

Data-model comparison of soil–water $\delta^{18}\text{O}$ at a temperate site in N. Spain with implications for interpreting speleothem $\delta^{18}\text{O}$



Laia Comas-Bru ^{a,*}, Frank McDermott ^{a,b}

^aUCD School of Earth Sciences, University College Dublin, Belfield, Dublin 4, Ireland

^bUCD Earth Institute, University College Dublin, Belfield, Dublin 4, Ireland

ARTICLE INFO

Article history:

Received 30 June 2015

Received in revised form 15 September 2015

Accepted 22 September 2015

Available online 28 September 2015

This manuscript was handled by Peter K. Kitanidis, Editor-in-Chief, with the assistance of Barbara Mahler, Associate Editor

Keywords:

Soil–water $\delta^{18}\text{O}$

La Garma cave

Stable oxygen isotopes

Modelling

SUMMARY

An understanding of how seasonal and longer-term $\delta^{18}\text{O}$ signals in meteoric precipitation ($\delta^{18}\text{O}_p$) are modified by percolation through soils is essential to link temporal changes in speleothem $\delta^{18}\text{O}$ to surface climatic conditions. This study focuses on modifications that occur in a relatively thick soil above a temperate cave site (La Garma, N. Spain). Monthly soil–water $\delta^{18}\text{O}$ ($\delta^{18}\text{O}_{sw}$) values at a depth of 60 cm through the year are only 14% of the range in $\delta^{18}\text{O}_p$, implying substantial homogenisation and attenuation of seasonal signals. A striking feature is that $\delta^{18}\text{O}_{sw}$ values at 60 cm depth are lowest in summer and highest in winter, the opposite (anti-phase) to that observed in rainfall. Soil–water residence times of up to circa 6 months in the upper 60 cm of soil, and a matrix flow, piston-type infiltration behaviour with mixing are inferred. Evaporative effects on recovered soil–water $\delta^{18}\text{O}$ are minimal at this wet temperate site, in contrast with published results from arid and semi-arid sites. A soil–water model is presented to estimate monthly $\delta^{18}\text{O}_{sw}$ as a function of air temperature and $\delta^{18}\text{O}_p$, incorporating effects such as variations in the amount of infiltrated water, changes in the ratio between evaporation and transpiration, mixing with antecedent soil moisture and small enrichments in ^{18}O linked to evaporation and summer moisture deficits. Our model reproduces the observed $\delta^{18}\text{O}_{sw}$ results, and produces $\delta^{18}\text{O}$ outputs in excellent agreement with $\delta^{18}\text{O}$ data for two monitored drip-water sites at La Garma cave that exhibit seasonal $\delta^{18}\text{O}$ variability. We conclude that simple evapotranspiration models that permit infiltration during months that have a positive hydrological balance only, tend to underestimate summer rainfall contributions. Overall, the study provides an improved framework for predicting $\delta^{18}\text{O}_{sw}$ trends at temperate sites such as La Garma that have a relatively thick soil cover, as well as for understanding seasonal ranges and trends in $\delta^{18}\text{O}$ in cave drip-sites.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Oxygen isotope ratios in precipitation ($\delta^{18}\text{O}_p$) correlate with key climate variables such as air temperature, precipitation amount and relative humidity on a range of spatial and temporal scales (Dansgaard, 1964; Merlivat and Jouzel, 1979; Rozanski et al., 1993). Such empirical relationships underpin palaeoclimate reconstructions based on $\delta^{18}\text{O}$ variations in speleothems (McDermott, 2004; Fairchild et al., 2006), pedogenic and lake carbonates (Cerling and Quade, 1993; Leng and Marshall, 2004), and tree rings (McCarroll and Loader, 2004; Xu et al., 2011). However, correct attribution of $\delta^{18}\text{O}$ variations to specific climate variables requires a detailed proxy- and site-specific understanding, because multiple factors influence the $\delta^{18}\text{O}_p$ signal and how it is ultimately recorded.

In the case of speleothems, this requires, *inter alia*, a good understanding of the dynamic and potentially complex mixing behaviour of infiltrating meteoric water in soils and the unsaturated zone of karst systems (Williams, 2008; Baker and Bradley, 2010; Bradley et al., 2010; Baker et al., 2012; Jex et al., 2013; Moerman et al., 2014; Genty et al., 2014).

Recently, two forward models that predict cave drip-water $\delta^{18}\text{O}$ based on $\delta^{18}\text{O}_p$ inputs and climate variables such as air temperature and precipitation amount have been published (Baker and Bradley, 2010; Wackerbarth et al., 2010). Forward modelling is preferable to simpler approaches that assume stationary relationships between speleothem O isotope ratios and $\delta^{18}\text{O}_p$ but it requires assumptions regarding potential isotope fractionation and water infiltration processes within the soil zone that are based on simple quantification of potential evapotranspiration that require validation, particularly in temperate regions. Much of the previous work on the $\delta^{18}\text{O}$ of soil–water ($\delta^{18}\text{O}_{sw}$) has focused on arid and semi-arid regions where evaporation causes ^{18}O

* Corresponding author. Tel.: +353 (0) 17162063.

E-mail address: laia.comasbru@ucd.ie (L. Comas-Bru).

enrichment as a result of diffusion of water to the atmosphere (Zimmermann et al., 1967; Barnes and Allison, 1984; Fontes et al., 1986; Shurbaji et al., 1995; Mathieu and Bariac, 1996; Hsieh et al., 1998; Newman et al., 1997; Gazis and Feng, 2004). In some semi-arid regions, these effects have been invoked to explain some of the observed $\delta^{18}\text{O}$ variability in cave drip-waters (Ayalon et al., 1998; Cuthbert et al., 2014). By contrast, comparatively little data are available for seasonal $\delta^{18}\text{O}_{\text{sw}}$ variability in temperate regions (Robertson and Gazis, 2006). The evolution of $\delta^{18}\text{O}_{\text{sw}}$ at temperate sites is likely to differ from that at arid and semi-arid sites because a positive soil–water balance may exist for much of the year and evaporative effects are consequently less important. On the other hand, unlike arid regions where pre-existing soil–water moisture is largely absent (e.g. Hsieh et al., 1998), temperate zone soils may retain a fraction of isotopically enriched soil–water during the dry season which can affect the isotopic evolution of soil–waters during the subsequent wet season.

The infiltration regime (e.g. slow matrix flow vs. rapid macro-pore flow) also exerts a control on $\delta^{18}\text{O}_{\text{sw}}$ variations with depth (Tooth and Fairchild, 2003). In some cases, non-synchronous variations in $\delta^{18}\text{O}_{\text{sw}}$ and $\delta^{18}\text{O}_{\text{p}}$ have been demonstrated (e.g. Gehrels et al., 1998; Tang and Feng, 2001; Gazis and Feng, 2004; Li et al., 2007), associated with slow matrix flow and piston-like behaviour in which more recently recharged water pushes older water deeper into the soil profile. In other cases, the oxygen isotopic composition of shallow soil–waters closely follows that of precipitation inputs, but individual strong precipitation events with low $\delta^{18}\text{O}_{\text{p}}$ have an immediate impact on $\delta^{18}\text{O}_{\text{sw}}$ to depths of 60 cm indicating 'by-pass', macro-pore flow behaviour (Brodersen et al., 2000). A related, but poorly understood issue is the extent to which mixing of waters within the soil zone, as distinct from within the unsaturated zone of the underlying bedrock, can partly homogenise seasonal or longer time-scale variability in $\delta^{18}\text{O}_{\text{p}}$ in the water that percolates into caves. An understanding of the processes causing this observed attenuation of the $\delta^{18}\text{O}_{\text{sw}}$ signal is important if speleothem time-series oxygen isotope data can be sampled and analysed at a finer temporal resolution than the timescale of homogenisation, or if the climate signal of interest has a strong seasonal expression (e.g. inter-annual variability in winter $\delta^{18}\text{O}_{\text{p}}$ associated with changes in the North Atlantic Oscillation; Baldini et al., 2008; Comas-Bru and McDermott, 2014).

In this study, oxygen isotope ratios have been measured in rain and soil–waters that were sampled monthly above La Garma cave in N. Spain (Fig. 1). To better understand the interplay between the various soil zone processes discussed above (evaporation, infiltration mechanisms and mixing), a simple soil–water model has been constructed to assess the extent to which the observed soil–water monthly variability can be estimated. Overall, this study provides improved insights into the temporal relationships between $\delta^{18}\text{O}_{\text{sw}}$ and $\delta^{18}\text{O}_{\text{p}}$ at different depths on seasonal timescales at a temperate site with a thick soil cover (>1 m).

