

## Drip water isotopes in semi-arid karst

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1 Drip water isotopes in semi-arid karst: implications for speleothem  
2 paleoclimatology

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14

15 **Abstract**

16 We report the results of the first multi-year monitoring and modelling study of the isotopic  
17 composition of drip waters in a semi-arid karst terrane. High temporal resolution drip rate  
18 monitoring combined with monthly isotope drip water and rainfall sampling at Cathedral Cave,  
19 Australia, demonstrates that drip water discharge to the cave occurs irregularly, and only after  
20 occasional long duration and high volume rainfall events, where the soil moisture deficit and  
21 evapotranspiration is overcome. All drip waters have a water isotopic composition that is heavier  
22 than the weighted mean annual precipitation, some fall along the local meteoric water line, others  
23 trend towards an evaporation water line. It is hypothesised that, in addition to the initial rainfall  
24 composition, evaporation of unsaturated zone water, as well as the time between infiltration events,  
25 are the dominant processes that determine infiltration water isotopic composition. We test this  
26 hypothesis using a soil moisture balance and isotope model. Our research reports, for the first time,  
27 the potential role of sub-surface evaporation in altering drip water isotopic composition, and its  
28 implications for the interpretation of speleothem  $\delta^{18}\text{O}$  records from arid and semi-arid regions.

29

30 **Keywords:** evaporation, water isotopes, recharge, karst, speleothems, semi-arid

31

## 32 **1. Introduction**

33 Within-cave monitoring of climate, hydrology and drip water biogeochemistry is recognised by the  
34 speleothem paleoclimate research community as being essential to the understanding of  
35 speleothem proxy records. Numerous monitoring studies have been reported in recent years, many  
36 of which are long-term (for example, Baker and Brunsdon, 2003; McDonald et al 2007) and include  
37 both monitoring and modelling approaches (for example, Treble et al., 2013). However, to date  
38 these research efforts have been mostly focussed on understanding processes relevant to  
39 temperate, sub-alpine and alpine caves. This bias has been predominantly due to the ease of access  
40 of cave sites, and the location of cave research groups, rather than the lack of importance of  
41 monitoring studies that would be relevant to speleothem records in semi-arid to arid climates.

42

43 The most widely used speleothem paleoclimate proxy is  $\delta^{18}\text{O}$ : originally sourced from precipitation,  
44 the speleothem water isotopic composition can be later modified due to interactions in the soil and  
45 vadose zones and within the cave. In semi-arid environments, the relationship between rainfall and  
46 soil water isotopic composition is relatively well understood thanks to series of field and laboratory  
47 studies (Allison 1982, Allison et al 1983, 1987; Allison and Hughes 1983; Barnes and Allison 1988).

48 The occasional rainfall events in a semi-arid climate will infiltrate the soil, leaving an isotopic  
49 signature of the precipitation event. Subsequent evaporation leads to a soil water isotope profile  
50 that is exponential in profile and isotopically enriched towards the surface. However, as evaporation  
51 is the dominant soil hydrological process, the soil volumetric water content is low as water is lost by  
52 evaporation. Therefore, on the occasions where the soil moisture deficit is exceeded and  
53 groundwater recharge occurs, it is likely that 'old' and isotopically enriched soil water is  
54 volumetrically small compared to the event water, and therefore water infiltrating to the vadose

55 zone is likely to have negligible water isotopic enrichment. In contrast to the relatively well  
56 understood soil water isotope processes, there are almost no studies that have investigated water  
57 isotope processes in the vadose zone in semi-arid to arid environments. In karst systems, Ingraham  
58 et al (1990) is a lone study that investigates the water isotopic composition of pool waters in the  
59 Carlsbad cave system of New Mexico, USA, to help constrain evaporative water fluxes within the  
60 cavern.

61

62 Here we report the results of a two-year drip water and rain water isotope monitoring study from  
63 Cathedral Cave at Wellington, New South Wales, Australia. Mean annual precipitation is 619 mm  
64 (1956-2005) and evaporation is 1825 mm (1965-2005; recorded at the nearby Wellington Research  
65 Centre, Australia Bureau of Meteorology). At this site  $ET \gg P$  and so the processes inferred from our  
66 monitoring of drip water isotopic composition are most relevant to semi-arid and arid climate  
67 regions. Additionally, we utilize the monitoring results to constrain a modified soil moisture balance  
68 model. Extending the approach of Cuthbert et al (2013), we add a soil and groundwater isotope  
69 component to understand the processes controlling drip water isotopic composition at our site.

70

## 71 **2. Methods and Site Description**

### 72 *2.1 Site background*

73 Our monitoring and modeling experiment was undertaken at Cathedral Cave in Wellington, New  
74 South Wales, Australia (32°37'S; 148°56'E) (Figure 1). The cave entrance, at 325.16 m elevation, is  
75 situated close to the top of a north-south trending ridge formed from Devonian Garra Formation  
76 limestone. To the west of this ridge, at an elevation of c. 300m, are the alluvial gravels of the Bell  
77 River. The geomorphology of the cave has been extensively researched (Osborne et al 2007) and is  
78 primarily orientated along the direction of jointing (150°), and contains abundant evidence of  
79 hypogene formation processes, arguably typical of many caves in SE Australia (Osborne et al., 2010)  
80 The cave descends approximately 25m from the entrance to the end of the cave, where the cave is

81 flooded as it intercepts the local groundwater at The Well (Figure 1). Groundwater is observed at an  
82 elevation of between 280-300m asl, depending on antecedent climate conditions. The cave is  
83 overlain by degraded box grass woodland, with bare soil and sparse tree cover (Blyth et al., 2014).

84

85 Our observations of the cave climatology are consistent with its morphology, which is a descending  
86 dead-end cave. Two entrances, located at the same elevation in the entrance series, could lead to  
87 limited ventilation in that part of the cave. Air exchange close to the entrance would also be  
88 expected through pressure and density effects on both the cave air and groundwater level. Air  
89 temperature measurements using Star-Oddi micro loggers show little variation ( $18.25 \pm 0.05^\circ\text{C}$ ,  
90 August 2011 to August 2012) in South Passage (our Site 2, Figure 1) over the long-term. Near the  
91 entrance (site 1, Figure 1), we have logged temperature variability over the short term and observe a  
92 range of 17-18 °C in January 2013 and 18-23 °C in February 2014. Relative humidity in the cave has  
93 been recorded using a Campbell HMP155A over short campaigns and was observed to be constant  
94 at 97% at Site 2 (Jan-Feb 2014), consistent with the presence of an adjacent groundwater body, and  
95 variable from 73-93% at site 1, consistent with ventilation within the entrance series. Within cave  
96 evaporation has been measured by measuring the volumetric water loss of 50ml water placed in  
97 petri dishes: at Site 1, average evaporation was 0.14 mm/d (over the period 7-15 January 2014) and  
98 0.08 mm/d (15 January - 6 March 2014) and at Site 2 was 0.004 mm/d (15 January – 6 March 2014).

99

100 The cave has been a focus of long-term hydrogeological monitoring by the investigators,  
101 commencing in 2009 and continuing, primarily using a network of in-situ Stalagmate © drip loggers.  
102 Jex et al (2012) describe drip water patterns and processes within the cave for a spatially dense  
103 network of drip-collection sites: it is a subset of drip waters from this network at Site 2 which are  
104 investigated here. Mariethoz et al (2012) utilized near-surface infiltration to identify non-linear and  
105 chaotic drip behavior and its relationship to surface connectivity. Most recently, and subsequent to

106 the results presented here, at Site 1, we have undertaken an artificial irrigation experiment to better  
107 understand infiltration processes (Cuthbert et al., in review; Rutledge et al., in revision).

108

## 109 *2. 2 Monitoring methods*

110 Our water isotope monitoring program was designed as follows. Monthly integrated rainfall samples  
111 were collected using standard IAEA protocols ([http://www-naweb.iaea.org/  
112 napc/ih/documents/userupdate/sampling.pdf](http://www-naweb.iaea.org/napc/ih/documents/userupdate/sampling.pdf)) at the nearby (7 km) UNSW Wellington Field Station.

113 Drip water was collected at fifteen monitoring sites within the South Passage of Cathedral Cave (Site  
114 2, Figure 1); five (sites 279, 280, 372, 395 and 396) were part of the network described by Jex et al.  
115 (2012). Isotope water samples were collected via funnels connected to 500ml or 1l HDPE bottles.  
116 Paraffin was placed in the bottles as a precaution to prevent evaporation within the bottles.  
117 Evaporation could be possible anywhere prior to collection, although our within-cave relative  
118 humidity measurements suggest that this is unlikely to occur within the cave at Site 2. Bottles were  
119 changed monthly, with fresh paraffin added, and an integrated 30 ml water sample transferred to  
120 sealed glass McCartney bottles with no headspace to prevent evaporation whilst in storage. These  
121 bottles were then stored until analysis, which occurred within two months. Water samples were  
122 collected at monthly intervals from March 2011 to March 2013.

123

124 Drip rates were monitored using a network of twenty-six Stalagmate © drip loggers in South Passage  
125 (Site 2) and a further four drip loggers situated closer to the surface (Site 1, including site 326 of Jex  
126 et al., 2012). This is the expanded network referred to by Jex et al (2012). Our intention was to  
127 measure the infiltration rate using Stalagmate © drip loggers for all isotope sample sites, but our  
128 monthly sampling frequently disturbed the drip logger alignment, and only seven of our fifteen  
129 isotope sample sites had reliable drip data. Drip rate data are presented in Table 1, together with a  
130 classification of the drip type (soda straw stalactite; non-soda straw stalactite, non-soda straw  
131 stalactite underneath flowstone).

132

133 Water isotopic composition of drip water and rainwater samples was determined using an LGR-24 d  
134 off-axis, integrated cavity output, cavity ringdown mass spectrometer (ICOS CRMS, Lis et al., 2007,  
135 Wassenaar et al 2008) at the University of New South Wales. Five internal reference standards  
136 (LGR#1 to LGR#5, with  $\delta^{18}\text{O}$  values of -19.5‰, -16.14‰, -13.1‰, -7.69‰, -2.8‰) and one external  
137 reference standard (VSMOW2, 0‰) was analysed as an external standard; and during the analysis  
138 period we participated in the 4<sup>th</sup> IAEA Inter Laboratory Comparison for stable isotopes of water  
139 (WICO2011, laboratory 082). Two samples analysed were outside the range of the  $\delta^{18}\text{O}$  standards,  
140 but by less than the analytical precision. Analytical precision for  $\delta^{18}\text{O}$  was 0.17 per mil for  $\delta^{18}\text{O}$  and  
141 0.6 per mil for  $\delta^2\text{H}$  (1 $\sigma$ ; calculated from within run internal references materials).

