

Spatial patterns in the oxygen isotope composition of daily rainfall in the British Isles

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Received: 19 June 2015 / Accepted: 7 December 2015
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Abstract Understanding the modern day relationship between climate and the oxygen isotopic composition of precipitation ($\delta^{18}\text{O}_\text{P}$) is crucial for obtaining rigorous palaeoclimate reconstructions from a variety of archives. To date, the majority of empirical studies into the meteorological controls over $\delta^{18}\text{O}_\text{P}$ rely upon daily, event scale, or monthly time series from individual locations, resulting in uncertainties concerning the representativeness of statistical models and the mechanisms behind those relationships. Here, we take an alternative approach by analysing daily patterns in $\delta^{18}\text{O}_\text{P}$ from multiple stations across the British Isles ($n = 10\text{--}70$ stations). We use these data to examine the spatial and seasonal heterogeneity of regression statistics between $\delta^{18}\text{O}_\text{P}$ and common predictors (temperature, precipitation amount and the North Atlantic Oscillation index; NAO). Temperature and NAO are poor predictors of daily $\delta^{18}\text{O}_\text{P}$ in the British Isles, exhibiting weak and/or

inconsistent effects both spatially and between seasons. By contrast $\delta^{18}\text{O}_\text{P}$ and rainfall amount consistently correlate at most locations, and for all months analysed, with spatial and temporal variability in the regression coefficients. The maps also allow comparison with daily synoptic weather types, and suggest characteristic $\delta^{18}\text{O}_\text{P}$ patterns, particularly associated with Cylonic Lamb Weather Types. Mapping daily $\delta^{18}\text{O}_\text{P}$ across the British Isles therefore provides a more coherent picture of the patterns in $\delta^{18}\text{O}_\text{P}$, which will ultimately lead to a better understanding of the climatic controls. These observations are another step forward towards developing a more detailed, mechanistic framework for interpreting stable isotopes in rainfall as a palaeoclimate and hydrological tracer.

Keywords Oxygen isotopes · Amount effect · NAO · British Isles

Electronic supplementary material The online version of this article (doi:[10.1007/s00382-015-2945-y](https://doi.org/10.1007/s00382-015-2945-y)) contains supplementary material, which is available to authorized users.

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1 Introduction

The relationship between climate and the oxygen isotope composition of precipitation ($\delta^{18}\text{O}_\text{P}$) is central to a wide range of palaeoclimate interpretation techniques, from direct archives of ancient precipitation preserved in ice (e.g. Barbante et al. 2006; Dansgaard et al. 1993; Johnsen et al. 2001; Petit et al. 1999), through indirect archives which include speleothem calcite, lake sediment biominerals and tree ring cellulose (e.g. Baker et al. 2011; Evans and Schrag 2004; Jones et al. 2006; Robertson et al. 2001; Tyler et al. 2008; von Grafenstein et al. 1996; Wang et al. 2008). Improved understanding of the climate-isotope relationship is therefore an important step towards improving the accuracy and rigour of palaeoclimate reconstructions both from individual records and through regional/global

data-assimilation projects (e.g. PAGES 2k Consortium 2013; Shakun and Carlson 2010). Much of our understanding of this key climate-isotope interaction is built around two approaches: the development and exploration of isotope-enabled climate models (Gedzelman and Arnold 1994; Hoffmann et al. 2006; Jouzel et al. 2000; Langebroek et al. 2011; Merlivat and Jouzel 1979; Schmidt et al. 2007) and the statistical examination of isotope monitoring data (Dansgaard 1964; Fischer and Baldini 2011; Rozanski et al. 1993; Treble et al. 2005). Despite significant developments in incorporating isotope systematics into climate models, the continued acquisition and exploration of precipitation isotope monitoring data remains crucial, both to assist in the validation and parameterisation of climate models but also to refine the interpretation of isotope based palaeoclimate records.

Empirical studies into the links between $\delta^{18}\text{O}_\text{P}$ and climatic/meteorological parameters are numerous and diverse. A widespread correlation between $\delta^{18}\text{O}_\text{P}$ and air temperature is manifest globally and for select continental regions, particularly from a spatial perspective and occasionally through time (Araguas–Araguas et al. 2000; Dansgaard 1964; Kohn and Welker 2005; Rozanski et al. 1993). Air temperature is an important factor in driving condensation within a vapour parcel and dictating the liquid–vapour isotopic fractionation (Dansgaard 1964). However, uncertainties exist regarding the association between air temperature at the land surface and vapour condensation temperature, which varies as a function of altitude even during the course of an individual rainfall event (Celle-Jeanton et al. 2001, 2004). Furthermore, the global correlation between air temperature and $\delta^{18}\text{O}_\text{P}$ is subject to covariance with other key elements of the global isotope hydrological cycle, including latitude, conditions at and distance from evaporation source, and precipitation amount (Bowen and Wilkinson 2002).