2. Site description and methods

2.1. Description of the study site

La Garma cave in N. Spain (43.43°N; 3.67°W) is located in Monte de la Garma, a low hill (186 m of altitude) of approximately three hectares situated 5 km from the mouth of the River Miera in the Cantabrian village of Omoño (Ribamontán al Monte) on the eastern side of Santander Bay (Northern Spain). The cave is part of a complex system of karstic galleries developed in Lower Cretaceous (Aptian) biomicritic limestones overlain by a laterally continuous c.150 m thick umbrisol (Jackson, 2009). The Lower Gallery at c. 80 m above sea level, is overlain by approximately

85–90 m of limestone at the drip-water sampling points discussed below (Fig. 1). The cave has developed largely along a NE–SW trending fault (Baldini, 2007). Drip-water sites in the cave both on and away from the fault zone have been monitored in previous studies (Baldini, 2007; Jackson, 2009; Baldini et al., 2015) and data from these studies provide additional tests for the soil–water infiltration/recharge model developed here. The area above the cave in which soil–water samplers were placed is partly vegetated with trees and undergrowth. The umbric soil with a hummus-rich surface layer is typical of that found under forest cover in high rainfall regions of Western Europe (WRB, 2014). Soil thickness varies across Monte de la Garma (typically 60–150 cm).

2.2. Regional climate

Hourly air temperature and precipitation data for Santander Airport station (43.25°N, 3.49°W; 52 m.a.s.l.), located 12.2 km from the sampling site, was provided by the Spanish Meteorological Institute (AEMET). The mean annual air temperature is 14.67 °C, and the long-term annual precipitation is 1204 mm, with a monthly annual range of 3.84 °C and 309.62 mm (1997–2013), respectively. According to the Köppen–Geiger climate classification scheme (Kottek et al., 2006), the site is type "Cfb". This corresponds to regions with a warm temperate climate (coldest month is –3 to 18 °C), fully humid (no dry summer or dry winter), a warm summer (mean temperature of the warmest month <22 °C, and a minimum mean temperature of 10 °C in at least four months). Whereas mean monthly air temperatures during the sampling period closely follow the long term means, large deviations in rainfall amounts are observed for some months (Fig. 2). For example, the site experienced a wetter than average winter (December 2012 and January 2013), and some exceptional storms (>30 mm/day) occurred in October 2012, November 2012, March 2013, April 2013 and May 2013.

2.3. Sample collection and analysis

Rain and soil–water samples were collected at monthly intervals above La Garma cave from June 2012 to May 2013. For operational reasons, the rainfall and soil–water sampling points were located at a point on the surface that is approximately 150 m north of the main cave galleries (Fig. 1c). Rain water was collected in accordance with the Global Network of Isotopes in Precipitation protocols (IAEA/WMO, 2014). Soil–waters were collected using Standard 1900 ceramic-cup soil–water samplers from Soil moisture Equipment Corp. at 15 cm (S1), 30 cm (S2) and 60 cm (S3). Each soil–water sample represents the integrated moisture for the period between vacuum/collection dates. Due to operational problems and/or the occurrence of soil-moisture deficits, it was not possible to retrieve soil–water samples for all of the planned sampling intervals (Table S1). Oxygen isotopic analysis of the water samples were conducted at the Stable-Isotope Laboratory (SILLA) of the University of Birmingham using an Isoprime continuous flow Isotope-Ratio Mass Spectrometer (CF-IRMS). The samples were equilibrated at 23 °C with a 5% CO₂ headspace for 7 h before analysis by CF-IRMS (Bieroza et al., 2014). Analytical precision is estimated to be 0.04‰ for $\delta^{18}\text{O}$ and 0.48‰ for δD . The hydrogen and oxygen isotope ratios (D/H, $^{18}\text{O}/^{16}\text{O}$) are expressed as ‰ values relative to V-SMOW.

2.4. Soil–water model

Not all of the precipitation that falls on a soil is available for infiltration, and so a weighting coefficient, I_m , that accounts for the fraction of infiltrating water each month was applied to model the monthly $\delta^{18}\text{O}_{\text{sw}}$. The oxygen isotopic enrichment of the

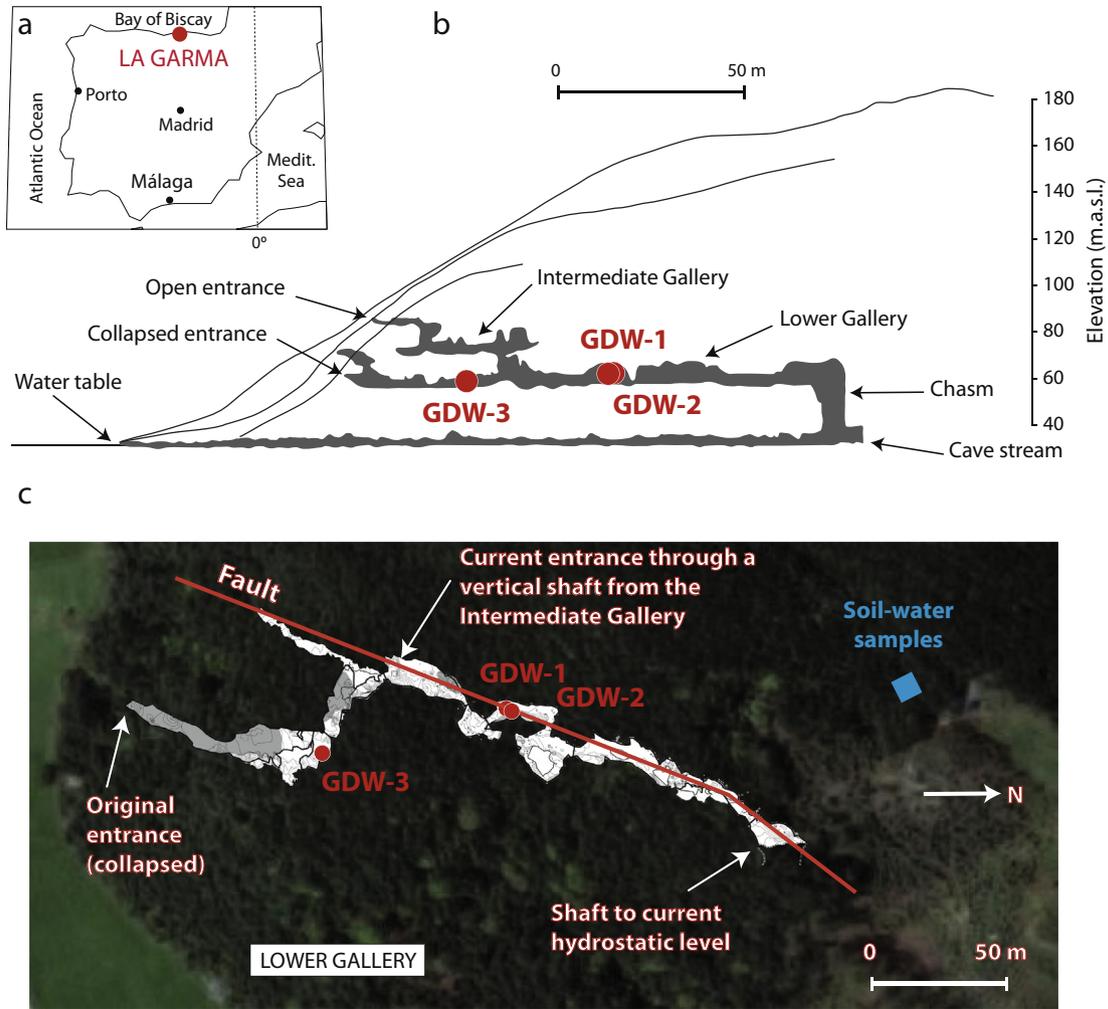


Fig. 1. (a) Location of La Garma cave (43°25'56"N; 3°40'08"W) within the Iberian Peninsula. (b) Cross-section of the cave showing the position of drip sites GDW-1, GDW-2 and GDW-3 relative to the cave galleries. (c) Plan view of the Lower Gallery, showing the soil-water and drip-site locations. Diagrams (b) and (c) have been modified after [Arias and Ontañón, 2013](#). Aerial view in panel (c) from Google® maps (2015).

soil-water by evaporation is described by a fractional distillation process under equilibrium conditions between water vapour and soil-water using a Rayleigh equation ([Rayleigh, 1896](#)). The isotope ratio of the infiltrating soil-water is given by [Hoefs \(1997\)](#):

$$\delta^{18}\text{O}_{\text{sw}} = \delta^{18}\text{O} \cdot I_m^{(\alpha-1) \cdot f_e} \quad (1)$$

where $\delta^{18}\text{O}$ is the isotopic composition of the initial water in the soil; $\delta^{18}\text{O}_{\text{sw}}$ is the isotopic composition when a fraction, I_m , remains; the fractionation factor α is given by [Majoube \(1971\)](#); f_e is the ratio between water lost by evaporation and transpiration.