142

### 143 2.3 Modelling methods

144 A model was developed to simulate groundwater recharge, shallow karst flow and isotopic  
145 composition of drip waters at the field-site and is illustrated schematically in Figure 2. A soil  
146 moisture balance (SMB) model was used for the topsoil which, based on Cuthbert et al (2013),  
147 makes use of a combined crop co-efficient approach ( $K_c$ ) taken from Allen et al. (1998). The total  
148 available water ( $TAW$ ) in the soil is defined as:

$$149 \quad TAW = (\vartheta_{FC} - \vartheta_{WP}) \cdot Z_r \cdot (1 - B) + (\vartheta_{FC} - 0.5\vartheta_{WP}) \cdot Z_e \cdot B \quad (1)$$

150 where  $\vartheta_{FC}$  &  $\vartheta_{WP}$  are fractional soil moisture contents at field capacity (FC) and wilting point (WP),  $Z_r$   
151 is the rooting depth of crop,  $Z_e$  is the thickness of the soil layer subject to drying by evaporation,  $B =$   
152 fractional area of bare soil (i.e. crop absent). The readily available water ( $RAW$ ) is defined as:

$$153 \quad RAW = p \cdot TAW \quad (2)$$

154 where  $p$  is a factor normally between 0.2 and 0.7 (Allen et al 1998, Table 22). If the soil moisture  
155 deficit in the topsoil ( $SMD_s$ ) is greater than the  $RAW$  then the actual evaporation rate ( $AE$ ) is reduced  
156 using a stress co-efficient ( $K_s$ ) as follows:

$$157 \quad AE = K_s PE \quad (3)$$

158 
$$K_s = (TAW - SMD_s) / (TAW - RAW) \quad (4)$$

159 where potential evapotranspiration,  $PE = K_c PE_0$  and  $PE_0$  is the reference crop (grass) potential  
160 evapotranspiration rate.

161

162 Using a daily input time series for rates of rainfall ( $RF$ ) and  $PE_0$ , the model algorithms calculate time  
163 series of  $AE$  and the rate of groundwater recharge ( $Rch$ ). Overland flow is very rare at the field site  
164 and has therefore been assumed to be zero with all rainfall ( $RF$ ) becoming infiltration. On days  
165 where the soil is under stress and rainfall occurs that is less than  $PE$  the rainfall is transpired plus a  
166 further amount from the soil equal to the remaining evaporative demand modified by the stress co-  
167 efficient. If rainfall exceeds the  $PE$  then the excess reduces the  $SMD$  and once this has become zero  
168 any additional excess becomes groundwater recharge.

169

170 Continuous time-series of potential evapotranspiration ( $PE_0$ ) and rainfall were obtained from nearby  
171 continuous automatic weather stations at the caves (Hill Station, operational from November 2011)  
172 and UNSW Research Station (operational until damaged by bushfire in December 2012) and the daily  
173 Bureau of Meteorology (BOM) station in Wellington (Station Number: 65034, located at Wellington  
174 Agrowplow (lat: 32.56° S / Long: 148.95 °E / 350 m asl), 6.5 km from the caves). For the rainfall data,  
175 double mass plots were derived for the three site combinations and the linear correlations used to  
176 infill missing data from the Hill Station.  $PE_0$  was calculated using the Penman-Montieth reference  
177 crop evapotranspiration using the UNSW Research Station data and a pan factor was derived from  
178 the BOM Station using a linear relationship between the two. Where data gaps persisted, the  
179 correlation between average monthly temperature and average monthly  $PE_0$  was used for filling  
180 data gaps.

181

182 To estimate the drip water  $\delta^{18}O$  composition reaching the cave monitoring points, rainfall events  
183 were assigned isotopic compositions based on the measured monthly values and the soil store was



184 assumed to be fully mixed. The soil store (S1) evolved through time ( $t$ , in increments of  $\Delta t = 1$  day)  
185 according to the following mass balance equation:

$$186 \quad S1_{t+\Delta t} = S1_t + (RF_t - AE_t - Rch_t) \cdot \Delta t \quad (5)$$

187 where  $S1_t$  and  $S1_{t+\Delta t}$  is the amount of water in the soil store (S1) in mm at times  $t$  and  $t+\Delta t$   
188 respectively. Using the suffix  $\delta$  to represent  $\delta^{18}\text{O}$  isotope compositions (per mil), the soil store  
189 isotopic composition was governed by the following equation:

$$190 \quad S1\delta_{t+\Delta t} = (S1\delta_t \cdot (S1_t - (AE_t + Rch_t) \cdot \Delta t) + RF\delta_t \cdot RF_t \Delta t) / S1_{t+\Delta t} \quad (6)$$

191 where  $S1\delta_{t+\Delta t}$  and  $S1\delta_t$  are the isotopic compositions of the soil store (S1) at time  $t$  and  $t+\Delta t$   
192 respectively and  $RF\delta_t$  is the isotopic composition of the rainfall at time  $t$ .

193 The model does not include isotopic fractionation in the soil zone for two reasons. First, at our site,  
194 recharge is erratic and comes from infrequent, large events, typical of arid and semi-arid  
195 environments. The soil is typically relatively dry before a recharge event, and even though prior soil  
196 water is likely to be enriched in heavy isotopes (Barnes and Allison, 1988), it is volumetrically very  
197 small compared to event water. Thus, during an event the residual isotopically enriched water is  
198 greatly diluted, the resulting soil isotopic concentration is very close to that of the incoming  
199 meteoric precipitation and this prior soil water cannot be used as a tracer of water movement  
200 (Sonntag et al, 1985). A second reason for not including fractionation in the soil zone in the model is  
201 that our field data (see section 3.2) shows that the predominant fractionation process occurs under  
202 high humidity. This cannot be accounted for by in-soil evaporation processes in unsaturated soils,  
203 where near surface evaporation results in fractionation with the slope of the  $\delta\text{D}-\delta^{18}\text{O}$  relationship  
204 typically  $< 4$  (Allison et al., 1983; Barnes and Allison, 1988).

205

206 The attenuation and isotopic evolution of the groundwater chemistry due to evaporation was then  
207 modelled by using a second store ( $S2$ ,  $S2\delta$  with initial values  $S2_0$  and  $S2\delta_0$  respectively). This filled  
208 from above with water leaving the soil as groundwater recharge, lost mass due to evaporation which

209 was assigned a constant value, and drained exponentially using a recession constant ( $\tau$ ) to simulate  
 210 drip water volume and  $\delta^{18}\text{O}$  to the deeper karst system ( $Dr, Dr\delta$ ) as follows:

$$211 \quad S2_{t+\Delta t} = S2_t + (Rch_t - E - Dr_t) \cdot \Delta t \quad (7)$$

$$212 \quad \text{with } Dr_t = \tau \cdot S2_t \quad (8)$$

213 The isotopic composition of the karst store (and any water leaving the store to become drip water)  
 214 was assumed to be governed by a simple mass balance if the depth of water in the store was greater  
 215 than a threshold value ( $S2_{lim}$ ):

$$216 \quad S2\delta_{t+\Delta t} = (S2\delta_t \cdot (S2_t - (Dr_t + E) \cdot \Delta t) + S1\delta_t \cdot Rch_t \cdot \Delta t) / S2_{t+\Delta t} \quad (9)$$

217 However, if  $S2_t < S2_{lim}$  then it was assumed, following Gonfiantini (1986, Eq.7, p117), that an  
 218 evaporative process in the shallow karst was of the form as follows:

$$219 \quad S2\delta_{t+\Delta t} = (S2\delta_t - m) \cdot f^n + m \quad (10)$$

220 Where  $m$  and  $n$  are empirical constants to be determined from model calibration, and  $f$  is the  
 221 proportion of water left in the store since the level fell below the threshold amount.

222

223 Rather than producing a calibrated model for each drip site with different parameters, our approach  
 224 was rather to attempt to match the range of observed isotopic values with the purpose of testing  
 225 our conceptual model and providing estimates of the range of model parameter combinations. The  
 226 SMB flow model was first tuned to capture the overall timing of the main drip events monitored in  
 227 South Passage by varying the SMB parameters; it was not attempted to match the volume of drip  
 228 water leaving the karst store against the measured drip data since the distribution of recharge  
 229 through the karst network is extremely complex and highly variable across all drip sites. This stage  
 230 of the model refinement was carried out manually since no single objective function could  
 231 reasonably be defined against which to automate the calibration. For the estimation of parameters  
 232 for the isotope model we applied a method similar to the widely used GLUE methodology (Beven &  
 233 Binley 1992) as follows. The aggregated modelled monthly drip water composition was compared  
 234 directly against the range of measured values assuming drip water is all sourced from a single

235 shallow store (albeit at different rates) by varying the parameters controlling the karst store and  
236 fractionation process. Sets of prior parameter distributions (ranges of estimated initial values) were  
237 defined based on physical plausibility and initial experimentation with the model to ensure a wide  
238 enough spread to avoid unwanted rejection of any physically plausible parameter sets. Monte-Carlo  
239 simulations were carried out for 50 000 random combinations of the prior parameter distributions.  
240 If all modelled values fitted within the range of the measured isotopic composition of the drip water  
241 across all samples for a given time step this model was deemed 'behavioural' and these models were  
242 retained (henceforth: physically plausible models). The parameter values of these physically  
243 plausible models were used to define the posterior parameter distributions..

244

### 245 **3. Results and Discussion**

#### 246 *3.1 Rainfall, evapotranspiration, and drip rates*

247 Rainfall, calculated  $PE_0$  and drip water data for the two-year period are presented in Figure 3.  
248 Average rainfall and  $PE_0$  for Feb 2011 to Feb 2013 are 666 and 982 mm/yr, higher and lower than the  
249 long term average respectively, reflecting the slightly cooler and wetter conditions experienced  
250 during the monitoring period where La Nina or neutral conditions prevailed. Drip rates are observed  
251 to be highly episodic, with only a few rainfall events of high duration and amount resulting in  
252 recharge and thus exfiltration in the cave. Drip water responses within the cave show significant  
253 variability between sites, as previously demonstrated by Jex et al. (2012). Particularly large drip  
254 rates, sometimes over 100 drips per 15 minutes (equivalent to  $\sim 1 \times 10^{-5} \text{ l s}^{-1}$ ), were observed during  
255 Jan-Mar 2012 and Jul-Aug 2012 with periods in between of much slower exfiltration ranging from 0  
256 to approx. 10 drips per 15 minutes ( $< \sim 1 \times 10^{-6} \text{ l s}^{-1}$ ).

257

#### 258 *3.2 Water Isotopes*

259 The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  composition of monthly integrated drip water and rainfall samples are summarized  
260 in Table 1, and  $\delta^{18}\text{O}$  time-series plotted in Figure 3. Figure 4 presents the plot of  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$ : also

261 presented on this plot are monthly grab samples collected from adjacent rivers (open squares) and  
262 ground water (open circles). River samples were obtained from the Macquarie River at the UNSW  
263 Research Station (7 km to the north-east of the caves) and the Bell River (2 km downstream of the  
264 Wellington Caves). Ground water samples were collected within the Wellington Caves Reserve, from  
265 Anticline Cave (200 m west of the cave entrance) and from 'The Well' in Cathedral Cave (shown in  
266 Figure 1).

267

268 Figure 4 demonstrates that the monthly rainfall samples fall along a local meteoric water line  
269 (LMWL) with an equation  $\delta^2\text{H} = 7.29 \delta^{18}\text{O} + 7.68$  ( $r=0.96$ , standard error of the slope = 0.43, standard  
270 error on the intercept = 2.08). The annual weighted mean isotopic composition of rainfall over the  
271 monitoring period was  $-4.28\text{‰}$  for  $\delta^{18}\text{O}$  and  $-23.54\text{‰}$  for  $\delta^2\text{H}$ , and the river and ground water grab  
272 samples all had a mean isotopic composition that reflected the weighted mean of precipitation  
273 (Table 1). In contrast, the drip water mean  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  composition ranged from  $-1.51\text{‰}$  to  $-$   
274  $3.45\text{‰}$ , and  $-1.16\text{‰}$  to  $-17.72\text{‰}$ , respectively. Mean drip water isotopic compositions were  
275 therefore  $0.83$  to  $2.77\text{‰}$  ( $\delta^{18}\text{O}$ ) and  $5.82$  to  $22.38\text{‰}$  ( $\delta^2\text{H}$ ) heavier than the weighted mean annual  
276 precipitation.

