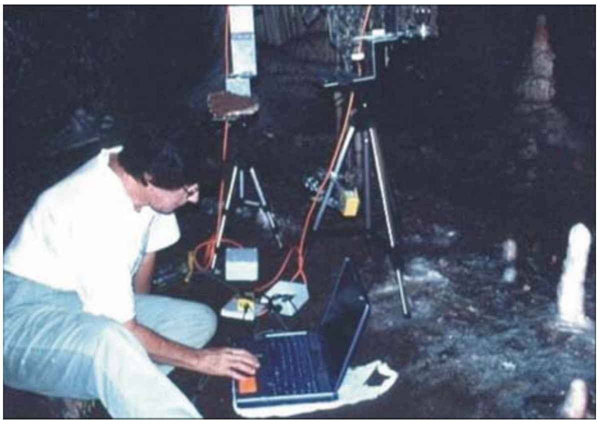

Plate 2: Downloading data from the automatic data loggers in Kooringa Cave. Photo: L. J. Henderson

MAJOR FINDINGS

Atmosphere and lithospere

The geochemical analyses of rainfall, dust, soil and bedrock indicated that each site preserved different hydrogeochemical signals. For example rainfall was enriched in nitrate at Cliefden reflecting the use of fertilisers.

Overall, rainfall geochemistry varied according to source origin, storm track, amount, and antecedent atmospheric conditions and meteoric precipitation is a significant reservoir of ionic species.

Similarly, dust deposited at each site showed differences due to the source and prevailing wind directions. Dust geochemistry indicated a terrestrial source at Cliefden and a dominance of marine-derived species at Wombeyan. Thus at each site, the lithological signal due to weathering processes, may be altered significantly by bulk deposition processes (rainfall and dust). Potentially, the drip water signal may differ considerably to that of the bedrock due to minimal bedrock contribution to the soil.

The importance of rainfall and dust events, in contributing to the development of a unique hydrogeology at each site was shown. The combination of high evaporation, low humidity and low rainfall at both sites ensures that added species are incorporated into the soils primarily as salts or evaporates and are available for reworking, dissolution and leaching at later stages dependant on the site hydrology.

Bedrock and soil leaching experiments indicated that soil water is the starting point in the evolution of the drip water geochemical signal but, the extent of its control is influenced by: the recharge patterns and the karst plumbing, i.e. fast macropore flow(1) (minimal soil water contribution) and slow micropore flow(2) (dominant soil water contribution) and the areal extent and depth of the soil.

Dependent on the availability and interconnectivity of macropore and/or micropore flow paths, and contribution from pre-event stored pore waters, the geochemical signature will always be different at each drip and, fall somewhere between the idealised end member signatures. Clearly, residence time (soil/water and bedrock/water contact times) is a significant factor.