The monthly weighting coefficient, I_m , was estimated using information about the monthly soil moisture budget as described below. The monthly potential loss of water due to direct evaporation and transpiration (PET) for the area above the site was estimated using a water-balance model ([Thornthwaite, 1948](#)) as implemented in the USGS Thornthwaite model ([McCabe and Markstrom, 2007](#)). This model uses the Hamon equation ([Hamon, 1961](#)) to estimate PET, and it assumes that none of the soil or plant surfaces is water-limited and that the extent to which PET occurs depends mainly on air temperature ([Mather, 1978](#); [Thornthwaite, 1948](#)):

$$\text{PET}_m = 13.97 \cdot d \cdot D^2 \cdot W_t \quad (2)$$

where PET_m is monthly potential evapotranspiration in mm, d is the number of days in a month, D is the mean monthly hours of daylight in units of 12 h, and, W_t is a saturated water vapour density term, in grams per cubic meter, calculated by:

$$W_t = (4.95 \cdot e^{(0.062 \cdot T)}) / 100 \quad (3)$$

where T is the mean monthly temperature in degrees Celsius ([Hamon, 1961](#)). Since water loss does not always proceed at the potential rate (PET_m) because of water supply limitations, the actual evapotranspiration (AET_m) is estimated from PET_m , monthly precipitation amount (P_m), soil moisture storage (ST_m) and soil moisture storage withdrawal (STW_m) using the Thornthwaite model ([McCabe and Markstrom, 2007](#)). In this methodology, the amount of moisture that can be removed from the soil (STW_m) depends on the moisture remaining in the soil from the previous month ($\text{ST}_{(m-1)}$), the soil moisture capacity (STC) and the difference between P_m and PET_m (Thornthwaite model; [McCabe and Markstrom, 2007](#)):

$$\text{STW}_m = \text{ST}_{(m-1)} - [\text{abs}(P_m - \text{PET}_m) \cdot (\text{ST}_{(m-1)} / \text{STC})] \quad (4)$$

The Thornthwaite method is known to overestimate PET_m in humid areas ([Schid, 1975](#); [Chen et al., 2005](#); [Trajkovic and Kolakovic, 2009](#)). The alternative Penman–Monteith methodology recommended by the Food and Agriculture Organization of the

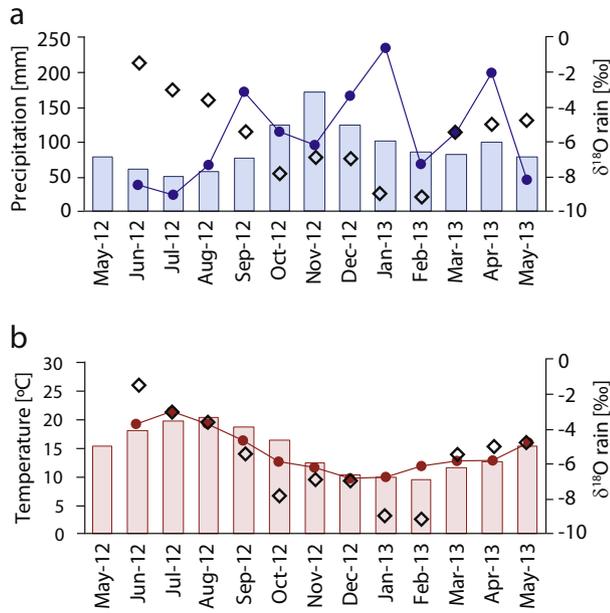


Fig. 2. Time series of precipitation, air temperature and rainfall $\delta^{18}O$ during the sampling periods (data symbols) compared with their long term means (vertical bars). (a) Precipitation amount in blue (left y-axis) and $\delta^{18}O_p$ as open black diamonds (right y-axis). (b) Air temperature in red (left y-axis) and $\delta^{18}O_p$ as open black diamonds (right y-axis). Precipitation and air temperature data were provided by the Spanish Meteorological Institute (AEMET) for the Santander Airport station. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

United Nations (Allen et al., 1998) yields PET_m values closer to measured values, but in the absence of relative humidity and wind speed data required for the Penman–Monteith methodology, the Thornthwaite method was used.

Calculations were done on a monthly basis, beginning with the soil moisture budget for January, assuming that the previous December had no soil moisture deficit. For those months in which water is supplied by frequent precipitation events, AET_m is assumed to equal PET_m . On the other hand, AET_m differs from PET when the soil moisture deficit falls below a critical threshold where vegetation has difficulty transpiring.

If the amount of infiltrated water ($ST_m = P_m - AET_m$), plus the soil moisture remaining from the previous month exceeds the STC , this surplus water is considered to be available for infiltration, and only the STC component is carried over in the computations for the following month. On the other hand, if the amount of infiltrated water ($ST_m = P_m - AET_m$), plus the soil moisture available from the previous month is less than the STC , no infiltration occurs, and the remaining moisture is allowed to mix with the infiltrated water of the following month. If a moisture deficit persists for several months, moisture stored initially in the STC decreases gradually until for example a precipitation event in autumn replenishes it, and eventually, a water surplus is re-established to allow infiltration to begin again. Otherwise, the monthly weighting coefficient could reach zero if a prolonged drought lasted for several months.

Consequently, if $ST_m + ST_{(m-1)} > STC$, infiltration occurs and

$$I_m = (ST_m + STC) / (P_m + STC) \quad (5)$$

where STC is the contribution of the antecedent moisture (i.e. the moisture that did not infiltrate and is carried over from the previous month). On the other hand, no infiltration occurs if $ST_m + ST_{(m-1)} < STC$, and in that case

$$I_m = (ST_m + ST_{(m-1)}) / (P_m + ST_{(m-1)}) \quad (6)$$

In the soil–water model, moisture of different isotopic compositions (i.e. one month, ST_m , and the preceding month, $ST_{(m-1)}$) is thus mixed in different proportions, depending on the balance between antecedent soil moisture and recharged water for each month. Isotopic mixing is conservative and a simple mass-balance model is used to calculate the $\delta^{18}O$ of the infiltrated water. To account for different degrees of $\delta^{18}O_{sw}$ homogenisation at depth, the model $\delta^{18}O_{sw}$ output described above is allowed to mix with antecedent water for several months at each depth (15, 30 and 60 cm). Mixing periods of 2–5 months have been tested (Supplementary Fig. S1). The monthly weighting factors used to compute the mixing are based on the relative contributions of each month to the total moisture according to the soil–water budget described above (Table 1).

Although soil macropore or preferential bypass flows have been reported in some studies at depths of up to 50 cm, following intense rainfall events (Tang and Feng, 2001; Gaziz and Feng, 2004), our monthly resolved soil–water $\delta^{18}O$ data do not require such flows to successfully estimate the observed $\delta^{18}O_{sw}$ data. Bypass infiltration processes within the unsaturated zone are also featured in full karst hydrogeological models designed to account for cave drip-water $\delta^{18}O$ variability (e.g. Baker and Bradley, 2010). However, here we emphasise that our model is intended only to explore soil–water $\delta^{18}O$ variability in temperate zone soils at depths of up to 60 cm, and therefore, does not include processes in the unsaturated zone of the bedrock. Comparison of modelled and observed $\delta^{18}O_{sw}$ data at 60 cm with seasonal drip-water $\delta^{18}O$ variability (see Section 4) is made on the basis that the monitored drip-sites GDW-1 and GDW-2 are located along a fault zone that provides a conduit for rapid transit through the bedrock (Fig. 1; Baldini et al., 2015). In effect, our model describes a simple piston-flow system, dominated by matrix flow in which new precipitation pushes existing soil moisture deeper into the soil profile, with variable degrees of mixing with pre-existing soil moisture, a fraction of which may be enriched in ^{18}O as a consequence of evaporation.

A sensitivity test using different values of f_e was employed to assess the model sensitivity to this parameter. For reference, the study by Wackerbarth et al. (2010) in central Germany with the same climate classification as the La Garma site ('Cfb'; Kottke et al., 2006) used $f_e = 0.2$ for summer (April–September) and $f_e = 0.5$ for winter (October–March). A sensitivity analysis of various f_e values (Table 2) demonstrates that the modelled $\delta^{18}O_{sw}$ output varies only within analytical uncertainty. Thus, the f_e values from Wackerbarth et al. (2010) were used in the model. In the absence of soil-moisture capacity (STC) measurement, a value of 150 mm was used for the site. Sensitivity tests confirmed that while the model output is sensitive to the STC value it is not unduly influenced by this parameter. For example the model produced a shift to higher $\delta^{18}O_{sw}$ of 0.14‰ in the mixed 60 cm water when a STC value of 200 mm was used instead of 150 mm.

3. Results

3.1. Rain and soil–water $\delta^{18}O$

Monthly rainfall $\delta^{18}O$ values at the La Garma site range from -9.15‰ to -1.49‰ (VSMOW), with highest values occurring during the summer months (Fig. 3). The mean annual weighted $\delta^{18}O_p$ of the rainfall samples is -6.39‰ . Significant correlations are observed between $\delta^{18}O_p$ and both mean air temperature ($p = 0.80$; significant at 99%) and rainfall amount ($\rho = -0.60$; significant at 95%). These correlations are consistent with longer $\delta^{18}O_p$ series and meteorological data from the Santander Airport GNIP station (IAEA/WMO, 2014), which yield ρ values of 0.56 and -0.56 (significant at 99%) for air temperature and rainfall amount,

Table 1
Monthly $\delta^{18}\text{O}_p$ contributions (x -axis) to modelled monthly $\delta^{18}\text{O}_{sw}$ (y -axis), in percentages.