277

278 We observe no relationship between drip water isotopic composition and hydrological properties  
279 such as the drip source classification, or drip rate (at the sites where that data is available) (Table 1).  
280 Comparing drip source classifications to drip water oxygen isotopic composition, soda-straw ( $n=8$ )  
281 and non-soda straw ( $n=5$ ) stalactite drip sources have mean isotopic compositions that are  
282 statistically similar (students t-test, 95% confidence level). Comparing mean, mean and maximum  
283 drip rates to oxygen isotopic composition, for the drip sites where data is available ( $n=7$ ), gave slopes  
284 of the  $\delta^{18}\text{O}$  vs drip rate relationship not significantly different from zero

285

286 Typically, from a theoretical perspective, the presence of a water isotopic composition that is  
287 heavier than the weighted mean of precipitation would be expected to be due to evaporation of  
288 lighter isotopes. The relative enrichment of  $\delta^2\text{H}$  to  $\delta^{18}\text{O}$  varies with the processes that determine  
289 evaporative enrichment: the relative humidity and turbulence of the overlying air mass (Gonfiantini,  
290 1986). In environments with limited air movement, the relative humidity can approach 100%; the  
291 slope of the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  regression will increase and the maximum amount of enrichment decreases  
292 with increasing relative humidity. Following Gonfiantini (1986), in environments with relative  
293 humidity larger than 95% the slope of the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  regression will be similar to that of the LMWL  
294 with an enrichment of up to 4‰ in  $\delta^{18}\text{O}$  possible. In environments with a lower humidity, the slope  
295 of the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  regression decreases, and the maximum amount of enrichment will be greater.  
296 Applying this theory to our results, Figure 4 demonstrates that drip waters as a whole scatter along  
297 the LMWL. However, considering each drip site individually, some sites have a slope of the  $\delta^2\text{H}$   
298 vs.  $\delta^{18}\text{O}$  regression that is, within the standard error uncertainty (Table 1), the same as the slope of  
299 the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  regression of the LMWL, indicative of evaporation in a high humidity environment.  
300 Others which have a lower slope of the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  regression than the LMWL, which could be  
301 attributed to evaporative enrichment in a less humid environment. Individual regression data is  
302 presented in Table 1.

303

304 In order to investigate these data further, Figure 5 presents the  $\delta^{18}\text{O}$  isotopic composition against  
305 time for drip sites grouped by their slopes of the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  regression. Sites which have a similar  
306  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  slope to the LMWL (slope of the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  regression  $>6.8$ ; sites 279, 280, 320, 372,  
307 387 and 398) have very similar time series. It is also notable that there is no relationship between  
308 the rainfall isotopic composition (Figure 3) and the way drip water isotopes vary during periods of no  
309 recharge. Sites which have the lowest slopes of  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  (slope of the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  regression  
310  $<4.8$ ; sites 319, 322, 330, 380, 396) also have similar time series. However, this group has greater  
311 isotopic variability between sites, with some having a wider range towards heavier isotopic

312 compositions. Notably, when comparing the slope of individual  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  regressions vs. mean  
313 isotopic composition, no relationship was observed, but a strong correlation is present between the  
314 slope of the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  regression and its correlation coefficient ( $r=0.92$ ). Sites with a steeper slope  
315 (e.g. that fall on the LMWL) have the strongest correlation between  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$ ; sites with a lower  
316 slope have the weakest correlation between  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$ .

317

318 Inspection of Figures 4 and 5 demonstrates that the drip sites can be interpreted in the following  
319 way:

320 Type 1. Some sites have variable  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  slopes  $>6.8$  and similar to the LMWL, and very  
321 similar time-series. Some sites have discontinuous dripping, with drip flow commencing after the  
322 high rainfall events, and the isotopic composition of this initial drip water varies between events.  
323 The isotopic composition of the water subsequently becomes heavier during drip flow recession  
324 periods. A conventional explanation would be that the drip water comes from a single water source.  
325 Isotopic enrichment must occur in this source, and the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  slope demonstrates that if  
326 evaporation is the explanation for the enrichment, it must occur in a humid ( $>95\%$  relative humidity)  
327 environment (Gonfiantini, 1986). Sites with slopes of the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  regression  $>6.8$  are  
328 distinguished in Figure 5. Figure 6 demonstrates that they show a spatial clustering, with no  
329 relationship to drip classification (Table 1)..

330

331 Type 2. Some sites have variable  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  slopes  $<6.8$  and lower than the LMWL, and more  
332 variability between the time-series. Similar to sites with slopes of the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  regression  $>6.8$ ,  
333 drip flow can be continuous or discontinuous and shows large variations when recharge occurs. Drip  
334 sites have an isotopic composition of the water which subsequently becomes heavier, even during  
335 periods of drip flow recession, with greater variability and enrichment of  $\delta^{18}\text{O}$  than sites with slopes  
336 of the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  regression  $>6.8$ . Sites are distinguished by their slope (5.8-6.8, 4.8-3.8, and  $<3.8$ )  
337 in Figure 5 and spatial distribution in Figure 6.

338

339 Type 3. One site has a low variability of  $\delta^{18}\text{O}$  and a mean composition that is heavier than the  
340 weighted mean of precipitation. It can be hypothesized that these sites have a relatively  
341 homogenized water source that has undergone isotopic enrichment. Only one such sample is  
342 present in our monitoring network, Site 319 (Figure 5, 6).

343

344 Combined isotope and drip rate data demonstrate that the drip water isotopic composition can be  
345 explained by the following processes:

346 1) A flow path where the resultant drip water has an initial isotopic composition that reflects  
347 the previous infiltration event, and which becomes increasingly isotopically heavy over time  
348 but falls on the LMWL. We hypothesise that this is water stored within the shallow  
349 unsaturated zone in which evaporation occurs, as observed in laboratory environments (e.g.  
350 Ingraham and Criss, 1993). The evaporation has to occur in an environment where  $\text{RH} > 95\%$ ,  
351 which enriches the isotopic composition close to the LMWL (Gonfiantini, 1986). For this to  
352 occur, the store has to be near-surface, to experience diurnal temperature changes  
353 necessary for continued evaporation. While allowing sufficient vapour transport to keep  
354 driving the evaporative process, it must also be relatively enclosed to permit continual  
355 drainage of evaporated (increasingly enriched) water whilst maintaining a high humidity.  
356 Although previously unreported as an isotopic process in karst, such a mechanism is possible  
357 in hot continental climates which experience large diurnal temperature variations; soil  
358 temperature variations lagged from the atmospheric temperature variations could drive  
359 circulation of air in and out of the soil/karst voids. The spatial clustering of these sites (slopes  
360 of the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  regression larger than 6.8 in Figure 6) suggests discrete water stores  
361 where evaporation is occurring.

362 2) A flow path similar to (1) above, but where water also experiences evaporative enrichment  
363 at lower relative humidity. For this to occur, the air-filled part of the store could be larger, or

364 better ventilated, or the enrichment could occur within a subsequent cave void if infiltration  
365 rates are low and relative humidity low. These sites are have slopes of the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$   
366 regression of  $<6.8$  in Figure 4.

367

368 Most infiltration sites comprise a mixture of these two end-member scenarios. For all drip sites  
369 combined, the slope correlates with the individual drip water isotope  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  correlation  
370 ( $r=0.92$ ), as noted previously. The strong association between the slope of the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$   
371 regression at a drip site and the strength of correlation between  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  (Table 1) suggests that  
372 the single,  $\text{RH}>95\%$  evaporation end-member is the primary source of fractionation, with some drips  
373 experiencing additional fractionation at lower RH.

374

### 375 *3.3 Modelled flow and water isotopes*

376 Figures 3 and 7 show the modelled karst potential groundwater recharge flux indicating that the  
377 combined SMB-karst model captures the timing of the main drip water events well. Calibrated  
378 model parameters are shown in Table 2.

379

380 The model is able also to simulate the observed patterns and magnitudes of the drip water isotopic  
381 composition using the parameters given in Table 2 and Figure 5. The set of physically plausible  
382 models, despite being 'free' to vary within the entire range of observable drip composition for Types  
383 1 to 3 identified above, included no models which consistently maintained  $\delta^{18}\text{O}$  values as low as Site  
384 319, of Type 3. This suggests that the 'single karst store' model structure works well for Types 1 and  
385 2 thus supporting our conceptual model. For Type 3, a mixed source of water is needed, derived  
386 from more than one store and so to successfully simulate such sites would require a modification of  
387 the existing numerical model to a more complex model structure.

388



389 If the karst evaporative process is 'switched off' (Figure 7) the modeled isotopic drip water reverts to  
390 lighter values which vary little from the mean rainwater isotopic composition. This shows that the  
391 observed drip water isotopic variations cannot simply be explained by transformation of the input  
392 precipitation signal using a standard model of soil and shallow karst processes. It is thus strongly  
393 indicative of evaporative equilibrium fractionation (i.e. at conditions >95% RH) in the karst being the  
394 dominant mechanism controlling the observed isotopic drip water compositions. Although the  
395 evaporative process is modeled empirically it has a sound theoretical basis with Equation 10 being of  
396 the form suggested by Gonfiantini (1986, Eq.7, p117). In the present case the variable  $f$  changes not  
397 only due to evaporative loss but also due to drainage from the karst store. Hence, a direct  
398 comparison between our parameters  $n$  and  $m$ , and Gonfiantini's  $A$  and  $B$  parameters cannot be  
399 made without further (laboratory) investigation to determine the precise form this relationship  
400 should take. The values of the physically based parameters retained in the posterior set are  
401 physically plausible and lend insight into the potential properties of the karst unsaturated zone at  
402 the fieldsite. Most parameters have clearly defined optima for example  $\tau \approx 0.03$  /d,  $S2_{lim} \approx 60$  mm  
403 and  $S2_0 \approx 200$  mm. The relatively large initial value for  $S2_0$  is suggestive of a period of substantial  
404 recharge occurring just prior to the drip isotope monitoring period. This is consistent with high  
405 observed driprates from the site in late 2010, observed prior to cave flooding (Jex et al., 2012).  
406 Furthermore, the ranges of  $S2$  and the drainage function,  $\tau$ , are also reasonable in comparison to  
407 other karst models (for example, Bradley et al., 2010). The model is relatively insensitive to the  
408 evaporation flux (which was set to a maximum of 0.15 mm/d, constrained by our in-cave  
409 evaporation rate at Site 1) in determining the timing of the positive isotopic value excursions since  
410 the optimum  $S2_{lim}$  values are relatively large in comparison. Hence the isotopic composition is  
411 primarily controlled by the empirical  $m$  and  $n$  parameters which control the fractionation of the karst  
412 store as it loses water by drainage and evaporation and which have very clearly defined parameter  
413 optima at  $n \approx 0.3$ ,  $m \approx -2$ .

414

415 The way the model is structured, the rate of fractionation is explicitly dependent on the fraction of  
416 water remaining in a shallow karst store. However, since the modeled drip rates are directly  
417 proportional to the size of this store (via the recession constant), the fractionation is thus also  
418 proportional to the drip rate, below a threshold value. Such a flow rate-dependent evaporative  
419 process has recently been directly observed during film flow over a speleothem-forming feature in  
420 the shallower part of the Cathedral Cave system (Cuthbert et al., in review). This could also be  
421 responsible for the fractionation observed in the deeper South Passage samples reported here.  
422 Furthermore, additional evaporative fractionation could occur within the cave passage, especially at  
423 low drip rates, either on the stalactite or on the sample collection bottle prior to collection below  
424 the paraffin seal (Dreybrodt and Deininger, 2013). However, the high relative humidity in South  
425 Passage, and lack of observed relationship between drip rate, drip classification and oxygen isotopic  
426 composition, suggests that these effects would be limited, at least at site 2.