Changes in precipitation amount are also expected to impart an influence upon $\delta^{18}\text{O}_\text{P}$, due to the combined effects of Rayleigh distillation prior to precipitation at the monitoring station, evaporation from falling raindrops and isotopic exchange between raindrops and ambient vapour beneath cloud level (Callow et al. 2014; Dansgaard 1964). The so called ‘amount effect’ is most prominently associated with convective tropical rainfall (Rozanski et al. 1993), however correlations between rainfall amount and $\delta^{18}\text{O}_\text{P}$ have also been frequently observed in data from maritime temperate regions (Baldini et al. 2008, 2010; Callow et al. 2014; Celle-Jeanton et al. 2001; Crawford et al. 2013; Darling and Talbot 2003; Treble et al. 2005). In addition to effects at the site of precipitation, variability in $\delta^{18}\text{O}_\text{P}$ is subject to the conditions at the source of moisture evaporation (e.g. sea surface temperatures and relative humidity), the trajectory of the air mass, synoptic weather patterns and

interaction with the land surface (Celle-Jeanton et al. 2001, 2004; Fischer and Baldini 2011; Heathcote and Lloyd 1986; Lachniet and Patterson 2009; Liebminger et al. 2006; Sodemann et al. 2008; Treble et al. 2005).

A major advance in our understanding of the controls over $\delta^{18}\text{O}_\text{P}$ has been the proliferation of studies utilising daily or event-scale monitoring in an attempt to address the mechanisms behind isotopic signatures at timescales relevant to the actual process (Baldini et al. 2010; Fischer and Baldini 2011; Heathcote and Lloyd 1986). Longer term $\delta^{18}\text{O}_\text{P}$ data—be they monthly, annual, centennial or millennial—are best viewed as composites of event scale processes, weighted by the amount of rainfall during each event. For this reason, regression models built around monthly or annual data can be subject to issues related to changes in seasonal weighting (Vachon et al. 2007) or simply an inability to capture the conditions during which precipitation occurred (Baldini et al. 2010). Recently, approaches have emerged which enable the integration of monthly resolved isotope data with daily meteorological data, therefore modelling the processes at timescales relevant to synoptic conditions (Fischer and Baldini 2011; Fischer and Treble 2008). However, with increased resolution comes increased noise, thus the representativeness of empirical models based upon single isotope time-series comes into question. There is therefore significant value in studies which combine daily monitoring with multiple sites in order to evaluate the relationships between regional meteorology and the isotopic composition of precipitation (e.g. Good et al. 2014) and such studies are scarce.

The British Isles is an interesting study location for isotopes in rainfall, with a maritime climate that is affected by the confluence of weather systems with distinctly different origins depending on the direction of flow (Heathcote and Lloyd 1986). Previous studies have addressed the climate-isotope relationships in the British Isles using single site daily, event based and monthly monitoring (Baldini et al. 2010; Darling and Talbot 2003; Fischer and Baldini 2011; Heathcote and Lloyd 1986; Jones et al. 2007). On the basis of nearly two year’s daily monitoring at Driby, Lincolnshire, Heathcote and Lloyd (1986) observed no correlation between air temperature and $\delta^{18}\text{O}_\text{P}$ and concluded that weather type and associated origin of moisture is the primary factor responsible for changes in daily $\delta^{18}\text{O}_\text{P}$. At Wallingford, Oxfordshire, Darling and Talbot (2003) observed weak and seasonally variable correlations between daily $\delta^{18}\text{O}_\text{P}$, temperature and precipitation amount – correlations which improve when monthly values are used. In a detailed analysis of event scale $\delta^{18}\text{O}_\text{P}$ in Dublin, Ireland, Baldini et al. (2008, 2010) demonstrate the primary role of precipitation amount and moisture source trajectory. On the basis of those data, Fischer and Baldini (2011), developed a series of daily empirical functions of increasing complexity