%	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
JAN	8.7							1.2	6.2	33.1	33.6	18.1
FEB	23.1	9.2							1.5	14.3	27.6	26.1
MAR	32.6	17.6	1.5							4.7	17.9	26.1
APR	33.4	31.2	7.3	4.3							6.5	16.6
MAY	17.7	31.0	17.9	19.5	9.4							4.2
JUN	8.0	24.0	21.1	29.0	16.9	0.6						
JUL		12.3	19.5	36.3	29.5	2.1	0.3					
AUG			9.5	37.3	42.9	5.6	3.7	1.0				
SEP				10.7	30.0	22.5	15.8	11.0	10.8			
OCT					4.3	8.1	11.1	12.6	24.2	39.8		
NOV						2.6	4.9	8.3	20.5	49.0	16.3	
DEC							1.7	4.2	14.8	48.1	25.8	5.9

Table 2
Output of the soil–water model at 15 cm using different values of the ratio between water lost by evaporation and transpiration (f_e). (*) Same values as used by Wackerbarth et al. (2010).

f_e (Oct–Mar)	f_e (Apr–Sep)	Model output at S1	Comments
0.4	0.1	–6.09	Increased seasonality
0.5	0.3	–6.09	Values used in this study (*)
0.9	0.6	–6.09	Decreased seasonality
0.9	0.3	–6.09	“
0.2	0.5	–6.09	Inversed seasonality
0.1	0.1	–6.09	No seasonality
0.3	0.3	–6.09	“
0.5	0.5	–6.09	“
1	1	–6.09	No uptake by plants
0	0	–6.10	No evaporation

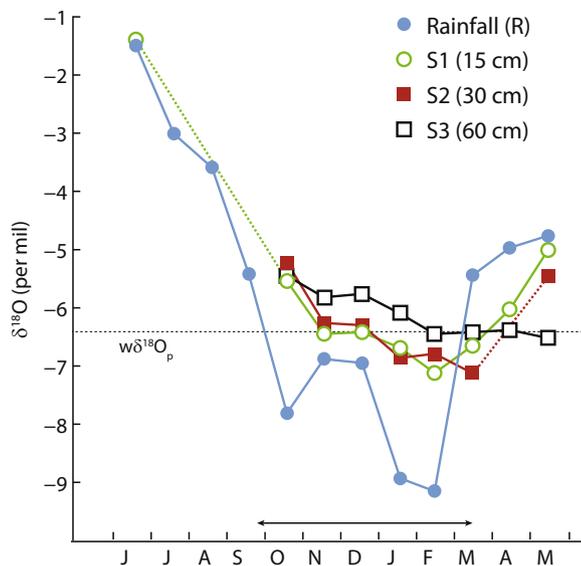


Fig. 3. Time series of the $\delta^{18}\text{O}_p$ and $\delta^{18}\text{O}_{sw}$ samples. Double arrowed horizontal line at the bottom of the panel indicates winter months for easier visualisation. Dashed horizontal line is the mean annual weighted $\delta^{18}\text{O}_p$ ($w\delta^{18}\text{O} = -6.39\text{‰}$).

respectively, for the period February 2000 to November 2010. The rainfall samples are offset slightly to lower $\delta^{18}\text{O}$ compared with most of the GNIP ($n = 130$) rainfall samples on which the Local Meteoric Water Line (LMWL) is based (Fig. 4a). A similar offset with respect to the LMWL is observed in the soil–water samples (Fig. 4b). None of the soil–water data plot below the LMWL.

Over the study period, the $\delta^{18}\text{O}_{sw}$ data at 15 cm and 30 cm follow the rainfall $\delta^{18}\text{O}$ trends although they are lagged by 1–2

months, and exhibit a much reduced range (5.7‰ at 15 cm, and 1.9‰ at 30 cm depth; Fig. 3). $\delta^{18}\text{O}_{sw}$ data for the deeper (60 cm) samples are even more strongly lagged (~ 3 months) and the range is more strongly attenuated (1.08‰) compared with that of the rainfall (7.66‰). At this soil depth, the range in $\delta^{18}\text{O}_{sw}$ is only about 14% of that of $\delta^{18}\text{O}_p$ (Figs. 3 and 5a).

Depth profiles (Fig. 5a) show a tendency for higher $\delta^{18}\text{O}_{sw}$ values in the shallow samples (15 cm) compared with the deeper samples (30 and 60 cm) during the summer. The opposite is observed during winter, when the lowest $\delta^{18}\text{O}_{sw}$ values occur at shallow levels, and the highest values are found at depth in the soil profile. An important result in the context of water that is potentially available for aquifer recharge is that for most months of the year, $\delta^{18}\text{O}_{sw}$ values at 60 cm depth were appreciably higher than the mean annual weighted $\delta^{18}\text{O}$ of the rainfall ($w\delta^{18}\text{O}_p = -6.39\text{‰}$; dashed lines in Figs. 3 and 5a), with highest values retrieved during some of the winter months (November to January), a time when $\delta^{18}\text{O}_p$ is characterised by low values. Because we do not have information about temporal variations in the soil moisture content at 60 cm depth, it is not possible to calculate the weighted mean annual $\delta^{18}\text{O}$ value for the soil–waters. On the basis of a Thornthwaite water balance model (McCabe and Markstrom, 2007, Fig. 5b), soil moisture deficits occur between May and August. No soil–water samples could be retrieved for August and September at any depth (Supplementary Table 1) despite the occurrence of some rainfall events >10 mm/day during this period (Fig. 2a).

3.2. Soil–water model results

Modelled monthly $\delta^{18}\text{O}_{sw}$ values for the shallow horizon (S1: 15 cm) fall within the observed range except for some months (Fig. 6a). For instance, the slightly higher $\delta^{18}\text{O}$ value of the July S1 sample compared with its rainfall counterpart (Supplementary Table S1 and Fig. 5a) is not reproduced in our model, and the modelled output at S1 is lower than observations (Fig. 6a and b). In contrast, excellent agreement is observed between the model output and observations at greater depths (S2: 30 and S3: 60 cm; Fig. 6a, c and d), where only the output of the model at 30 cm is only marginally lower than observed (Fig. 6c).

Consistent with the observations, modelled $\delta^{18}\text{O}_{sw}$ values at depths (30 and 60 cm) for the winter months are higher than the observed mean annual weighted $\delta^{18}\text{O}$ of the rainfall, while the opposite occurs in the model output from summer months (Fig. 6a). Mixing periods of 2, 3 and 3 months are required at 15, 30 and 60 cm respectively, to reproduce the observed monthly $\delta^{18}\text{O}_{sw}$ patterns. This indicates that homogenisation of the monthly $\delta^{18}\text{O}_p$ signal at 60 cm depth occurs over about 6 months (Fig. 6b–d and Supplementary Fig. S4). Table 1 illustrates the monthly contribution of $\delta^{18}\text{O}_p$ to $\delta^{18}\text{O}_{sw}$ at 60 cm. Owing to the

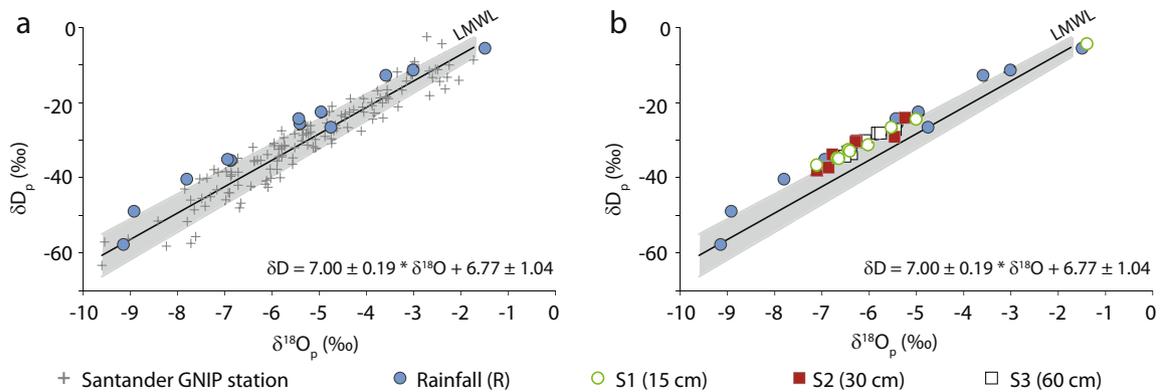


Fig. 4. Isotopic compositions of rainfall and soil–water samples. (a) Rainfall samples collected in this study and all the monthly samples available from the GNIP station at Santander Airport (43.48°N, 3.8°W; IAEA/WMO, 2014; grey crosses). The LMWL was derived using the 130 unweighted samples available from the GNIP station; (b) Rain and soil–water samples collected in this study compared to the LMWL. The shaded areas show the 95% confidence intervals of the LMWL the equation of which is shown in each panel.