427 It is notable that the recharge events which reset the isotopic composition of the karst store and drip  
428 waters in South Passage occur on timescales of hours to days and time-steps of this order of  
429 magnitude are needed to predict their occurrence. It is well known that soil moisture balance  
430 models are very sensitive to the choice of time-stepping (Howard & Lloyd 1979). However, most  
431 climate models operate on monthly or coarser time-steps and, when coupled with hydrologic  
432 models, structural errors such as those due to time-stepping within a soil-moisture accounting  
433 algorithm are rarely considered (Holman et al., 2012). Our results therefore have significant  
434 implications for how to model adequately the effect of climate change, for example variations in  
435 rainfall intensification, on recharge and speleothem-forming processes in karst environments.

436

### 437 *3.4 Implications for speleothem records*

438 Our results inform the climatic interpretation of speleothem records in the arid and semi-arid  
439 environment in Australia and elsewhere. We have shown that drip water may be enriched by several  
440 per mil owing to evaporative processes; this is of similar magnitude, but opposite in direction, to the

441 fractionation predicted by the estimated atmospheric cooling of up to 9 °C at the Last Glacial  
442 Maximum in continental Australia (Galloway, 1965; Miller et al., 1997). Thus if both processes are  
443 happening concurrently the speleothem signal could be confounded and affect the imprint of  
444 atmospheric temperature in the speleothem record (Fairchild and Baker, 2012). Additionally, we  
445 expect that the speleothem isotopic record from these environments may exhibit a considerable  
446 range in isotopic values driven by shifts in the frequency-magnitude relationships of infiltration  
447 events. This may be recorded on an event-scale but, more relevant to the detection in speleothem  
448 isotopic records, is the decadal-centennial timescale on which recharge will be influenced by  
449 variability in the dominant climate modes over Australia and more generally in other semi-arid and  
450 arid areas globally. Variability in climate modes on these timescales has been observed in proxy  
451 records in the Australasian region (e.g. van Ommen et al., 2010). Finally, we draw a link between  
452 these results and previous studies that have demonstrated a sensitivity between the timing of  
453 speleothem growth and the P-ET balance. Speleothems 'switching on' during cooler time periods  
454 (the Last Glacial Maximum and stadial periods) is attributed to reduced evaporation in southern  
455 Australia's arid margin (Ayliffe et al., 1998; Cohen et al., 2011). The results of our study may inform  
456 the interpretation of speleothem isotopic records from this region as the water balance changes  
457 within stadial and glacial events.

458

## 459 **Conclusions**

460 Groundwater recharge in semi-arid environments is episodic; the initial isotopic composition of  
461 recharge reflects the isotopic composition of the few rainfall events which are large enough to  
462 overcome existing soil moisture deficits. This initial isotopic composition may be affected by  
463 subsequent evaporation. At our monitoring site, observed drip waters had a mean  $\delta^{18}\text{O}$  up to 2.77‰  
464 heavier than the weighted mean of precipitation. Here, evaporation from a partially air-filled water  
465 store in a high humidity environment is an important process. Our modelling approach  
466 demonstrated that this isotope enrichment had to include evaporation from a shallow subsurface

467 karst water store, such as a solutionally widened fracture or proto-cave. The degree of enrichment  
468 would be site specific, and dependent on the relative size of the store and its climatic properties  
469 (temperature variability, relative humidity), its drainage rate and the time between infiltration  
470 events. We have identified and modelled unsaturated zone evaporation as an important process in  
471 determining infiltration water  $\delta^{18}\text{O}$  for the first time. We propose that at other caves in semi-arid to  
472 arid regions, evaporation will also be a likely source of isotope enrichment, but this requires  
473 confirmation.

474

475 At Cathedral Cave, infiltration  $\delta^{18}\text{O}$  is a complex function of (1) the isotopic composition of recharge  
476 water, (2) the time since the last recharge event (3) water store climate and physical properties and  
477 (4) water flow routing from the store to the drip site, including evaporation during the degassing  
478 process that forms speleothems (Dreybrodt and Deininger, 2013). This makes the interpretation of  
479 individual stalagmite  $\delta^{18}\text{O}$  records potentially complex. The range of mean drip water  $\delta^{18}\text{O}$  between  
480 sample sites gives an indication of this hydrological uncertainty: in our case this is 1.94‰ (mean  
481 from -1.51‰ to -3.45‰). This is greater than the total range of hydrological uncertainty in  
482 stalagmite  $\delta^{18}\text{O}$  currently modelled for both modern (Baker and Bradley, 2009; Bradley et al. 2010;  
483 Treble et al. 2013), historical (Jex et al. 2013), and Last Glacial Maximum (Baker et al. 2013)  
484 environments: all use hydrology modelling approaches that exclude unsaturated zone evaporation  
485 as a process.

486

487 Interpretation of speleothem  $\delta^{18}\text{O}$  archives, typically from temperate, sub-alpine or cool climates, is  
488 one where evidence is presented either (1) for speleothem deposition that is at or close to  
489 equilibrium, or (2) that deposition has occurred out of equilibrium, such that kinetic fractionation  
490 has occurred (Fairchild and Baker, 2012). The relevant processes in these environments are relatively  
491 well observed (e.g. Spötl et al., 2005; Lachniet, 2009) and modelled (Dreybrodt and Scholz, 2011).  
492 However, in semi-arid to arid environments, subject to surface, soil and unsaturated zone

493 evaporation, our understanding of the interpretation of speleothem  $\delta^{18}\text{O}$  is still developing. In this  
494 study, we attribute at least part of the observed  $\delta^{18}\text{O}$  isotope composition of stalagmite forming drip  
495 waters to evaporation in the unsaturated zone, and propose that this process is likely to occur at  
496 other sites where  $\text{ET} > \text{P}$ , such as those reported in central Texas (Pape et al., 2010). Thus,  
497 interpretation of stalagmite  $\delta^{18}\text{O}$  in these regions could be a function of this process, as well as the  
498 previously recognised within-cave processes such as kinetic effects (due to the differing rate  
499 constants of calcite precipitation for the heavy and light isotopes; Dreybrodt, 2008; Dreybrodt and  
500 Scholz, 2011) and evaporation during degassing (Dreybrodt and Deininger, 2013). As well as having  
501 relevance to the interpretation of speleothem records from modern day regions where  $\text{ET} > \text{P}$  and  
502 infiltration is infrequent, our findings are also relevant to the interpretation of Quaternary  
503 speleothem records from regions where the modern day climate is temperate or Mediterranean, but  
504 in the past experienced some degree of aridity.

505

#### 506 **Supplementary Materials**

507 Rainfall double mass plots, isotope and drip rate data are available on-line as supplementary  
508 spreadsheets.

509

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520

## 521 **References**

522 Allison, G.B., 1982. The relationship between  $^{18}\text{O}$  and deuterium in water in sand columns  
523 undergoing evaporation. *Journal of Hydrology*, 55, 163-169.

524 Allison, G.B. and Hughes, M.W., 1983. The use of natural tracers as indicators of soil-water  
525 movement in a temperate semi-arid region. *Journal of Hydrology*, 60, 157-173

526 Allison, G.B., Barnes, C.J. and Hughes, M.W., 1983. The distribution of deuterium and  $^{18}\text{O}$  in dry  
527 soils. 2. Experimental. *Journal of Hydrology*, 64, 377-397.

528 Allison, G.B., Colin-Kaczala, C., Filly, A. and Fontes, J.Ch. 1987. Measurement of isotopic equilibrium  
529 between water, water vapour and soil  $\text{CO}_2$  in arid zone soils. *Journal of Hydrology*, 95, 131-141

530 Allen, R.G., Pereira, L.S., Raes, D., and Smith, M. 1998. Crop evapotranspiration - Guidelines for  
531 computing crop water requirements - FAO Irrigation and drainage paper 56. FAO, Rome, Italy.

532 Ayliffe, L.K., Marianelli, P.C., Moriarty, K.C., Wells, R.T., McCulloch, M.T., Mortimer, G.E. and  
533 Hellstrom, J.C., 1998. 500ka precipitation record from southeastern Australia: Evidence for  
534 interglacial relative aridity. *Geology* 26, 147-150.

535 Baker, A. and Brunson, C., 2003. Non-linearities in drip water hydrology: an example from Stump  
536 Cross Caverns, Yorkshire. *Journal of Hydrology*, 277, 151-163.

537 Baker, A. and Bradley, C. 2010. Modern stalagmite  $\delta^{18}\text{O}$ : instrumental calibration and forward  
538 modelling. *Global and Planetary Change*, 71, 201-206.

539 Baker, A., Bradley, C. and Phipps, S.J., 2013. Hydrological modelling of stalagmite  $\delta^{18}\text{O}$  response to  
540 glacial-interglacial transitions. *Geophysical Research Letters*. 40, Issue 12, 3207–3212

541 Barnes, C.J. and Allison, G.B., 1988. Tracing of water movement in the unsaturated zone using stable  
542 isotope of hydrogen and oxygen. *Journal of Hydrology*, 100, 143-176.

543 Beven, K., and Binley, A., 1992. The future of distributed models: model calibration and uncertainty

544 prediction. *Hydrological processes*, 6, 279-298.

545 Bradley, C., Baker, A., Jex, C. and Leng, M.J. 2010. Hydrological uncertainties in the modelling of cave  
546 drip-water  $\delta^{18}\text{O}$  and the implications for stalagmite palaeoclimate reconstructions. *Quaternary*  
547 *Science Reviews* 29, 2201-2214.

548 Cohen, T.J., Nanson, G.C., Jansen, J.D., Jones, B.G., Jacobs, Z., Treble, P., Price, D.M., May, J.H., Smith,  
549 A.M., Ayliffe, L.K., and Hellstrom, J.C., 2011. Continental aridification and the vanishing of Australia's  
550 megalakes. *Geology* 39, 167-170.

551 Cuthbert, M.O., Mackay, R. and Nimmo, J.R. 2013. Linking soil moisture balance and source-  
552 responsive models to estimate diffuse and preferential components of groundwater recharge.  
553 *Hydrology and Earth System Science*, 17, 1003-1019.

554 Cuthbert, M.O., Rau, G.C., Andersen, M.S., Roshan, H., Rutledge, H., Marjo, C., Markowska, M.,  
555 Graham, P.W., Mariethoz, G. and Baker, A., in review. Controls on cave dripwater temperatures and  
556 implications for speleothem paleoclimate archives. *Geophysical Research Letters*.

557 Dreybrodt, W. 2008. Evolution of the isotopic composition of carbon and oxygen in a calcite  
558 precipitating  $\text{H}_2\text{O}-\text{CO}_2-\text{CaCO}_3$  solution and the related isotopic composition of calcite in stalagmites.  
559 *Geochimica et Cosmochimica Acta*, 72, 4712-4724.

560 Dreybrodt, W. and Scholz, D. 2011. Climatic dependence of stable carbon and oxygen isotope signals  
561 recorded in speleothems: From soil water to speleothem calcite. *Geochimica et Cosmochimica Acta*,  
562 75, 734-752

563 Dreybrodt, W. and Deininger, M., 2013. The impact of evaporation to the isotope composition of DIC  
564 in calcite precipitating water films in equilibrium and kinetic fractionation models. *Geochimica et*  
565 *Cosmochimica Acta*, doi 10.1016/j.gca.2013.10.004

566 Fairchild, I.J. and Baker, A., 2012. *Speleothem Science*. Wiley-Blackwell.

567 Galloway, R.W., 1965. Late Quaternary climates in Australia. *Journal of Geology* 73, 603-618.

568 Gonfiantini, R., 1986. Environmental Isotopes in Lake Studies. In Fritz P. and Fontes J. Ch. (Eds)  
569 Handbook of Environmental Isotope Geochemistry, Volume 2: The Terrestrial Environment, pp113-  
570 168. Elsevier.