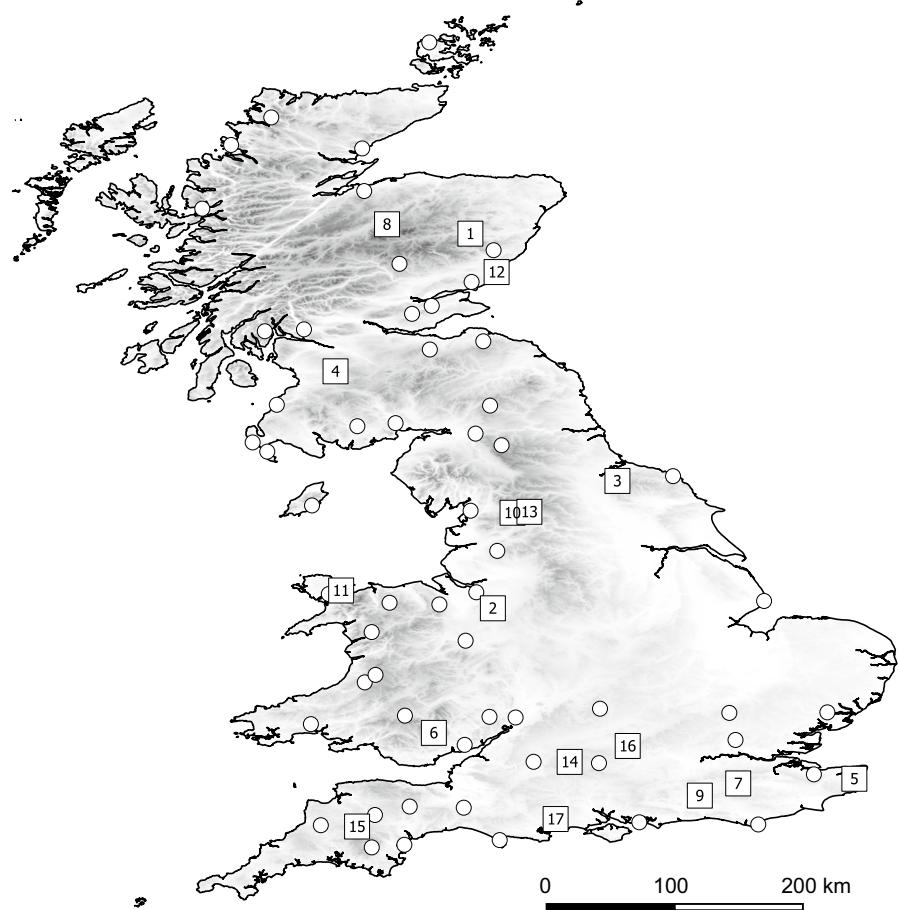


Fig. 1 Topographic map of the British Isles (dark shaded areas = higher elevation), including the location of the sampling sites used in this study. Open circles are those sites only sampled in

January 2012, whereas open boxes indicate the sites sampled during all months. The numbers in the squares indicates the site number, as detailed in Table 1

to characterise $\delta^{18}\text{O}_{\text{P}}$ as a function of precipitation amount and moisture source. The Fischer and Baldini (2011) daily functions, and approach in general, offer tremendous potential for improving the interpretation of palaeoclimate archives. However, the broader applicability of those functions, as with the traditional Dansgaard (1964) type relationships, is dependent upon understanding how the coefficients and model skill vary in space and through time. In particular, the causal mechanism between rainfall amount and $\delta^{18}\text{O}_{\text{P}}$, and how that relationship evolves through the lifespan of a rainfall event, remains poorly understood. Here, in an attempt to better evaluate the spatial and temporal heterogeneity of daily isotope functions, and to address the issue of signal versus noise in daily $\delta^{18}\text{O}_{\text{P}}$ data, daily monitoring of $\delta^{18}\text{O}_{\text{P}}$ was carried out at multiple locations across the relatively small spatial gradient of the British Isles. We report daily $\delta^{18}\text{O}$ measurements over 57 days, sampling rainfall events across each of the four seasons from up to 70 sites. These data indicate daily spatial $\delta^{18}\text{O}$

gradients within the British Isles of up to 17 ‰, highlighting the role of the evolution of weather systems in driving local scale variability in $\delta^{18}\text{O}_{\text{P}}$. We use these data to evaluate the empirical relationships between $\delta^{18}\text{O}_{\text{P}}$ and daily weather, and to qualitatively assess the potential for developing a synoptic typology for $\delta^{18}\text{O}_{\text{P}}$ in the British Isles.

2 Sites and methodology

Daily precipitation water samples were collected from up to 70 sites within England, Wales, Scotland and Northern Ireland (Fig. 1; Table 1). The samples were collected as part of a pilot study for the British Isotopes in Rainfall Project (BIRP)—a community engagement initiative, in collaboration with volunteer weather observers and the UK Met Office. Initially, 17 volunteers were engaged, contacted via the Climate Observers Link (COL) or via existing monitoring programmes (Table 1). This group was

Table 1 Details of sites sampled during March 2010, October 2010 and July 2011. Site numbers relate to those mapped in Fig. 1

Site	Site no.	Latitude (°N)	Longitude (°E)	Height (m.a.s.l.)	Sample months			Notes
					March 2010	October 2010	July 2011	
Aboyne	1	57.07	-2.79	126		15	11	
Acton	2	53.07	-2.55	44	10		10	Temperature data from MIDAS (site 1132; Reaseheath Hall; 2 km NE)
Carlton-in-Cleveland	3	54.43	-1.22	88	11	15	14	
Darvel	4	55.60	-4.23	217	10	14	15	
Eastry	5	51.25	1.31	32	10	15	11	
Ebbw Vale	6	51.74	-3.18	303	10	15	14	
Edenbridge	7	51.20	0.07	47	10			
Glenmore Lodge	8	57.17	-3.68	344		13	17	Temperature data from MIDAS (site 118; Cairngorm Chairlift; 4 km S)
Horsham	9	51.07	-0.34	37	10	13	8	
Lawkland	10	54.09	-2.34	176	10			Temperature data from MIDAS (site 513; Bingley; 44 km SW)
Llansadwrn	11	53.26	-4.17	107	11	19	15	
Lunan Vale	12	56.66	-2.51	19		15	15	Temperature data from MIDAS (site 15045; Crombie Country Park; 19 km SW)
Malham Tarn	13	54.10	-2.16	384		15	13	
Marlborough	14	51.43	-1.73	142	10	15	2	
Okehampton	15	50.74	-4.00	170		15	14	Temperature data from MIDAS (site 1345; East Okement Farm; 4 km S)
Wallingford	16	51.60	-1.11	50		10	9	
West Moors	17	50.82	-1.88	17	10	13	12	
Total samples					102	202	180	