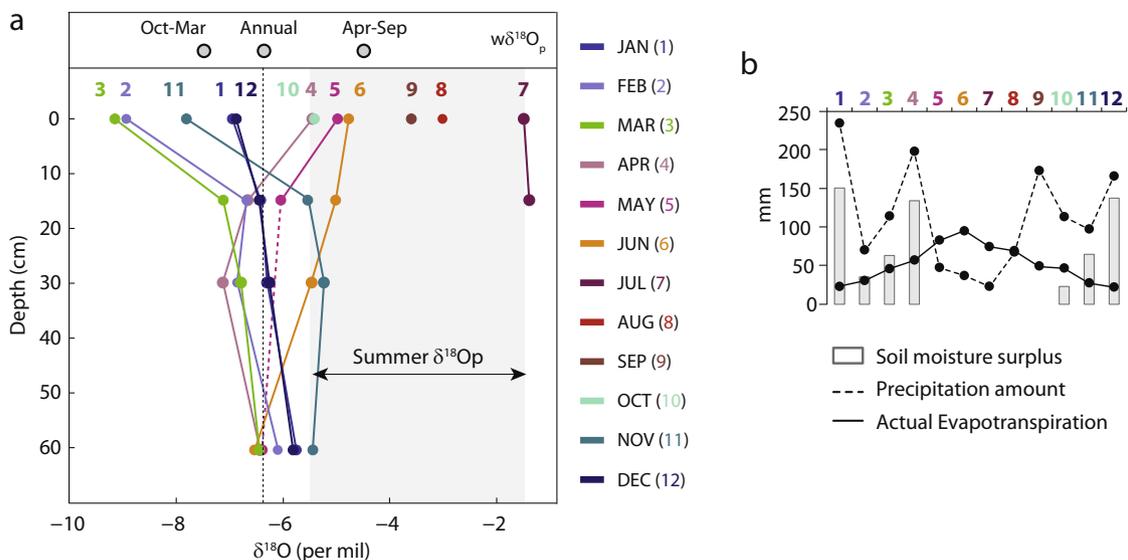


Fig. 5. Depth profiles of measured $\delta^{18}O_{sw}$ and water balance plots. (a) $\delta^{18}O_p$ (at 0 cm depth) and $\delta^{18}O_{sw}$ depth profiles (S1: 15 cm, S2: 30 cm and S3: 60 cm). Weighted mean winter, annual and summer $\delta^{18}O_p$, calculated with the rainfall data presented in this study, are indicated at the top of the panel. Grey area in (a) indicates the range of summer (April–September) $\delta^{18}O_p$. (b) Water balance plot calculated with the mean air temperature and precipitation amount for the sampling intervals using a Thornthwaite Monthly Water Balance Model (McCabe et al., 2007).

mixing factors implied by the soil–water model, the October–March (April–September) contribution to the annual $\delta^{18}O_{sw}$ at 60 cm is 61.4% (38.6%). Approximately 21% of the October–March $\delta^{18}O_{sw}$ signal at 60 cm reflects residual inputs from summer rainfall.

4. Discussion

Our results differ from the majority of studies that were completed at arid and low rainfall sites (Barnes and Allison, 1984; Fontes et al., 1986; Shurbaji et al., 1995; Mathieu and Bariac, 1996; Hsieh et al., 1998; Newman et al., 1997; Gazis and Feng, 2004), because unlike the temperate zone site studied here, these are characterised by little or no antecedent moisture at the end of the dry season. The steep slope defined by our soil–water data on a D/H vs. $\delta^{18}O$ diagram (Fig. 4) and the absence of significant departures from the LMWL (Fig. 4) provides little evidence for evaporative isotopic enrichment of soil–waters prior to recharge at this temperate site, in contrast with results from drier sites

(Hsieh et al., 1998; Robertson and Gazis, 2006). This supports results from Bradley et al. (2010), where evaporation is found to be negligible at relatively temperate and wet sites. However, the presence of vegetation could in principle induce additional isotopic enrichment in soil–waters if partly evaporated throughfall water is an important component (Brodersen et al., 2000). We cannot rule out the possibility that the absence of recoverable water in a few of the summer months may have resulted from evapotranspiration or as a result of insufficient vacuum in the samplers to extract soil water.

Two important results arise from our study. First, to account for the observed $\delta^{18}O_{sw}$ data, some infiltration of summer rains into the deeper (circa 60 cm) soil profile must occur, despite indications from simple ‘Thornthwaite-type’ evapotranspiration models that soil moisture deficits occur in summer (Fig. 5b). This result is consistent with recent observations of cave drip-water $\delta^{18}O$ at two temperate-zone cave sites in SE and SW France (Genty et al., 2014) and it highlights the limitations of simple ‘Thornthwaite-type’ models for forward modelling of soil–water moisture $\delta^{18}O$ at temperate sites. The study by Genty et al. (2014) demonstrated

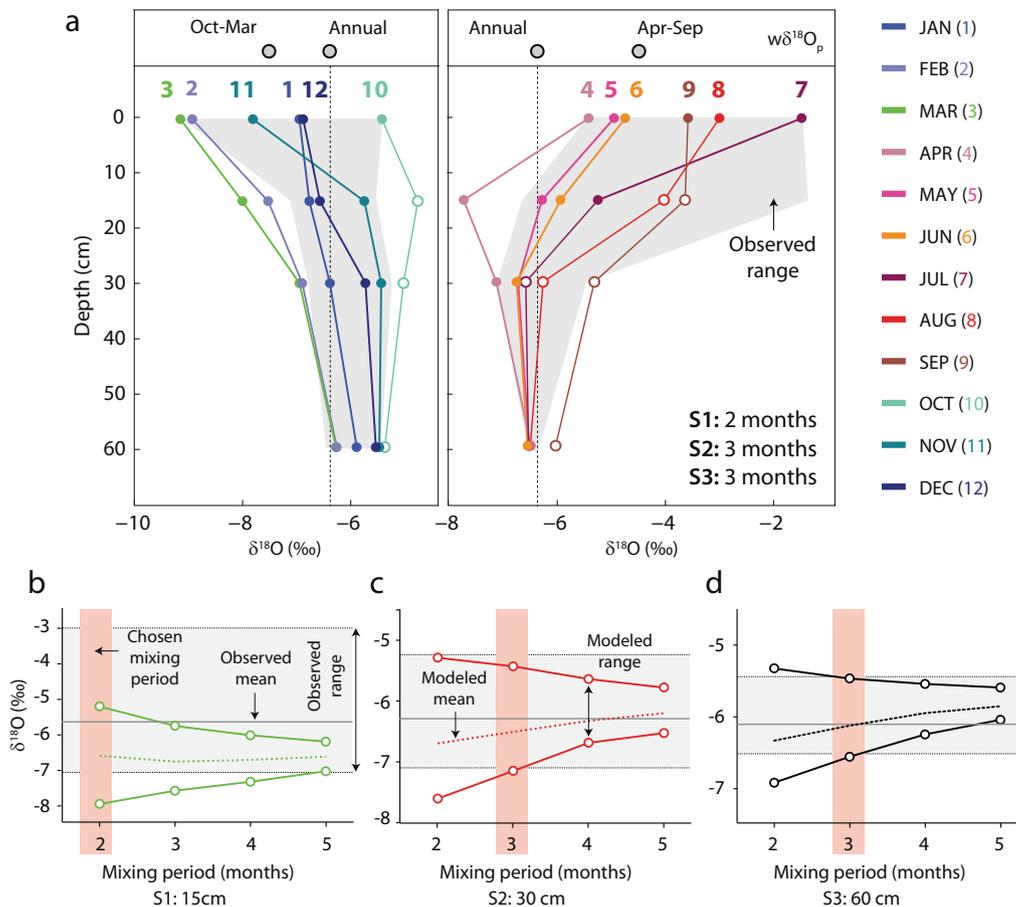


Fig. 6. Results of the soil–water model using $\text{STC} = 150 \text{ mm}$, $f_e = 0.2$ for summer (April–September) and $f_e = 0.5$ during winter (October–March). See Section 2.4 for further details. (a) Depth profiles of modelled monthly $\delta^{18}\text{O}_{\text{sw}}$. Grey shaded area in (a) is the range of measured monthly $\delta^{18}\text{O}_p$ and $\delta^{18}\text{O}_{\text{sw}}$ (as in Fig. 5). Open symbols in (a) represent depths/months when samples could not be retrieved and thus, are not included in the grey shaded area. Mean winter, annual and summer $\delta^{18}\text{O}_p$, calculated with the rainfall data presented in this study, are indicated at the top of the panel. (b) Modelled $\delta^{18}\text{O}_{\text{sw}}$ range and mean at 15 cm (S1) compared to observations for a number of mixing months (x-axis); (c) same as (b) for 30 cm depth (S2); (d) same as (b and c) for 60 cm depth (S3). The applied mixing periods (x-axis in b–d) are calculated as illustrated in Supplementary Fig. 1. For example, the mixing applied in S2 (c) uses as input the results obtained with the mixing period chosen for S1 (b). The same is true for S3 (d) and the results from S2 (c). $\delta^{18}\text{O}_{\text{sw}}$ ranges and means in (b), (c) and (d) are calculated for the same number of months as available observed data (i.e. open symbols in (a) are omitted in the calculations).