571 Holman I. P., Allen, D. M., Cuthbert M. O. and Goderniaux P. 2012. Towards best practice for  
572 assessing the impacts of climate change on groundwater. Hydrogeology Journal, 20: 1-4.

573 Howard, K. W. F., and Lloyd, J. W. 1979. The sensitivity of parameters in the Penman evaporation  
574 equations and direct recharge balance. Journal of Hydrology, 41(3), 329-344.

575 Ingraham, N.L., Chapman, J.B. and Hess, J.W., 1990. Stable isotopes in cave pool systems: Carlsbad  
576 Cavern, New Mexico, U.S.A. Chemical Geology, 86, 65-74.

577 Ingraham, N.L. and Criss, R.E., 1993. Effect of surface area and volume on the rate of isotopic  
578 exchange between water and water vapour. Journal of Geophysical Research, 98, D11, 20547-20553.

579 Jex, C.N., Mariethoz, G., Baker, A., Graham, P., Andersen, M.S., Acworth, I., Edwards, N. and Azcurra,  
580 C., 2012. Spatially dense drip hydrological monitoring and infiltration behaviour at the Wellington  
581 Caves, South East Australia. Int Journal of Speleology, 41(2) 285-298.

582 Jex, C.N., Phipps, S.J., Baker, A, and Bradley, C. 2013. Reducing uncertainty in the climatic  
583 interpretations of speleothem  $\delta^{18}\text{O}$ . Geophysical Research Letters, 40, 2259–2264

584 Lachniet, M.S. 2009. Climatic and environmental controls on speleothem oxygen-isotope values.  
585 Quaternary Science Reviews, 28, 412-432

586 Lis, G., Wassenaar, I.L. and Hendry, M.J., 2007. High-precision laser spectroscopy D/H and  $18\text{O}/16\text{O}$   
587 measurements of microliter natural water samples. Analyt. Chem. 80,287-293

588 Mariethoz, G., Baker, A., Sivakumar, B., Hartland, A. and Graham, P. 2012. Chaos and irregularity in  
589 karst percolation. Geophys. Res. Lett., L23305

590 Miller, G.H., Magee, J.W., and Jull, A.J.T., 1997. Low-latitude glacial cooling in the Southern  
591 Hemisphere from amino-acid racemisation in emu eggshells. Nature 385, 241-244.



592 McDonald, J., Drysdale, R., Hill, D., Chisari, R. and Wong, H. 2007. The hydrochemical response of  
593 cave drip waters to sub-annual and inter-annual climate variability, Wombeyan Caves, SE Australia.  
594 *Chemical Geology*, 244, 605-623.

595 Nimmo, J. R. 2010. Theory for Source-Responsive and Free-Surface Film Modeling of Unsaturated  
596 Flow, *Vadose Zone J.*, 9, 295-306, doi:10.2136/vzj2009.0085

597 Osborne R.A.L., 2007. Cathedral Cave, Wellington Caves, New South Wales, Australia. A multiphase,  
598 non-fluvial cave. *Earth Surface Processes and Landforms*, 32, 2075-2103.

599 Osborne, R.A.L., 2010. Rethinking eastern Australian caves. Geological Society, London, Special  
600 Publications, 346, 289-308.

601 Pape, J.R., Banner, J.L., Mack, L.E., Musgrove, M., and Guilfoyle, A., 2010, Controls on oxygen isotope  
602 variability in precipitation and cave drip waters, central Texas, USA: *Journal of Hydrology*, 385, 203-  
603 215.

604 Rutledge, H., Baker, A., Marjo, C., Andersen, M.S., Graham, P.W., Cuthbert, M.O., Rau, G.C., Roshan,  
605 H., Markowska, M., Mariethoz, G. and Jex, C., submitted. Dripwater organic matter and trace  
606 element geochemistry in a semi-arid karst environment: implications for speleothem  
607 paleoclimatology. *Geochimica et Cosmochimica Acta*.

608 Sonntag, C., Christmann, D. and Munnich, K.O., 1985. Laboratory and field experiments on  
609 infiltration and evaporation of soil water by means of deuterium and oxygen-18. In: Proc. IAEA/GSF  
610 Meeting, Vienna, 1984, IAEA TECDOC 357: 145-159

611 Spötl, C., Fairchild, I.J., and Tooth, A.F., 2005. Cave air control on dripwater geochemistry, Obir caves  
612 (Austria): implications for speleothem deposition in dynamically ventilated caves. *Geochimica et*  
613 *Cosmochimica Acta*, 69, 2451-2468.

614 Treble, P.C., Bradley, C., Wood, A, Baker, A., Jex, C.N., Fairchild, I.J., Gagan, M.K., Cowley, J. and  
615 Azcurra, C., 2013. An isotopic and modelling study of flow paths and storage in Quaternary  
616 calcarenite, SW Australia: implications for speleothem paleoclimate records. *Quaternary Science*  
617 *Reviews*, 64, 90-103

618 Van Ommen, T.D. and Morgan, V., 2010. Snowfall increase in coastal East Antarctica linked with  
619 southwest Western Australian drought. *Nature Geoscience* 3, 267-272.

620 Wassenaar, L.I., Hendry, M.J., Chostner, V.L. and Lis G.P. 2008. High Resolution Pore Water  $\delta^2\text{H}$  and  
621  $\delta^{18}\text{O}$  Measurements by  $\text{H}_2\text{O}(\text{liquid})\text{-H}_2\text{O}(\text{vapor})$  Equilibration, *Environmental Science and Technology*,  
622 2008, 42 9262–9267

623

624 **Table captions**

625

626 Table 1. Drip water and local river and groundwater isotopic composition. For each drip site, a 'drip  
627 water line' and its correlation coefficient is shown, along with the standard error of both gradient  
628 (M) and intercept (C). Drip types are classified as soda straw stalactite (So), non soda-straw stalactite  
629 (St) and non-soda-straw stalactite within flowstone (F)

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631 Table 2. Parameter values estimated by manual calibration and used to generate model simulations  
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633 ranges defined in Figure 7.

634

635 **Figure captions**

636

637 Figure 1. Cathedral Cave sampling locations. Boxes show the two monitoring sites: 1. the near-  
638 entrance site monitoring drip rate and 2. the deeper South Passage site monitoring drip rate and  
639 drip water isotopes. The locations of monitoring sites at the latter are shown in more detail in Figure  
640 3c. Also labelled is 3: groundwater sample location 'The Well'. The cave survey is reproduced with  
641 permission of the Sydney University Speleological Society.

642 Figure 2. Schematic illustration of the modelled processes. Variables are all defined in the main text.

643 Figure 3. (a) Rainfall (grey line) and potential evaporation (black line); (b) modelled groundwater  
644 potential recharge; (c) drip rate for all Stalagmate drip loggers over the study period; (d) rainfall  
645 (dashed line) and drip water (solid line) monthly isotope samples.

646 Figure 4. (a)  $\delta^2\text{H}$  vs  $\delta^{18}\text{O}$  for monthly rainfall (closed circles) and infiltration (small closed squares).  
647 Local river water samples (open squares) and groundwater samples (open circles) are also  
648 presented. (b) Trend lines of the data presented in (a): Local Meteoric Water Line (dashed line) and  
649  $\delta^2\text{H}$  vs  $\delta^{18}\text{O}$  regressions for each drip water site (solid lines). Regression equations and correlation  
650 coefficients are presented in Table 1. (b

651 Figure 5. Water  $\delta^{18}\text{O}$  isotope time series shaded by slope of  $\delta^2\text{H}$  vs  $\delta^{18}\text{O}$  regression.  $>6.8$ , light grey  
652 dotted lines;  $6.8-5.8$ , grey dot-dash lines;  $5.8-4.8$ , dark grey dashed line;  $<4.8$ , black solid lines. Solid  
653 grey lines represent the periods of infiltration (Figure 2c).

654 Figure 6 Spatial distribution of Site 2 water isotope samples: see inset, Figure 1 for location within  
655 Cathedral Cave. Site ID and drip classification are as presented in Table 1. Shading and fill of the  
656 symbols shows the slope of  $\delta^2\text{H}$  vs  $\delta^{18}\text{O}$  regression as presented in Table 1.

657 Figure 7 (a) Results from Monte-Carlo modelling of drip water compositions shown against  
658 observations (solid lines, except dashed Site 319), and observed rainfall and modelled groundwater

659 potential recharge. Shaded area represents the isotopic distribution of the physically plausible model  
660 results (1927 out of 50 000). The model output for the most frequently used parameter values are  
661 highlighted (dots) and for no karst evaporation/fractionation (dot-dash) (b) Frequency distributions  
662 of the posterior parameter sets, normalised across the range of prior parameter values. Each  
663 parameter was free to vary between zero and the value defined in brackets. For example, m was  
664 free to vary randomly between 0 and -5 but most models that had a reasonable fit have values of  
665 around -0.2.

**\*Highlights (for review)**

- 1 Isotopic composition of cave drip waters in a semi-arid karst terrane are reported.
- 2 Their isotopic composition is heavier than the weighted mean annual precipitation.
- 3 Modelling confirms sub-surface evaporation affects drip water isotopic composition.
- 4 Relevant to the interpretation of speleothem records from arid and semi-arid regions.
- 5