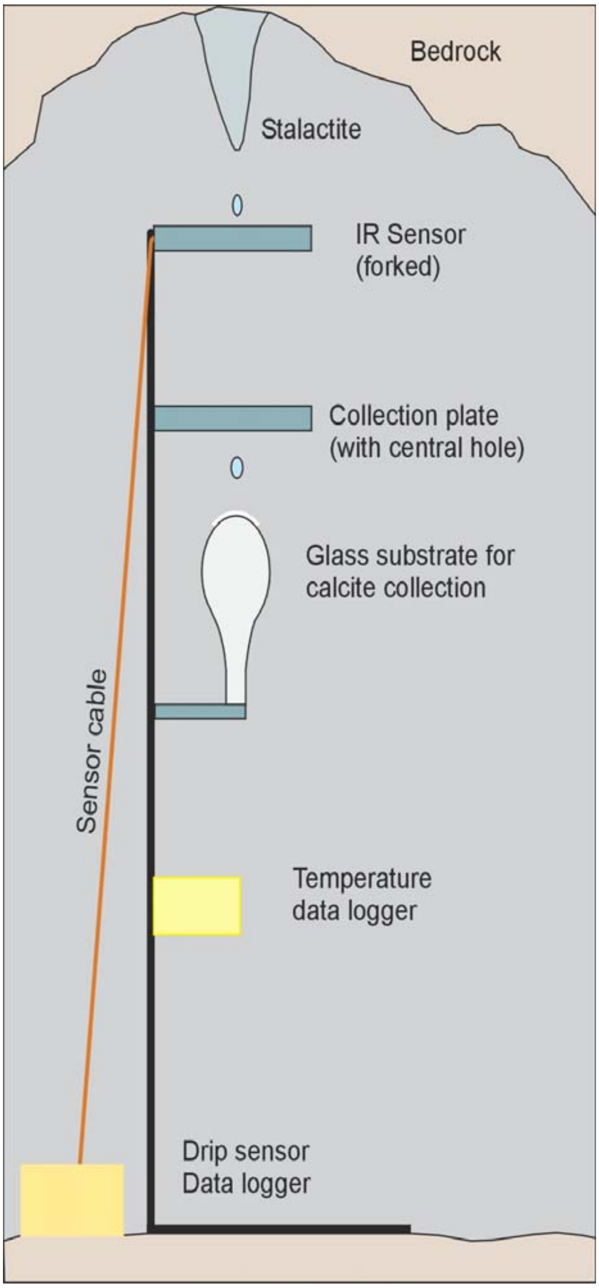

Figure 3: Schematic of discharge monitoring apparatus. Discharge recorded by the IR sensor was downloaded from the data logger ~ monthly intervals. Bottle for water collection for chemical analysis was placed on the collection plate Calcite was precipitated onto the glass substrate and collected at intervals as determined by growth rate and frequency of visits. Diagram: L. J. Henderson.

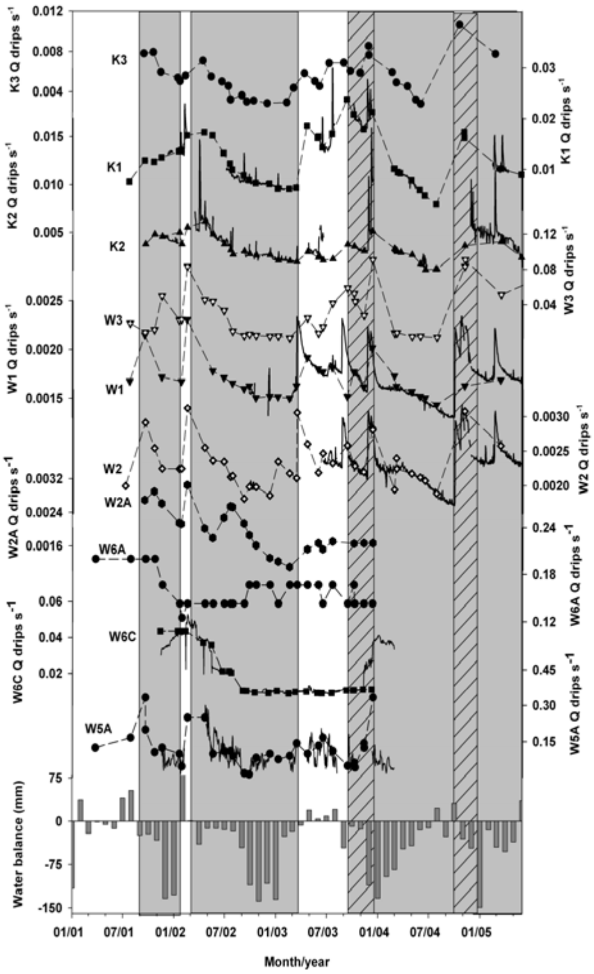

Figure 4: Discharge and site water balance profile for all sites in according to bedrock thickness. Symbols are manual readings and solid lines are automatic drip-sensor values. The grey shaded phases are water-deficit periods. The stippled areas are periods of transient water excess due to spring/summer storms, resulting in recharge to the shallow sites.

Hydrology

At Wombeyan the discharge of 10 drip sites located beneath bedrock thicknesses of 12, 22 and 45 metres was monitored either continuously (using automated infrared sensors) or at discrete ~monthly intervals and compared with local rainfall and water balance data.

The long-term average rainfall, temperature and evaporation data indicate that a strong seasonal drip/discharge pattern should occur at Wombeyan Caves. The expectation is that during winter, low evaporative conditions will allow for increased recharge to the caves, resulting in increased discharge (Goede and Hitchman 1984). However, the high variability of rainfall (~ 29%), due to ENSO and associated air-mass circulation patterns was experienced during this study. Drip discharge decreased during the summer months at most sites.

In addition, expected winter recharge was perturbed by the 2002/2003 and 2004 droughts. Both droughts produced a negative water balance during winter months. In fact, there was no effective precipitation during winter 2004, which resulted in a steady decline in discharge to the lowest flows recorded at the shallow drips for the duration of the study. However, all sites were hydrologically active throughout the study, even during long periods of ENSO related water deficit and high summer evaporation, which suggests a significant storage component in the soil and bedrock (vadose zone) (Smart and Friederich 1987; Baker *et al.* 1999; Baker and Brunsdon, 2003; Tooth and Fairchild 2003).