Values within the 'Sample months' columns indicate the number of samples collected in each month, at each site. Details of nearby Met Office stations used to complement data where no local temperature measurements were taken are given in the 'Notes' column

subsequently augmented by further weather observers with ongoing association with the U.K. Met Office. Precipitation water samples were collected using a standard Met Office rain gauge at 9 a.m. GMT each day. Having measured the amount of rainfall for the previous 24 h, the rain water samples were transferred to 4 or 8 ml Nalgene® HDPE bottles, depending on rainfall amount, taking care to ensure bottles were full to avoid any exchange of sample oxygen with air in the bottle. The bottles were labelled, stored at 4 °C and sent to the British Geological Survey at the end of each month. Details of sampling practice were communicated to participants via an online video (<http://tinyurl.com/>)

(BIRP2010), with further instructions provided via post to each sampler.

Precipitation samples were collected during the course of four campaigns, conducted in March 2010, October 2010, July 2011 and January 2012, thereby capturing a sub-sample of each of the seasons. Collection days were inevitably limited by the occurrence of precipitation events and availability of volunteers, and thus the sample set for each site and month range from 2 to 19 samples (Table 1). In addition to collecting precipitation water, at the majority of stations a range of meteorological data was recorded. Every station provided rainfall amount data, and the majority also

provided air temperature recordings. Where local temperature readings were not taken, temperature data from a nearby Met Office station was used (Table 1). Because precipitation samples were collected at 9 a.m. each day, the date of precipitation in each instance was assigned as the previous day, both for precipitation amount data and isotope composition, following standard practice for the U.K. Met Office. The daily North Atlantic Oscillation (NAO) index was obtained from the U.S. National Oceanic and Atmospheric Administration (NOAA) Climate Prediction Center (<http://www.cpc.ncep.noaa.gov>).

Oxygen and hydrogen isotopes of water were analysed at NERC Isotope Geosciences Facility at the British Geological Survey. For D/H analysis, the hydrogen was liberated by Cr reduction, while $^{18}\text{O}/^{16}\text{O}$ were equilibrated with CO_2 using an ISOPREP 18 device. Mass spectrometry was performed on a VG SIRA ($\delta^{18}\text{O}$) and IsoPrime ($\delta^2\text{H}$) in conjunction with laboratory standards calibrated against NBS standards. Long term analytical errors are 0.05 ‰ for ^{18}O and <1 ‰ for $\delta^2\text{H}$.

Spatial patterns in daily $\delta^{18}\text{O}_P$ were mapped using the *filled.contour* program in R, which uses the function *akima* to perform bivariate data interpolation (Akima 1978). Backward trajectories of air parcels arriving at the British Isles were computed using the web-based HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Hess 1997, 1998; Draxler and Rolph 2015; Rolph 2015) for a matrix of 63 locations between 5.7°W, 50°N and 2.7°E, 58°N. Back trajectories were computed for air parcels arriving at 1500 m.a.s.l. at six-hourly intervals prior to the time of water sampling at 9:00 h. Principle locations of moisture uptake were estimated as the first point in a particular trajectory whereby the specific humidity increased by >0.5 g/kg and atmospheric pressure was >900 hPa, following Krklec and Dominguez-Villar (2014).

3 Results

3.1 Regression between daily $\delta^{18}\text{O}_P$, maximum air temperature and precipitation amount

For the statistical analysis of daily precipitation isotope data, we treat the data from January 2012 separately from those from March 2010, October 2010 and July 2011. This is because the January 2012 sample contains observations from ~4 times as many locations, yet over 3 days, which contrasts with the fewer (15–17) locations over up to 19 days for the other sampling months. In all instances, relationships with precipitation amount are explored using a power coefficient ($P^{0.5}$), to ensure a Gaussian distribution

of regression residuals, following the reasoning outlined in Fischer and Treble (2008) and Fischer and Baldini (2011); nonlinear relationships are known in climate-isotope studies, such as in the discussion of Rayleigh fractionation later in this paper, and root transformations are often applied to precipitation data in climatology because precipitation data are typically skewed. Daily maximum temperatures (T_{\max}) are used, since they relate to the temperature around noon on the day of precipitation, whereas mean daily temperatures for the period of sampling (9 a.m.–9 a.m.) are not consistently available.