Figure 1  
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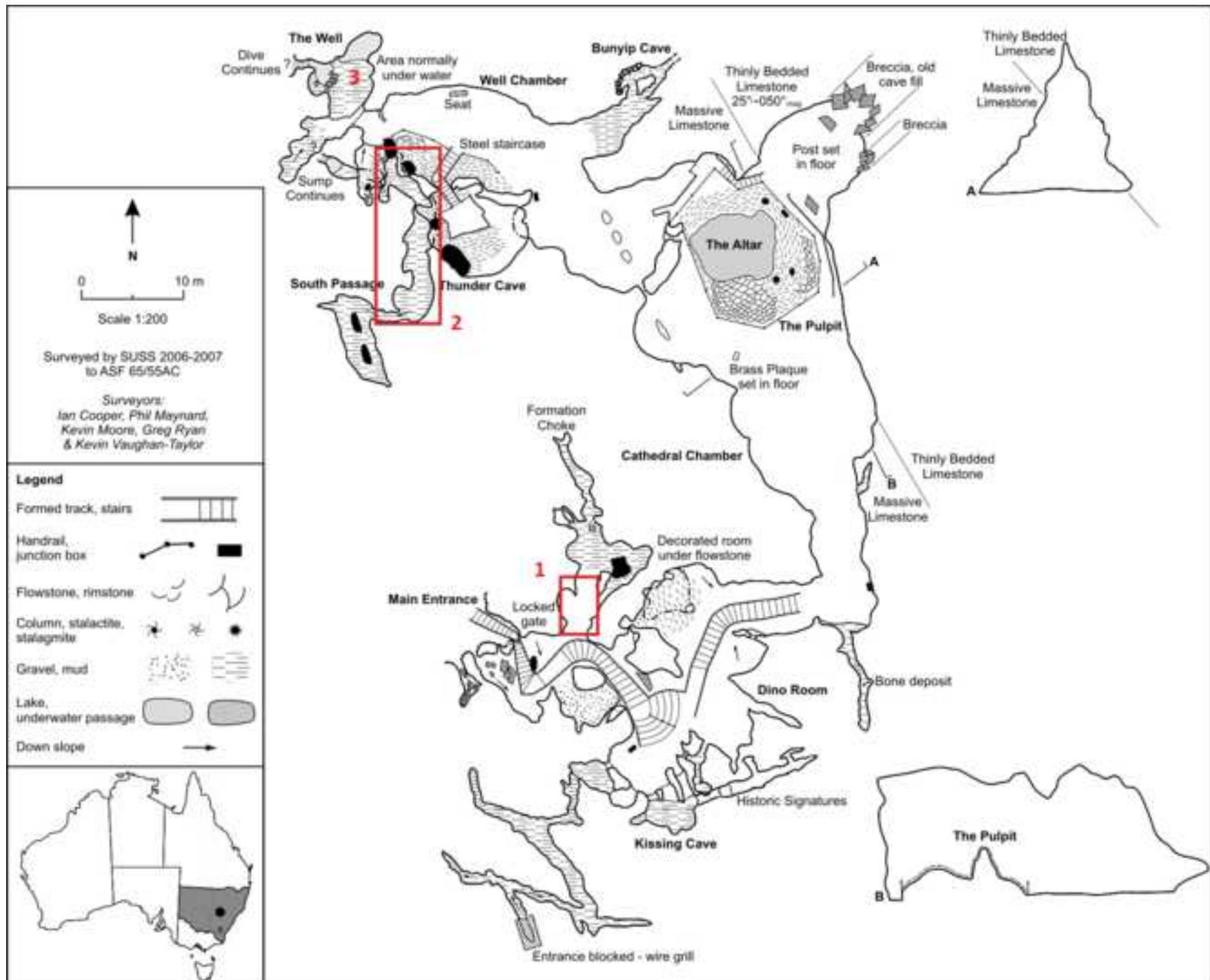
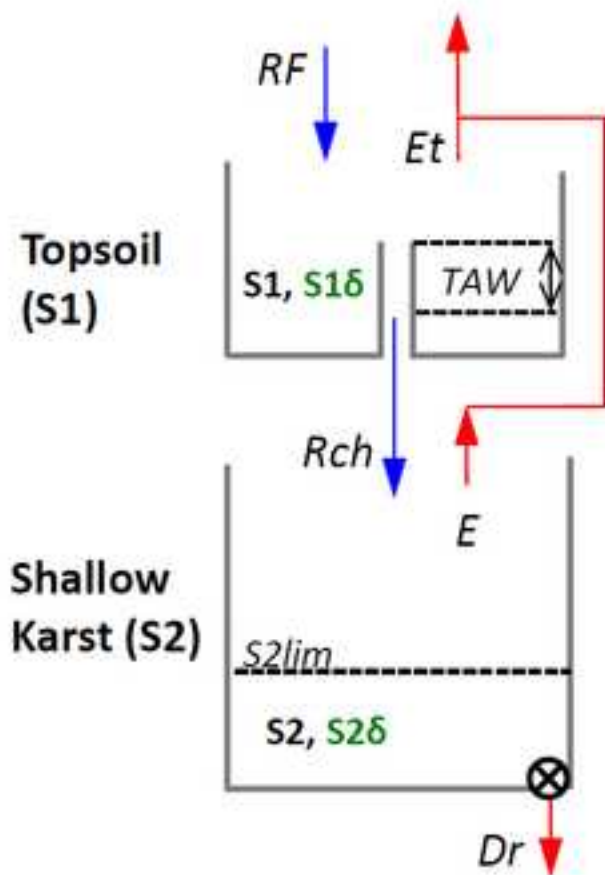


Figure 2  
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$$S1_{t+\Delta t} = S1_t + (RF_t - AE_t - Rch_t) \cdot \Delta t$$

$$S1\delta_{t+\Delta t} = (S1\delta_t (S1_t - (AE_t + Rch_t) \cdot \Delta t) + RF\delta_t \cdot RF_t \cdot \Delta t) / S1_{t+\Delta t}$$

$$S2_{t+\Delta t} = S2_t + (Rch_t - E - Dr_t) \cdot \Delta t$$

$$Dr_t = \tau \cdot S2_t$$

If  $S2_t > S2lim$

Then  $S2\delta_{t+\Delta t} = (S2\delta_t (S2_t - (Dr_t + E) \cdot \Delta t) + S1\delta_t \cdot Rch_t \cdot \Delta t) / S2_{t+\Delta t}$

Else  $S2\delta_{t+\Delta t} = (S2\delta_t - m) \cdot f^n + m$



Figure 3  
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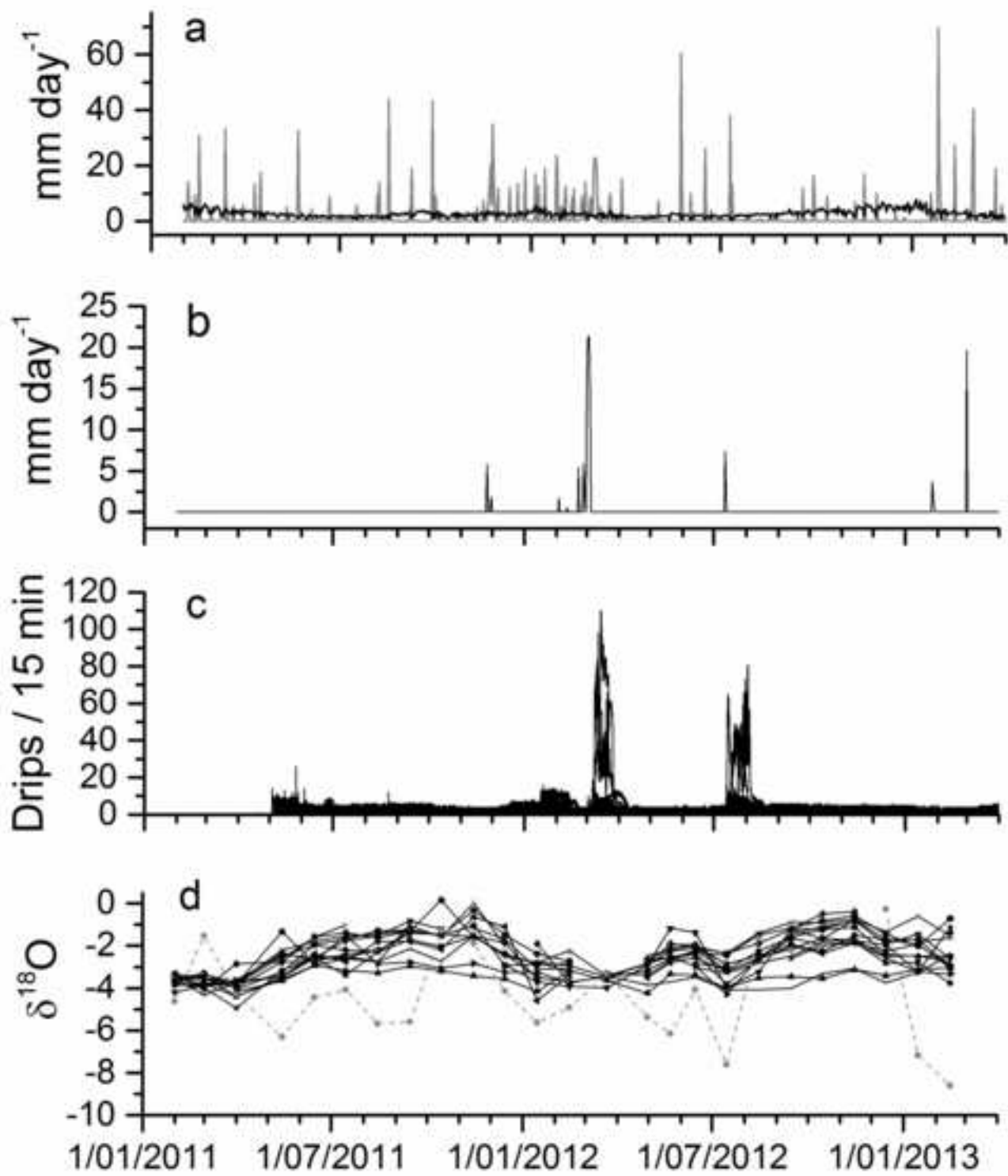