12-14 m bedrock depth (Kooringa Cave)

The discharge of all three drips (K1, K2 and K3) is generally in phase and follows changes in the water balance as triggered by effective precipitation (Figure 4). Response time to individual recharge events range between 8 days to several hours, dependant on the level of vadose storage: e.g. after 17 days without rainfall K1 and K2 took 8 days to record an increase in discharge to a recharge event (due to low vadose storage and the presence of ventilated pore spaces), but seven days later 25 mm rainfall caused increased discharge within 2 days.

22 m bedrock depth (Mulwaree/Upper Wollondilly Cave)

The four drips at this depth (W1, W2, W2A and W3) are generally in phase with each other and show a similar oscillation structure to the water balance (Figure 4). However, their respective hydrographs show dissimilar (gradual) recession limbs when compared to the hydrographs of the drips in Kooringa Cave. This indicates that there is an absence of well-connected macropore routes and small aperture fissures at the greater depth (Williams 1983). Thus, water to the drips is "pushed out" under hydraulic head rather than direct delivery through well-connected flow paths as evidenced by the drips in Kooringa Cave.

45 m bedrock depth (Lower Wollondilly Cave)

The three drips in Lower Wollondilly (W5A, W6A and W6C) each display unique hydrological behaviour, with no apparent recharge/discharge connection as evident in the near-surface drips (Figure 4).The discharge behaviour of W5A is highly variable and unlike any of the other drips.

At W5A some (but not all) of the troughs in discharge are spaced at near-monthly intervals, perhaps suggesting a lunar cycle link. Peaks and troughs are multi-modal and there are rapid decreases in discharge, with decreases approximating 200% within two hours. Flow-switching is extremely rapid and shows no relationship between rainfall and discharge, although the application of a running mean gives a broad in-phase relationship with the water balance, suggesting the influence of hydraulic head pressure fluctuations.

Whilst the exact reason for the flow-switching is uncertain, its presence indicates the unsuitability of this drip to record an interpretable high-resolution (sub-annual to inter-annual) geochemical signal in speleothem calcite.

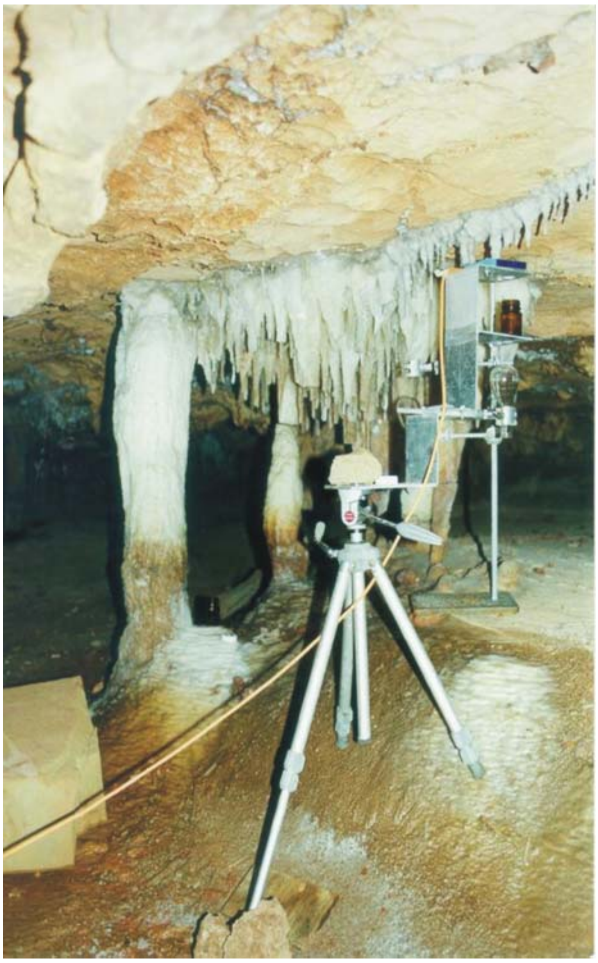

Plate 3: The automatic discharge monitoring apparatus set up in Wollondilly Cave at a bedrock thickness of 45 m. Photo: J. McDonald.

W6A shows little short-term variability with no apparent response to rainfall events. This drip has a low variability with only 5 discrete discharge values for the entire period. W6A maintains a high discharge implying access to substantial storage, maintained by recharge and minor changes in the head driving flow (Smart and Friederich 1987; Tooth and Fairchild 2003).

W6C appears to show an intermittent response coincident with a high-volume rainfall event, suggesting either a threshold necessary to initiate a discharge increase via overflow, or influence of hydraulic head initiating a source change (Smart and Friederich 1987; Tooth and Fairchild 2003).