The relationship between $\delta^{18}\text{O}_P$, T_{\max} and $P^{0.5}$ is explored first using all daily data (excluding January 2012), and then with data subset according to month and site in order to ascertain the consistency of relationships in time and space. Due to the paucity of data, monthly subsets from each site were not analysed individually. When all daily data are combined, there are weak yet statistically significant ($p < 0.001$) relationships between $\delta^{18}\text{O}_P$, $P^{0.5}$ and T_{\max} ($r^2 = 0.17$ and 0.02 respectively) but not NAO (Fig. 2). Significant regressions can also be observed between $\delta^{18}\text{O}_P$ and $P^{0.5}$ when data are subset according to month, with slope coefficients varying between March 2010 (slope = -1.45, $r^2 = 0.24$), October 2010 (slope = -0.97, $r^2 = 0.14$) and July 2011 (slope = -0.85, $r^2 = 0.19$) (Fig. 3a–c). Significant regressions ($p < 0.05$) did not exist between $\delta^{18}\text{O}_P$ and T_{\max} for monthly subsets for March or October 2010 (Fig. 3d, e), however a weak ($r^2 = 0.04$, $p = 0.01$) relationship was observed for July 2011 (Fig. 3f). The mean T_{\max} for the three sampled months varied markedly, from 10.54 °C in March 2010, 12.74 °C in October 2010 and 17.21 °C in July 2011 (Fig. 3d–f). There were no significant regressions ($p < 0.05$) between $\delta^{18}\text{O}_P$ and NAO where data were subset according to month (Fig. 3g–i).

When data are subset according to sampling location (incorporating data from each month excluding January 2012), significant regressions between $\delta^{18}\text{O}_P$ and $P^{0.5}$ can be observed with $p < 0.05$ at 11 of the 17 sites (Fig. 4). Those sites that did not exhibit significant precipitation effects were Edenbridge (EDEN), Glenmore Lodge (GLEN), Horsham (HOR), Lunan Valley (LUNA), Wallingford (WALL) and West Moors (WMOR) (Fig. 4). Five sites exhibited significant $P^{0.5}$ effects with $r^2 > 0.3$, and those were Acton (ACT), Aboyne (ABYE), Carlton-in-Cleveland (CACL), Darvel (DAR) and Lawkland (LAW). Given the paucity of data, it was not possible to rigorously test for differences in the within-site $P^{0.5}$ versus $\delta^{18}\text{O}_P$ relationships between months, although there is no obvious indication that data from March 2010, October 2010 or July 2011 exhibit markedly different response patterns to the regression models based on all months combined (Fig. 4).

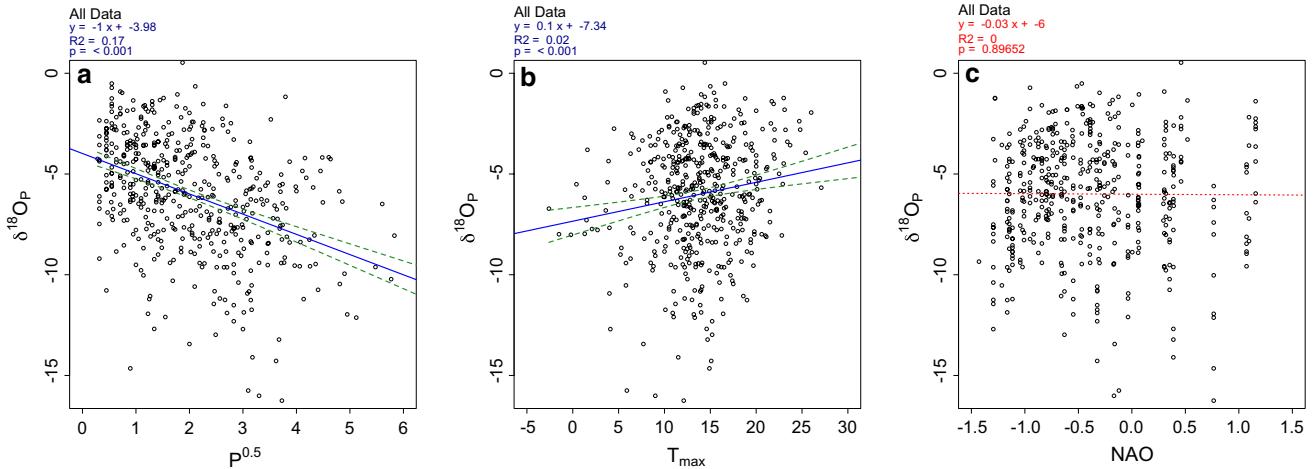


Fig. 2 Scatter plots of daily $\delta^{18}\text{O}_\text{P}$ vs. **a** precipitation amount (square root transformed; $P^{0.5}$), **b** daily maximum temperature (T_{\max}) and **c** North Atlantic Oscillation index (NAO) for all samples collected during March 2010, October 2010 and July 2011, excluding January 2012. Regression coefficients are given inset. Solid blue lines signifi-

cant linear model fit, dashed green lines 95 % confidence intervals. Non-significant linear models are illustrated with dotted red lines. Blue text relates to significant regression models, whereas red text indicates non-significant models. This colour coding of text and lines applies to all of the following regression plots