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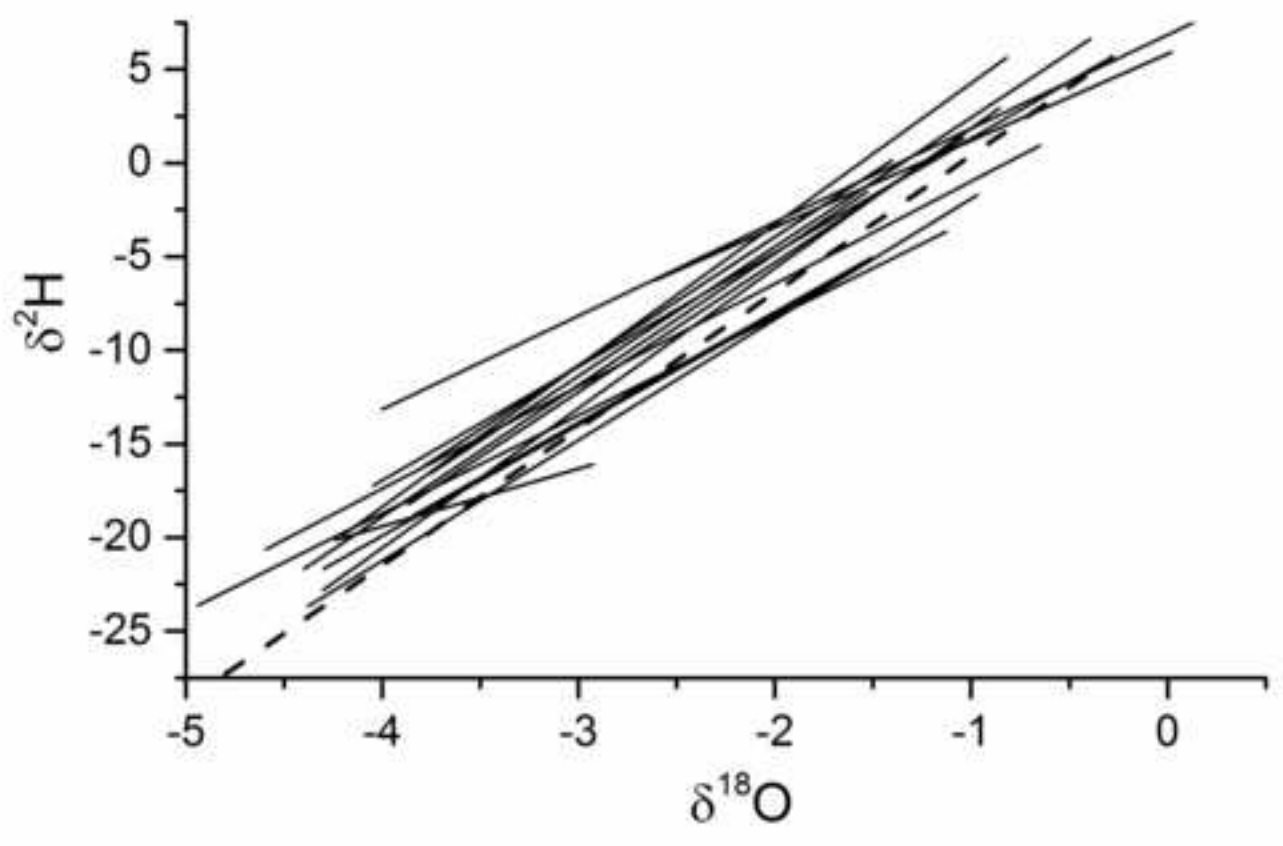
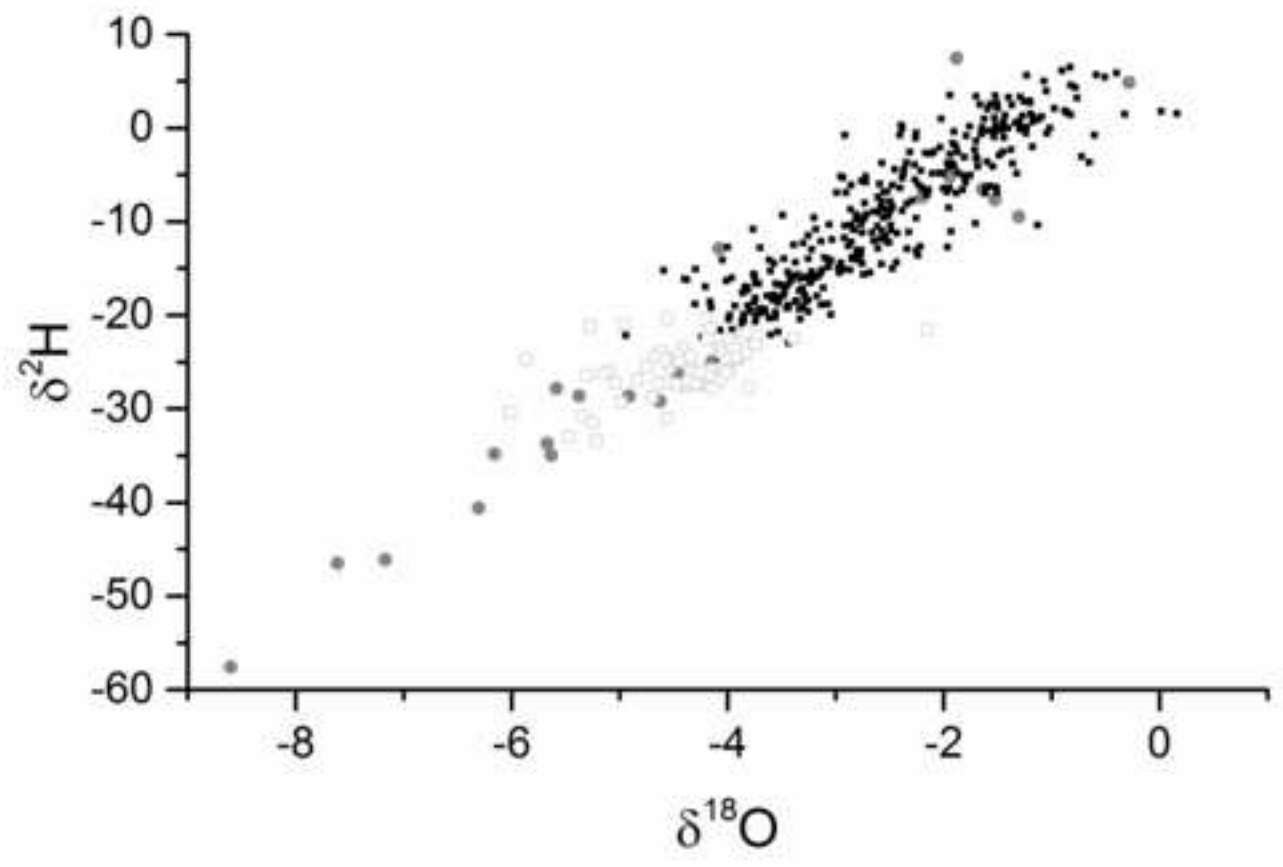


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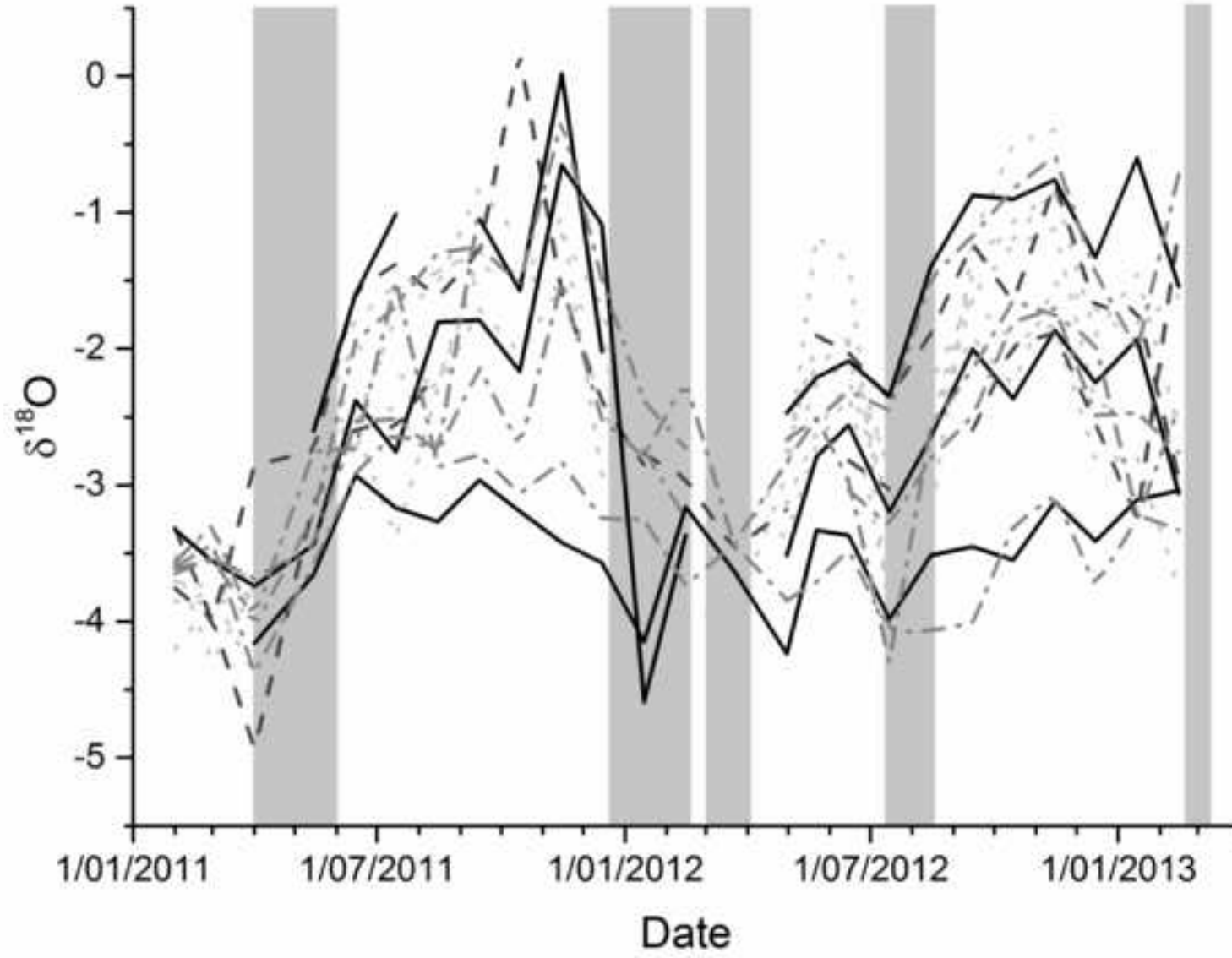


Figure 6  
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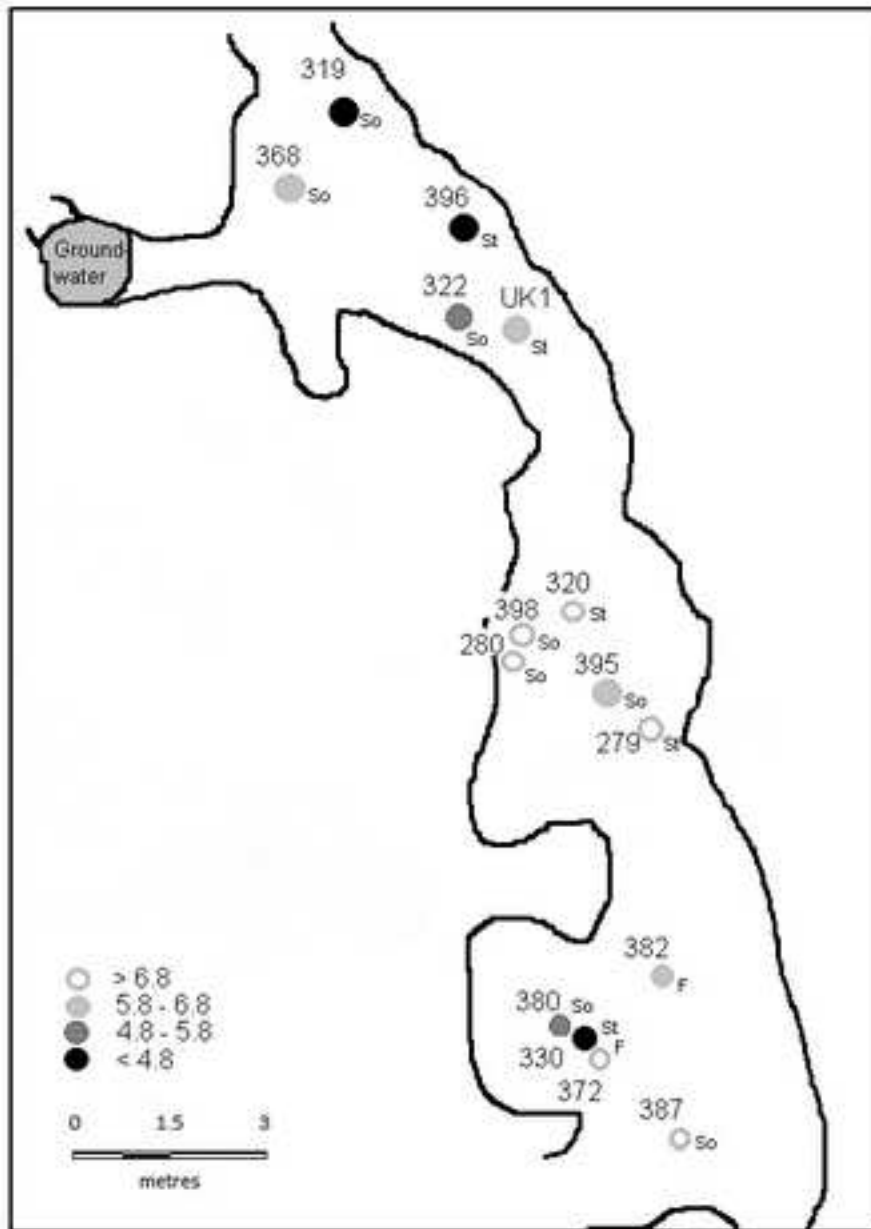