that modelled drip-water values would be much lower than the weighted mean $\delta^{18}\text{O}_p$ value if only those months with a modelled positive water balance had contributed to the cave drips. A similar requirement for contributions to deep soil–waters by summer precipitation, despite a modelled moisture deficit, was observed in the study of Gehrels et al. (1998) in temperate central Netherlands. Overall, this appears to be a robust observation at temperate zone sites. In part this discrepancy may arise because, as introduced earlier, ‘Thornthwaite type’ models overestimate potential evapotranspiration in relatively humid climates. For example, in accordance with the ‘Thornthwaite-based’ estimations of soil moisture deficits (Fig. 5b), no soil–waters could be retrieved for August and September at any depth (Supplementary Table 1). However, the $\delta^{18}\text{O}$ depth profile for November can only be explained (and modelled) if some water from late-summer rains had remained in the soil (Figs. 5a and 6a). A combination of effects could explain this observation. First, the effect of evapotranspiration on effective recharge may be overestimated as a result of using monthly data to calculate these ‘Thornthwaite type’ models. In this case, intense or long-duration rainfall events that could be capable of generating recharge do not appear to be effective when averaged over a month. Second, during September and October the soil was likely to have been too dry to efficiently transmit water into the sampler, despite some rain events taking place. Under these conditions

water would be held too tightly by surface tension with the soil to be extracted by the samplers.

Use of a water infiltration model in which only hydrologically effective precipitation is considered (no infiltration in months with $\text{AET}_m > P_m$; e.g. as implemented in the model of Wackerbarth et al., 2010) produced modelled annual mean $\delta^{18}\text{O}_{\text{sw}}$ values lower than the observed ranges, particularly in winter (Supplementary Fig. S2a–c). It appears that simple ‘Thornthwaite type’ schemes that permit rainfall inputs during months with a positive hydrological balance only, produce winter-biased results because no contributions from pre-existing soil moisture is considered when the first autumn rains occur following the summer soil moisture deficit. By contrast, our model permits the summer months to have an influence on the isotopic composition of the infiltrated water through its soil water storage component (STC), and it thus produces higher mean $\delta^{18}\text{O}_{\text{sw}}$ values that are in better agreement with observed soil–water values (Fig. 6a–c).

A second robust result is that both the measured and the model $\delta^{18}\text{O}$ values exhibit strong homogenisation of the $\delta^{18}\text{O}_p$ signal at depths of 60 cm (Figs. 5 and 6). As a result, the range in $\delta^{18}\text{O}_{\text{sw}}$ at 60 cm depth is only 14% that of $\delta^{18}\text{O}_p$. Whilst this study does not aim to provide a hydrogeological karst model to estimate cave-drip water $\delta^{18}\text{O}$ values, we note that a comparable degree of attenuation has been observed in $\delta^{18}\text{O}$ values from monitored cave

seepage waters at two drip-sites within La Garma cave between September 2004 and October 2005 (GDW-1 and GDW-2; Baldini et al., 2015). In these drip-sites, located along a fault zone that facilitates rapid flow (Baldini et al., 2015; Fig. 1c), the range in monthly drip-water $\delta^{18}\text{O}$ is only 16% that of $\delta^{18}\text{O}_p$. Demonstration that a large degree of oxygen isotopic homogenisation can occur within the upper 1 m of the soil zone has implications for how the soil compartments of hydrogeological forward models are designed to generate synthetic drip-water $\delta^{18}\text{O}$ time-series (e.g. Baker and Bradley, 2010). In this regard, we note that the strong attenuation of seasonal $\delta^{18}\text{O}_p$ signals observed here is relevant for karst sites that are overlain by relatively thick soils or glacial tills, but is unlikely to be relevant for karst that is overlain by thin, poorly developed soils.

Despite the observed large degree of attenuation of the original $\delta^{18}\text{O}_p$ signal at a depth of 60 cm, it is clear that seasonal changes of $\delta^{18}\text{O}_{sw}$ are ultimately driven by the seasonal $\delta^{18}\text{O}_p$ variability. During the sampling period, summer $\delta^{18}\text{O}_p$ values were higher than winter values by 2.97‰, but our soil–water data show the opposite trend at deeper soil horizons, with $\delta^{18}\text{O}_{sw}$ values being lower during summer (by 0.52‰; Fig. 5a). This anti-phase behaviour and substantial attenuation of the $\delta^{18}\text{O}_{sw}$ signal relative to $\delta^{18}\text{O}_p$ indicates an average soil–water infiltration time of about 6 months, consistent with the mixing factors required by our model (Supplementary Fig. S1), and suggests a predominantly matrix flow, piston-type behaviour in the soil zone at this site. Similar observations were reported in drip-water $\delta^{18}\text{O}$ data from La Garma cave, where the mean winter (DJF) $\delta^{18}\text{O}$ values were unexpectedly higher than the summer (JJA) means by 0.50‰ and 0.32‰ at the GDW-1 and GDW-2 drip-sites, respectively (Baldini et al., 2015). Baldini et al. (2015) estimated the drip-water residence time to be of 7.5 months for the GDW-1 site, suggesting that the water may experience a transit time of <2 months between the deepest soil horizon described in our model/observations (60 cm) and the monitored drip-sites GDW-1 and GDW-2. This is consistent with the previous classification of these drip-sites as ‘seasonal drips’ (Smart and Friederich, 1986) on the basis of their rate of discharge and coefficient of variation (Jackson, 2009). In this type of drip-site, drip-rate and discharge is determined to a larger extent by variations in annual rainfall and evaporation than by an aquifer reservoir, explaining their fast, ‘flashy’ nature (Jackson, 2009). Palaeoclimate studies using $\delta^{18}\text{O}$ in speleothems require an understanding of how different factors affect the relationship between $\delta^{18}\text{O}$ values of contemporaneous rainwater and drip-water. In particular, our results show that by only considering how the $\delta^{18}\text{O}$ of infiltrated water is modified in the upper 60 cm of the soil, we are able to better constrain the causes of drip-water, and thus speleothem, $\delta^{18}\text{O}$ seasonal variability at least for the GDW-1 and GDW-2 drip-sites located along the fault zone at La Garma cave. It is important to note, however, that at other locations in the cave, greater attenuation of the seasonal $\delta^{18}\text{O}_p$ signals and mixing occurring over multiple years within the unsaturated zone of the karst is likely, at least at slow drip-sites such as GDW-3, located off the fault zone (Fig. 1c). This site exhibits a ‘dual porosity’ aquifer system with elements of rapid response (e.g. fracture filling giving rise to increased hydraulic level) and a base-flow corresponding to a longer-term storage component in the aquifer as evidenced by drip-rate measurements (Supplementary Fig. S3). In contrast with the GDW-1 and GDW-2 drip-sites, this slow-dripping seepage flow site displays almost constant $\delta^{18}\text{O}$ values with little or no preservation of the seasonal $\delta^{18}\text{O}_p$ signal (Baldini, 2007).

5. Conclusions

A new monthly resolved time-series dataset of soil–water $\delta^{18}\text{O}$ for three depths (15, 30 and 60 cm), coupled with contemporaneous $\delta^{18}\text{O}$ measurements on rainfall, provides new insights into

the processes of rainwater infiltration and mixing in a thick umbricol developed on karstified Cretaceous limestone in a partly forested temperate region in N. Spain. The study provides two results that are important for studies that require better constraints on the seasonal effects on infiltration of rainfall as well, as the timescales of mixing in the upper 0.6 m of a thick temperate zone soil. First, the observed temporal variations in soil–water $\delta^{18}\text{O}$ require that some stored summer rainfall must be included in the soil–water budget, even for months in which a moisture deficit is predicted by simple evapotranspiration models. The latter is consistent with results from a recent study of temporal variability in cave drip-water $\delta^{18}\text{O}$ at two French cave sites (Genty et al., 2014). A simple soil–water model driven by piston-flow, but permitting mixing between newly infiltrated and antecedent moisture closely reproduces the observed $\delta^{18}\text{O}_{sw}$ at depth in the soil. The model is quite insensitive to the balance between evaporation and transpiration, indicating that evaporation is negligible at this temperate zone site, in accordance with our D/H vs. $\delta^{18}\text{O}$ results, and with inferences by Bradley et al. (2010).