Five of the 17 site-specific regressions between T_{\max} and $\delta^{18}\text{O}_\text{P}$ are significant to $p < 0.05$, data from Acton (ACT), Ebber Vale (EBBV), Glenmore Lodge (GLEN), Marlborough (MARL) and Wallingford (WALL) (Fig. 5). The slope coefficients for those relationships range between +0.14 at Glenmore Lodge (GLEN) to +0.37 at Acton (ACT). For most sites, particularly those with significant T_{\max} effects, there is visible clustering of data according to month (Fig. 5). There is only one site, Edenbridge (EDEN) which exhibits a significant ($p < 0.05$, $r^2 = 0.58$) positive relationship with NAO, however only a single month (March) was monitored at that site (Fig. 6). Two additional sites—West Moors (WMOR) and Horsham (HOR) also exhibited significant regressions between March $\delta^{18}\text{O}_\text{P}$ and NAO (Supplementary Information, Figure S1).

The spatial distribution of regression coefficients for $P^{0.5}$ and T_{\max} versus $\delta^{18}\text{O}_\text{P}$ are mapped in Fig. 7. Sites which exhibit significant regression coefficients between $\delta^{18}\text{O}_\text{P}$ and $P^{0.5}$ are distributed across the British Isles, however the sites with the largest r^2 and lowest (most negative) slopes versus $P^{0.5}$ are those in northern England and Scotland, with the exception of Acton (ACT) in central England (Fig. 7a, b). Two sites in Scotland, Glenmore Lodge (GLEN) and Lunan Valley (LUNA), exhibit no significant relationship with $P^{0.5}$ (Fig. 7a, b). Only five sites produced a significant regression between $\delta^{18}\text{O}_\text{P}$ and T_{\max} , of which four are situated in central and southern England (Fig. 7c, d). One northern site—Glenmore Lodge (GLEN), Scotland, also exhibited a significant relationship with temperature, whilst three sites on the southern coast of England exhibited no significant temperature effect (Fig. 7c, d).

3.2 Spatial distribution of daily $\delta^{18}\text{O}_\text{P}$

Over the sampling period, the geographical distribution of $\delta^{18}\text{O}_\text{P}$ across Great Britain varied markedly from day to day. On some occasions, e.g. 13th March 2010 (Figure S2), 17th October 2010 (Figure S3) and 21st July 2011 (Figure S4), $\delta^{18}\text{O}_\text{P}$ values were largely homogenous (within a 2 % range) across the entire spatial gradient. However, on other occasions, e.g. 4th October 2010, 27th October 2010 (Figure S3) and 9th July 2011 (Figure S4), marked spatial gradients in $\delta^{18}\text{O}_\text{P}$ occurred, up to a maximum range of 17 %. The degree of spatial homogeneity may, in part, relate to the sampling frequency and location of precipitation samples for a particular day, however the day to day differences in spatial range measured from ~15 sites is equivalent to that observed over the 3 days sampled in January 2012 (Fig. 8), where the spatial gradient varies from 17 % on 23rd January 2012 to 10 % on 25th January 2012, despite over 60 stations being sampled on both occasions. Most frequently, daily $\delta^{18}\text{O}_\text{P}$ patterns show a decrease along a south-west to north-east gradient, although there are numerous exceptions to this rule, with occasional inversions in the direction of that gradient and bimodal distributions (e.g. 20th March 2010, 22nd October 2010 and 6th July 2011; Figures S2–S4). The most depleted $\delta^{18}\text{O}_\text{P}$ values measured were collected at sites in Scotland and northern England. Although a larger density of samples is preferable in order to trace spatial patterns in daily $\delta^{18}\text{O}_\text{P}$, reduction in sample number to as few as four sites still allows for some coherent patterns to be observed. On days where precipitation