However, there are also abrupt decreases in discharge indicative of flow switching between two reservoirs and increased daily variability is evident at higher discharge, pointing to a deep complexity in the behaviour of this drip.

The results from these three drips, all in near proximity to each other, highlights the need for the careful selection of stalagmites when trying to elucidate an interpretable palaeohydrological signal.

On the other hand, the occurrence of a quasi-linear response between the site water balance and some near-surface drips is encouraging. Potentially, several of these drips are suitable for palaeoclimate studies if changes in their hydrology can be related to coincident changes in chemistry.

Hydrochemistry

For drip water chemistry to be meaningful in palaeoclimate studies, a linear relationship between hydrology and one or more chemical parameters is desirable (Baker and Brundson 2003).

The most promising chemical parameters for the interpretation of water-bedrock interactions and hence palaeohydrology found in this study are magnesium (Mg) and strontium (Sr) via their molar ratios with respect to calcium (Ca) (Fairchild *et al.* 2000).

If Mg/Ca and Sr/Ca are increasing and covarying, and Ca is coincidently decreasing then prior calcite precipitation (PCP) is indicated (Fairchild *et al.* 2000).

Prior calcite precipitation occurs when CO_2-rich percolating waters degas into ventilated air pockets (during aridity), causing calcium carbonate ($CaCO_3$) to precipitate. As Ca is preferentially removed, the solution becomes enriched in trace elements (e.g. Mg and Sr).

It is proposed that at Wombeyan, accompanying the increased water deficit of the 2002-2003 El Niño event and the 2004 drought, dewatering of fractures and fissures, and decreased hydraulic head in the soil and bedrock fracture network, promotes enhanced degassing and precipitation of $CaCO_3$ into the air-filled pores (McDonald *et al.* 2004).

Thus, at this site, if Mg/Ca and Sr/Ca of cave drip waters changes in line with the process of prior calcite precipitation, with values and duration in excess of those expected during a "normal" summer/winter annual cycle, they may be used as palaeohydrological proxies.

KEY FINDINGS

- There is a sympathetic relationship between Mg/Ca and Sr/Ca at all sites
- PCP is proved at K1, K2, K3, W2, W3, W6A and W6C
- There is an inverse relationship between Mg/Ca and Sr/Ca with Ca at all sites
- Discharge and Mg/Ca and Sr/Ca trend inversely at all sites in Kooringa and Upper Wollondilly
- There are no trends between discharge and Mg/Ca and Sr/Ca at the Lower Wollondilly sites.
- Discharge and Ca are positively co-variant (statistically significant) only at K1, K2 and W3.

However, when a quantification of the relationships between Mg/Ca, Sr/Ca and discharge is made, a statistically significant correlation is found only sites K1 and K2. These two sites also show strong correlation between Ca and discharge, which suggests a hydrochemical link, and thus a strong link to climate via drip hydrochemistry.

FUTURE DIRECTIONS

A major impediment to the understanding of factors that control drought and rainfall variability in Australia is the lack of pre-instrumental data. The significance that Mg/Ca and Sr/Ca are robust palaeohydrological proxies at certain shallow caves and the impact for south eastern Australian palaeoclimate studies is immense.

This finding has application in palaeoclimate studies and climate modelling. Precision radiometric dating coupled with high-resolution geochemical analyses make it possible to reconstruct rainfall histories at sub-annual resolution.

The reconstruction of a drought history at Wombeyan Caves (in the Sydney Water Catchment) from suitable stalagmites potentially allows for the understanding of long-term rainfall variability and will be of use to hydrologists and water management authorities.

Currently, water levels in the dams supplying Sydney are ~ 35% capacity, the lowest ever recorded, whilst the demand increases due to a rise in population. The brevity of the instrumental record makes imperative that natural archives be accessed and interpreted rigorously.

However, equally significant are the misinterpretations which can occur when speleothem feed waters do not record a reliable palaeohydrological signal. This is certainly of concern for potential palaeohydrological studies considering these ratios and uncertainty in these cases urge the consideration of multiple proxies, as well as the use of multiple speleothems.

Overall, this study points towards the critical importance of site selection and urges that it be based on a modern drip water hydrological study.

Importantly, the study stresses the advantages of non-destructive contemporaneous studies to select speleothems potentially suitable for palaeoenvironmental reconstructions, and reducing the need for unnecessary removal of speleothems for study.

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NOTES

(1) Macropore flow is the fast movement of water through structural features in soil such as worm holes and well-developed fissures in the bedrock.
(2) Micropore flow is the slow movement of water derived from soil aggregates and the bedrock matrix.

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