Second, seasonal scale $\delta^{18}\text{O}_p$ variability is largely homogenised and attenuated in soil–water samples collected at 60 cm depth, a feature that is also captured by our soil–water model. The muted seasonal range in $\delta^{18}\text{O}_{sw}$ (14% of $\delta^{18}\text{O}_p$) above La Garma cave is similar to that observed at two monitored drip-sites that are located along a fault zone that provides a conduit for rapid flow (Baldini et al., 2015). As a result of a c. 6 month mixing time, $\delta^{18}\text{O}_{sw}$ values at 60 cm depth show the opposite seasonal trends compared with $\delta^{18}\text{O}_p$. Overall, this work presents an improved framework for predicting soil–water $\delta^{18}\text{O}$ trends in temperate sites that have a relatively thick soil cover, as well as for understanding seasonal trends observed in $\delta^{18}\text{O}$ of soil waters that are available to feed drip-sites within La Garma cave.

Acknowledgements

This work was funded by Science Foundation Ireland through its ‘Research Frontiers Programme’ (10/RFP/GEO2747). We would like to thank Patricia Fernández Sánchez and Prof. Pablo Arias Cabal (University of Santander, Spain) for carefully collecting the samples presented here. The helpful technical advice from Mr. Michael Murphy (UCD School of Earth Sciences) is greatly appreciated. The authors are grateful to the journal editor, Prof. Peter K. Kitandis and two anonymous reviewers for their insightful comments and advice that greatly improved the manuscript.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhydrol.2015.09.053>.

References

- Allen, R.G., Pereira, L.S., Raes, D., Smith, M., 1998. Crop evapotranspiration Guidelines for computing crop water requirements. FAO Irrigation and Drainage. Paper 56. Rome: FAO – Food and Agriculture Organization of the United Nations.
- Arias, P., Ontañón, R., 2013. Pleistocene foragers on the Iberian Peninsula: Their culture and environment. Cantabrian portable art in its context: an approach to the study of the Paleolithic graphic expression in northern Spain. Festschrift in honour of Gerd-Christian Weniger for his sixtieth birthday, Mettmann: Neanderthal Museum, pp. 261–281.
- Ayalon, A., Bar-Matthews, M., Sass, E., 1998. Rainfall-recharge relationships within a karstic terrain in the Eastern Mediterranean semi-arid region, Israel: $\delta^{18}\text{O}$ and δD characteristics. J. Hydrol. 207, 18–31. [http://dx.doi.org/10.1016/S0022-1694\(98\)00119-X](http://dx.doi.org/10.1016/S0022-1694(98)00119-X).
- Baldini, L.M., 2007. An investigation of the controls on the stable isotope signature of meteoric precipitation, cave seepage water, and Holocene stalagmites in