Figure 7a  
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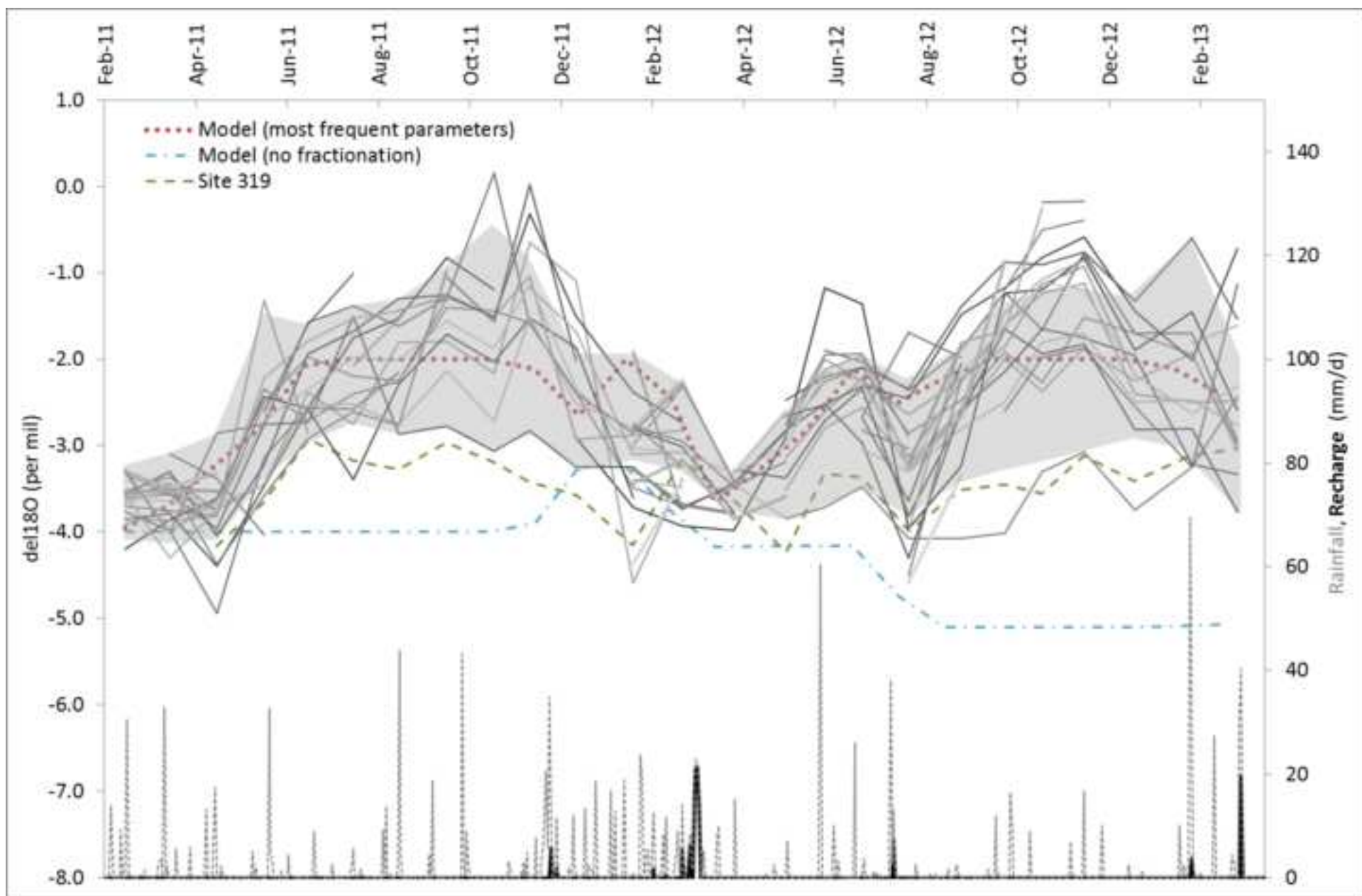


Figure 7b  
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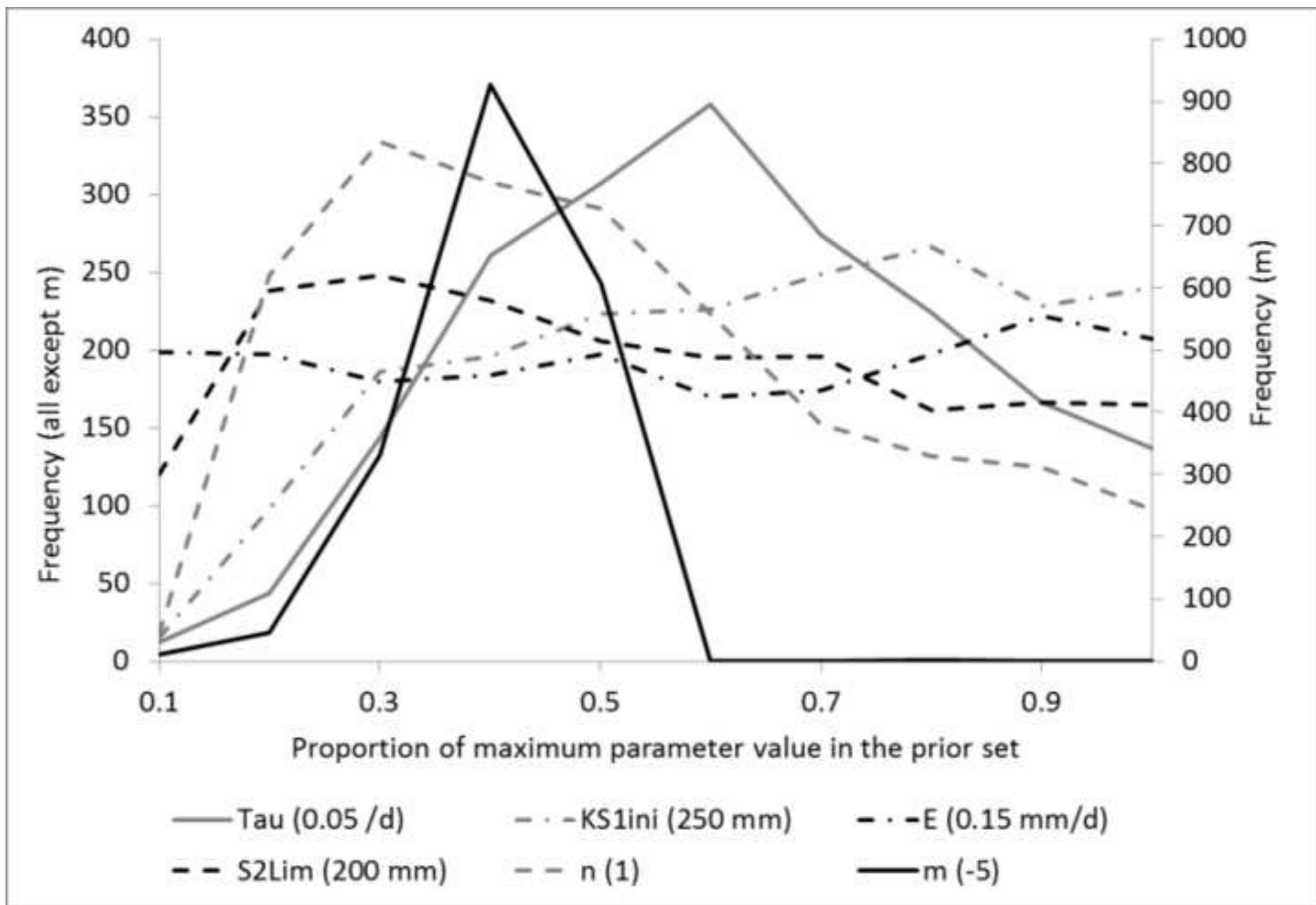


Table 1

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- 1 Table 1. Drip water and local river and groundwater isotopic composition. For each drip site, a 'drip water line' and its correlation coefficient is shown, along
- 2 with the standard error of both gradient (M) and intercept (C). Drip types are classified as soda straw stalactite (So), non soda-straw stalactite (St) and non-
- 3 soda-straw stalactite within flowstone (F)

Site ID	Drip Type	Mean (drips/15min)	Median (drips/15 min)	Maximum (drips/15 min)	$\delta^{18}O$		$\delta^2H$		Number of samples	$\delta^2H = M * \delta^{18}O + C$				
					mean	sd	mean	sd		N	M	C	r	
279	St	8.28	1.00	368.00	-2.81	0.84	-10.52	6.75	24	7.03	0.81	9.22	2.38	0.88
280	So	0.89	1.00	3.00	-2.50	0.78	-7.38	6.18	25	6.85	0.82	9.76	2.13	0.87
319	So	1.85	2.00	14.00	-3.45	0.38	-17.72	1.99	23	3.08	0.92	-7.08	3.21	0.59
320	St	3.04	0.00	110.0	-2.43	1.16	-6.53	9.42	24	7.54	0.62	11.81	1.67	0.93
322	So	0.32	0.00	3.00	-1.98	0.91	-3.08	5.76	22	5.00	0.87	6.85	1.88	0.79
330	St	nd	nd	nd	-2.62	0.90	-9.84	6.10	24	4.49	0.86	5.47	2.36	0.81
368	So	nd	nd	nd	-2.90	0.71	-13.42	5.06	25	5.91	0.82	3.74	2.45	0.83
372	F	0.36	0.00	2.00	-2.36	0.90	-7.82	6.94	23	6.91	0.74	8.51	1.85	0.90
380	So	nd	nd	nd	-2.88	0.84	-12.85	5.34	19	5.23	0.88	2.24	2.63	0.82
382	F	nd	nd	nd	-1.96	0.98	-4.51	6.72	24	6.09	0.67	7.39	1.45	0.89
387	So	nd	nd	nd	-2.24	1.03	-6.13	7.70	18	6.90	0.73	9.33	1.80	0.92
395	So	3.90	3.00	11.00	-2.76	0.64	-12.43	4.79	24	5.90	0.99	3.84	2.79	0.79
396	St	nd	nd	nd	-1.51	0.73	-1.16	4.62	18	4.63	1.05	5.83	1.74	0.73
398	So	nd	nd	nd	-2.19	0.96	-7.06	7.63	22	7.47	0.63	9.33	1.49	0.94
UK1	St	nd	nd	nd	-3.30	0.75	-16.71	5.79	20	6.45	0.98	4.54	3.31	0.83
RAIN					-4.28	2.18	-23.54	16.48	24	7.29	0.43	7.68	2.08	0.96
Rivers														
MACQUARIE					-4.27	0.75	-24.58	3.06	18					
BELL					-4.45	0.59	-26.24	3.68	18					
Groundwater														
ANTICLINE					-4.43	0.53	-25.50	1.44	18					
WELL					-4.46	0.44	-26.41	2.34	18					

**Table 2**[Click here to download Table: Cuthbert et al\\_Table\\_2.docx](#)

1

<i>Parameter</i>	<i>Description</i>	<i>Value</i>	<i>Units</i>
$SMD_i$	initial soil moisture deficit	TAW	mm
$\theta_{FC}$	field capacity of soil	25	%
$\theta_{WP}$	wilting point of soil	5	%
$Z_e$	soil depth subject to evaporative drying	0.1	m
$Z_r$	rooting depth	0.47	m
$K_c$	crop coefficient	1	-
$p$	RAW to TAW ratio	0.5	-
$B$	proportion of bare soil	0.1	-
$S1\delta_0$	Initial $\delta^{18}O$ of soil store	-4	‰
$S2\delta_0$	Initial $\delta^{18}O$ of karst store	-4	‰

2

3 Table 2. Parameter values estimated by manual calibration and used to generate model simulations  
4 shown in Figure 3 & 7. Parameters not shown were subject to a Monte-Carlo analysis and have  
5 ranges defined in Figure 7.

6



**Supplementary table 1**

[Click here to download Supplementary material for on-line publication only: Cuthbert et al Supplemental Table 1 Rainfall Double](#)

**Supplementary table 2**

[Click here to download Supplementary material for on-line publication only: Cuthbert et al Supplementary Table 2 Drip rate data](#)

**Supplementary table 3**

[Click here to download Supplementary material for on-line publication only: Cuthbert et al Supplementary Table 3 Drip water and](#)