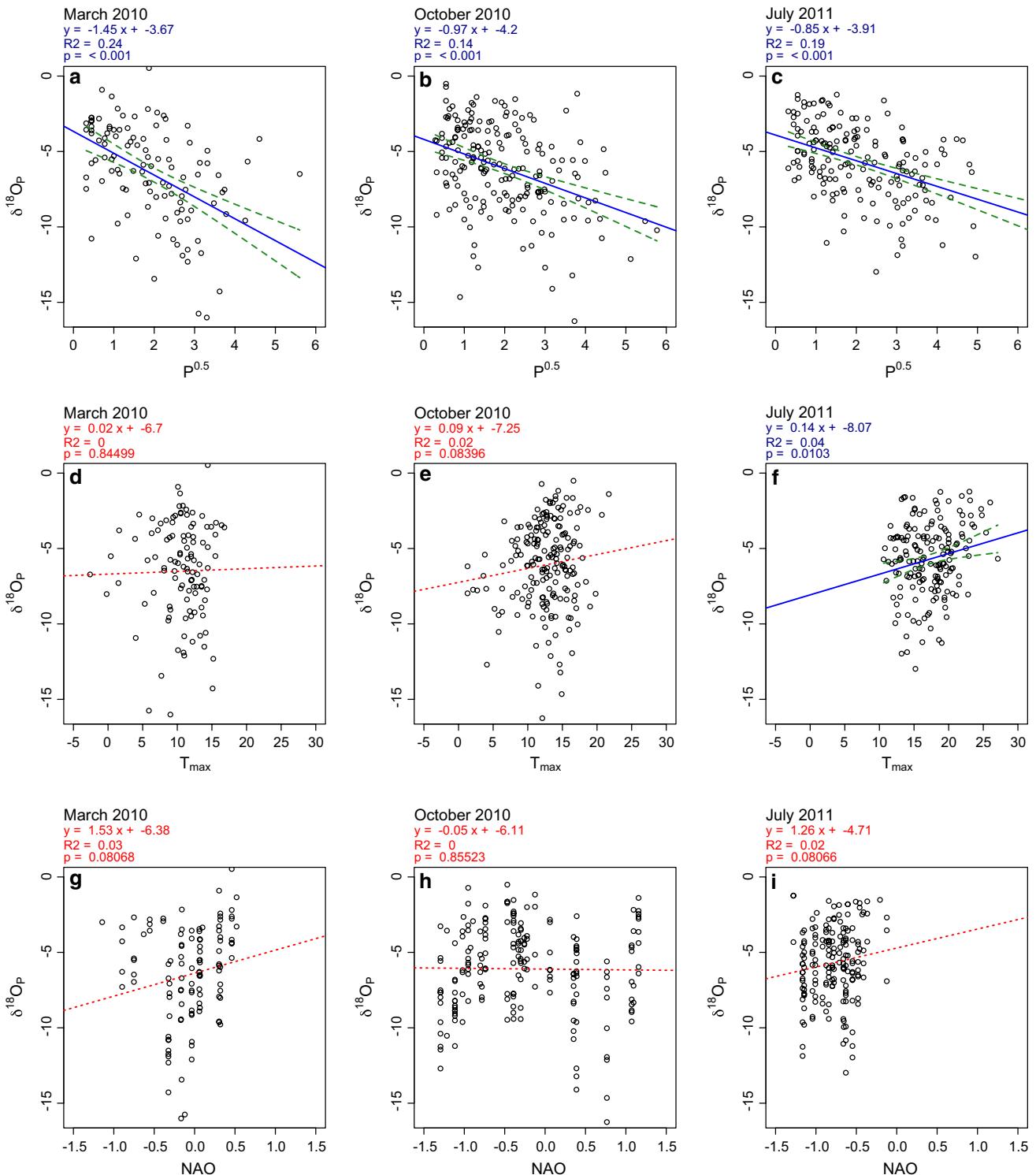


Fig. 3 Scatter plots of daily $\delta^{18}\text{O}_P$ vs. **a, d, g** precipitation amount (square root transformed, $P^{0.5}$), **b, e, h** daily maximum temperature (T_{max}) and **c, f, i** North Atlantic Oscillation index (NAO) for all samples subset according to month of sampling collected during March 2010, October 2010 and July 2011

fell at all locations, the pattern which emerges from 14 sampling sites (e.g. 17th July 2011, Figure S4) is not dissimilar to those which can be observed based upon >80

sites (e.g. 24th January 2012; Fig. 8c). Maps of the mean $\delta^{18}\text{O}_P$ values for March 2010, October 2010 and July 2011 are provided in the supplementary information (Figure S5).