- Europe Ph. D. thesis. UCD School of Geological Sciences, University College Dublin, Ireland, p. 338.
- Baldini, L.M., McDermott, F., Foley, A.M., 2008. Spatial variability in the European winter precipitation $\delta^{18}\text{O}$ -NAO relationship: Implications for reconstructing NAO-mode climate variability in the Holocene. *Geophys. Res. Lett.* 35, L04709. <http://dx.doi.org/10.1029/2007GL032027>.
- Baldini, L.M., McDermott, F., Baldini, J.U., Arias, P., Cueto, M., Fairchild, I.J., Hodmann, D.L., Matthey, D.P., Müller, W., Nita, D.C., Ontañón, R., García-Moncó, C., Richards, D.A., 2015. Regional temperature, atmospheric circulation, and sea-ice variability within the Younger Dryas Event constrained using a speleothem from northern Iberia. *Earth Planet. Sci. Lett.* 419, 101–110. <http://dx.doi.org/10.1016/j.epsl.2015.03.015>.
- Baker, A., Bradley, C., 2010. Modern stalagmite $\delta^{18}\text{O}$: instrumental calibration and forward modelling. *Glob. Planet. Change.* 71, 201–206. <http://dx.doi.org/10.1016/j.gloplacha.2009.05.002>.
- Baker, A., Bradley, C., Phipps, S.J., Fischer, M., Fairchild, I.J., Fuller, L., Spötl, C., Azcurra, C., 2012. Millennial-length forward models and pseudoproxies of stalagmite $\delta^{18}\text{O}$: an example from NW Scotland. *Clim. Past* 8, 1153–1167. <http://dx.doi.org/10.5194/cp-8-1153-2012>.
- Barnes, C.J., Allison, G.B., 1984. The distribution of deuterium and ^{18}O in dry soils: 3. Theory for non-isothermal water movement. *J. Hydrol.* 74 (1–2), 119–135. [http://dx.doi.org/10.1016/0022-1694\(84\)90144-6](http://dx.doi.org/10.1016/0022-1694(84)90144-6).
- Bierzoza, M., Baker, A., Bridgeman, J., Boomer, I., 2014. Stable isotopic composition of raw and treated water. *Water Manage.* 167, 414–429. <http://dx.doi.org/10.1680/wama.13.00065>.
- Bradley, C., Baker, A., Jex, C.N., Leng, M.J., 2010. Hydrological uncertainties in the modelling of cave drip-water $\delta^{18}\text{O}$ and the implications for stalagmite palaeoclimate reconstructions. *Quat. Sci. Rev.* 29 (17–18), 2201–2214. <http://dx.doi.org/10.1016/j.quascirev.2010.05.017>.
- Brodersen, C., Pohl, S., Lindenlaub, M., Leibundgut, C., Wilpert, K.v., 2000. Influence of vegetation structure on isotope content of throughfall and soil-water. *Hydrol. Process.* 14, 1439–1448. [http://dx.doi.org/10.1002/1099-1085\(20000615\)14:8<1439::AID-HYP985>3.0.CO;2-3](http://dx.doi.org/10.1002/1099-1085(20000615)14:8<1439::AID-HYP985>3.0.CO;2-3).
- Cerling, T.E., Quade, J., 1993. Stable carbon and oxygen isotopes in soil carbonates. In: Swart, P.K., Lohmann, K.C., McKenzie, J., Savin, S. (Eds.), *Climate Change in Continental Isotopic Records*. Geophysical Monograph, vol. 78. Amer. Geophys. Union, Washington DC 20009, USA, pp. 217–231. <http://dx.doi.org/10.1029/GM078p0217>.
- Chen, D., Gao, G., Xu, C., Guo, J., Ren, G., 2005. Comparison of the Thornthwaite method and pan data with the standard Penman–Monteith estimates of reference evapotranspiration in China. *Clim. Res.* 28 (2), 123–132. <http://dx.doi.org/10.3354/cr028123>.
- Comas-Bru, L., McDermott, F., 2014. Impacts of the EA and SCA patterns on the European twentieth century NAO–winter climate relationship. *Q. J. R. Meteorol. Soc.* 140, 354–363. <http://dx.doi.org/10.1002/qj.2158>.
- Cuthbert, M.O., Baker, A., Jex, C.N., Graham, P.W., Treble, P.C., Andersen, M.S., Acworth, R.L., 2014. Drip water isotopes in semiarid karst: implications for speleothem paleoclimatology. *Earth Planet. Sci. Lett.* 395, 194–204. <http://dx.doi.org/10.1016/j.epsl.2014.03.034>.
- Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus* XVI 4, 436–468. <http://dx.doi.org/10.1111/j.2153-3490.1964.tb00181.x>.
- Fairchild, I.J., Smith, C.L., Baker, A., Fuller, L., Spoetl, C., Matthey, D., McDermott, F., 2006. Modification and preservation of environmental signals in speleothems. *Earth Sci. Rev.* 75 (1–4), 105–153. <http://dx.doi.org/10.1016/j.earscirev.2005.08.003>.
- Fontes, J.-C., Youssfi, M., Allison, G.B., 1986. Estimation of the long term, diffuse groundwater discharge in the Northern Sahara using stable isotope profiles in soil water. *J. Hydrol.* 86, 315–327. [http://dx.doi.org/10.1016/0022-1694\(86\)90170-8](http://dx.doi.org/10.1016/0022-1694(86)90170-8).
- Gaziz, C., Feng, X., 2004. A stable isotope study of soil water: evidence for mixing and preferential flow paths. *Geoderma* 119 (1–2), 97–111. [http://dx.doi.org/10.1016/S0016-7061\(03\)00243-X](http://dx.doi.org/10.1016/S0016-7061(03)00243-X).
- Gehrels, J.C., Peeters, J.E.M., DeVries, J.J., Dekkers, M., 1998. The mechanism of soil water movement as inferred from ^{18}O stable isotope studies. *Hydrol. Sci. J.-des Sci. Hydrol.* 43 (4), 579–594. <http://dx.doi.org/10.1080/02626669809492154>.
- Genty, D., Labuhn, I., Hoffmann, G., Danis, P.A., Mestre, O., Bourges, F., Wainer, K., Massault, M., Van Exter, S., Régnier, E., Orengo, Ph., Falourd, S., Minster, B., 2014. Rainfall and cave water isotopic relationships in two South-France sites. *Geochim. Cosmochim. Acta.* 131, 323–343. <http://dx.doi.org/10.1016/j.gca.2014.01.043>.
- Hamon, W.R., 1961. Estimating potential evapotranspiration. *J. Hydraulic Eng.* 87, 107–120.
- Hoefs, J., 1997. *Stable Isotope Geochemistry*, 4th ed. Springer-Verlag, Berlin.
- Hsieh, J.C.C., Chadwick, O.A., Kelly, E.F., Savin, S.M., 1998. Oxygen isotopic composition of soil water: quantifying evaporation and transpiration. *Geoderma* 82 (1–3), 269–293. [http://dx.doi.org/10.1016/S0016-7061\(97\)00105-5](http://dx.doi.org/10.1016/S0016-7061(97)00105-5).
- IAEA/WMO, 2014. Global Network of Isotopes in Precipitation. The GNIP Database. Accessible at: <<http://www.iaea.org/water>>.
- Jackson, A.S., 2009. Variable sensitivity of European Holocene speleothems to climate change: case studies from selected caves Ph.D. thesis. UCD School of Geological Sciences, University College Dublin, Ireland, p. 202.
- Jex, C.N., Phipps, S.J., Baker, A., Bradley, C., 2013. Reducing uncertainty in the climatic interpretations of speleothem $\delta^{18}\text{O}$. *Geophys. Res. Lett.* 40, 2259–2264. <http://dx.doi.org/10.1002/grl.50467>.
- Kottek, M., Grieser, J., Beck, C., Rudolf, B., Rubel, F., 2006. World Map of the Köppen-Geiger climate classification updated. *Meteorologische Zeitschrift* 15 (3), 259–263. <http://dx.doi.org/10.1127/0941-2948/2006/0130>.
- Leng, M.J., Marshall, J.D., 2004. Palaeoclimate interpretation of stable isotope data from lake sediment archives. *Quat. Sci. Rev.* 23 (7–8), 811–831. <http://dx.doi.org/10.1016/j.quascirev.2003.06.012>.
- Li, F., Song, X., Tang, C., Liu, C., Yu, J., Zhang, W., 2007. Tracing infiltration and recharge using stable isotope in Taihang Mt. North China. *Environ. Geol.* 53, 687–696. <http://dx.doi.org/10.1007/s00254-007-0683-0>.
- Majoube, M., 1971. Fractionnement en oxygène¹⁸ et en deutérium entre l'eau et sa vapeur. *J. Chem. Phys.* 197, 1423–1436.
- Mather, J.R., 1978. *The climatic water balance in environmental analysis*. D.C. Heath and Company, Lexington Brooks, Mass.
- Mathieu, R., Bariac, T., 1996. An isotopic study (^2H and ^{18}O) of water movements in clayey soils under a semiarid climate. *Water Res. Res.* 32 (4), 779–789. <http://dx.doi.org/10.1029/96wr00074>.
- McCabe, G.J., Markstrom S.L., 2007. A monthly water-balance model driven by a graphical user interface. Report, U. S. Geological Survey Open-File report 2007–1008.
- McCarroll, D., Loader, N.J., 2004. Stable isotopes in tree rings. *Quat. Sci. Rev.* 23 (7–8), 771–801. <http://dx.doi.org/10.1016/j.quascirev.2003.06.017>.
- McDermott, F., 2004. Palaeo-climate reconstruction from stable isotope variations in speleothems: a review. *Quaternary Sci. Rev.* 23 (7–8), 901–918. <http://dx.doi.org/10.1016/j.quascirev.2003.06.021>.
- Merlivat, L., Jouzel, J., 1979. Global climatic interpretation of the deuterium–oxygen 18 relationship for precipitation. *J. Geophys. Res. Oceans* 84 (C8), 5029–5033. <http://dx.doi.org/10.1029/JC084iC08p05029>.
- Moerman, J.W., Cobb, K.M., Partin, J.W., Meckler, A.N., Carolin, S.A., Adkins, J.F., Lejau, S., Malang, J., Clark, B., Tuen, A.A., 2014. Transformation of ENSO-related rainwater to dripwater $\delta^{18}\text{O}$ variability by vadose water mixing. *Geophys. Res. Lett.* 41 (22), 7907–7915. <http://dx.doi.org/10.1002/2014GL061696>.
- Newman, B.D., Campbell, A.R., Wilcox, B.P., 1997. Tracer-based studies of soil water movement in semi-arid forests of New Mexico. *J. Hydrol.* 196, 251–270. [http://dx.doi.org/10.1016/S0022-1694\(96\)03320-3](http://dx.doi.org/10.1016/S0022-1694(96)03320-3).
- Rayleigh, J.W.S., 1896. Theoretical considerations respecting the separation of gases by diffusion and similar processes. *Phil. Mag. Series 5* (42), 493–498.
- Robertson, J.A., Gaziz, C.A., 2006. An oxygen isotope study of seasonal trends in soil water fluxes at two sites along a climate gradient in Washington State (USA). *J. Hydrol.* 328 (1–2), 375–387. <http://dx.doi.org/10.1016/j.jhydrol.2005.12.031>.
- Rozanski, K., Araguás-Araguás, L., Gonfiantini, R., 1993. Isotopic patterns in modern global precipitation. In: Swart, P.K., Lohmann, K.C., McKenzie, J., Savin, S. (Eds.), *Climate Change in Continental Isotopic Records*. Geophysical Monograph, vol. 78. Amer. Geophys. Union, Washington DC 20009, USA, pp. 1–36. <http://dx.doi.org/10.1029/GM078p0001>.
- Schid, H., 1975. Berechnung der potentiellen Verdunstung und deren vergleich mit aktuellen Verdunstungswerten von Lysimetern. *Archiv für Meteorologie, Geophysik und Bioklimatologie, Serie B* 23 (4), 331–342.
- Shurbaji, A.-R.M., Phillips, F.M., Campbell, A.R., Knowlton, R.G., 1995. Application of a numerical model for simulating water flow, isotope transport, and heat transfer in the unsaturated zone. *J. Hydrol.* 171, 143–163. [http://dx.doi.org/10.1016/0022-1694\(95\)02756-F](http://dx.doi.org/10.1016/0022-1694(95)02756-F).
- Smart, P., Friederich, H., 1986. Water movement and storage in the unsaturated zone of a maturely karstified carbonate aquifer, Mendip Hills, England. In: *Proceedings of the Environmental Problems in Karst Terranes and Their Solutions Conference*. National Water Well Association, Dublin OH, pp. 59–87.
- Tang, K., Feng, X., 2001. The effect of soil hydrology on the oxygen and hydrogen isotopic compositions of plants' source water. *Earth Planet. Sci. Lett.* 185, 355–367. [http://dx.doi.org/10.1016/S0012-821X\(00\)00385-X](http://dx.doi.org/10.1016/S0012-821X(00)00385-X).
- Thornthwaite, C.W., 1948. An approach toward a rational classification of climate. *Geograph. Rev.* 38, 55–94.
- Tooth, A.F., Fairchild, I.J., 2003. Soil and karst aquifer hydrological controls on the geochemical evolution of speleothem-forming drip waters, Crag Cave, southwest Ireland. *J. Hydrol.* 273, 51–68. [http://dx.doi.org/10.1016/S0022-1694\(02\)00349-9](http://dx.doi.org/10.1016/S0022-1694(02)00349-9).
- Trajkovic, S., Kolakovic, S., 2009. Evaluation of reference evapotranspiration equations under humid conditions. *Wat. Res. Man.* 23 (14), 3057–3067. <http://dx.doi.org/10.1007/s11269-009-9423-4>.
- Wackerbarth, A., Scholz, D., Fohlmeister, J., Mangini, A., 2010. Modelling the $\delta^{18}\text{O}$ value of cave drip water and speleothem calcite. *Earth Planet. Sci. Lett.* 299, 387–397. <http://dx.doi.org/10.1016/j.epsl.2010.09.019>.
- Williams, P.W., 2008. The role of the epikarst in karst and cave hydrogeology: a review. *Int. J. Speleol.* 37 (1), 1–10.
- WRB, 2014. World Reference Base for Soil Resources 2014. International soil classification system for naming soils and creating legends for soil maps. Report, World Soil Resources Reports No. 106. FAO, Rome.
- Xu, C., Sano, M., Nakatsuka, T., 2011. Tree ring cellulose $\delta^{18}\text{O}$ of *Fokienia hodginsii* in northern Laos: a promising proxy to reconstruct ENSO? *J. Geophys. Res.: Atmos.* 116 (D24), D24109. <http://dx.doi.org/10.1029/2011JD016694>.
- Zimmermann, U., Ehhalt, D., Muennich, K.O., 1967. Soil water movement and evapotranspiration: changes in the isotopic composition of the water. *Proc. Symp. on Isotopes in Hydrology, Int. At. Energy Agency, Vienna*. 83, 567–585.