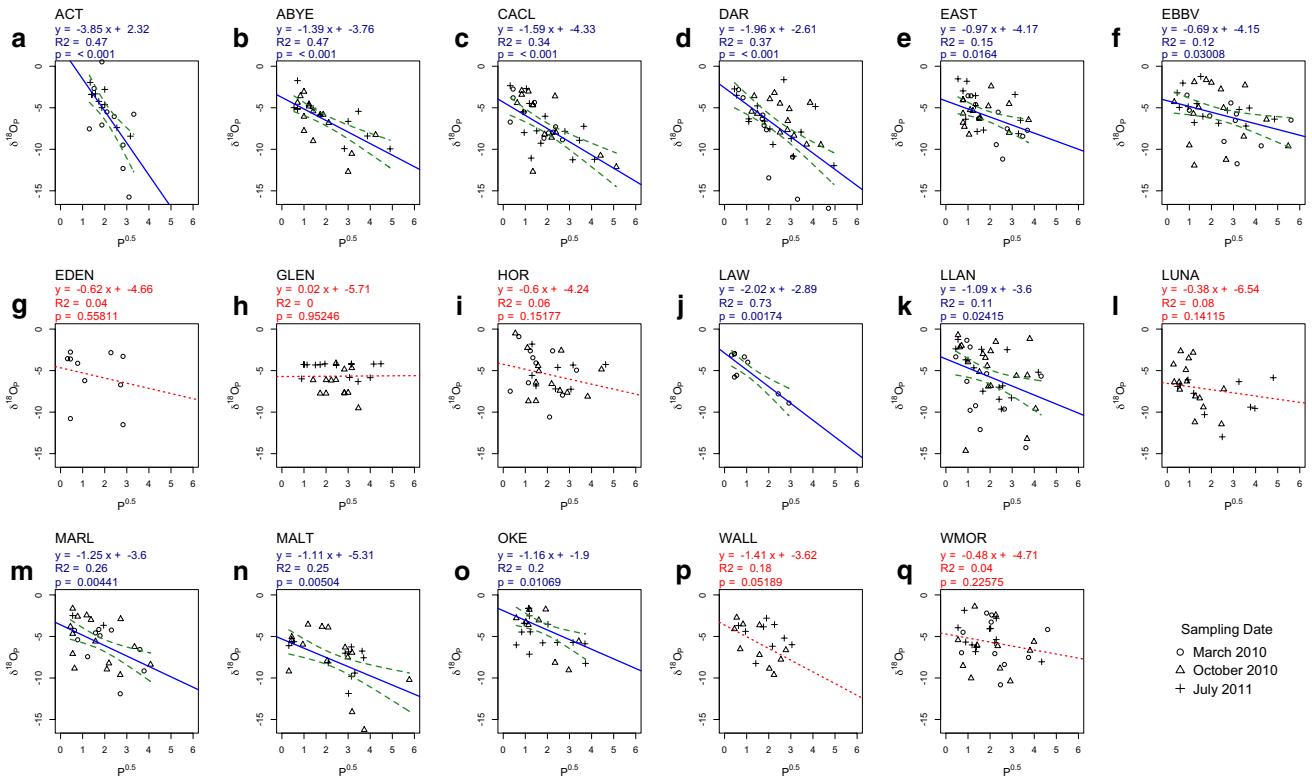


Fig. 4 Scatter plots of daily $\delta^{18}\text{O}_\text{P}$ versus precipitation amount (square root transformed, $P^{0.5}$) subset by site for all samples collected during March 2010 (open circles), October 2010 (open triangles) and July 2011 (crosses)

Spatial patterns in $\delta^{18}\text{O}_\text{P}$ are clearly best captured in January 2012, where the sample density was highest (Fig. 8). On 23rd January 2012, the lowest $\delta^{18}\text{O}_\text{P}$ values of $-18.5\text{\textperthousand}$ were obtained from rain falling in eastern-central Scotland, with a pattern of increasing $\delta^{18}\text{O}_\text{P}$ to the north, west and particularly to the south of that location (Fig. 8c). On this date, western England and Wales, Northern Ireland and southeast England experienced the highest $\delta^{18}\text{O}_\text{P}$ values of up to $0.58\text{\textperthousand}$, with a southward pattern of increasing $\delta^{18}\text{O}_\text{P}$ along the eastern coast of England (Fig. 8c). On 24th January 2012, a marked longitudinal gradient was observed, with declining $\delta^{18}\text{O}_\text{P}$ along an east-northeast trajectory (Fig. 8f). Lowest $\delta^{18}\text{O}_\text{P}$ values on 24th January were observed along the eastern coast of England and Scotland (Fig. 8f). The 25th January 2012 saw a shift towards low $\delta^{18}\text{O}_\text{P}$ (-15 to $-10\text{\textperthousand}$) in the north west of Scotland, Northern Ireland, north west England and northern Wales, with higher $\delta^{18}\text{O}_\text{P}$ in the south of England (Fig. 8i). HYSPLIT modelling indicates that two moisture bearing air masses crossed the British Isles on January 23rd, 2012 (Fig. 8a, b). The first parcel collected water vapour over the Norwegian Sea, east of Iceland and collided with the northern British Isles along a north-westerly trajectory

(Fig. 8a). The second air mass collected moisture from the central Atlantic Ocean and collided with the British Isles along a south-westerly trajectory. On the 24th January 2012, HYSPLIT modelling indicates that the majority of moisture was derived from the central Atlantic, impacting the British Isles along a westerly/south-westerly trajectory (Fig. 8d). On the 25th January 2012, HYSPLIT modelling indicates moisture arriving from a south-westerly trajectory, having markedly changed direction beforehand above the Bay of Biscay to the south (Fig. 8g). HYSPLIT back trajectories for six hourly intervals on the 3 days sampled in January 2012 are provided in the supplementary information (Figures S6–S8).

The relationship between the spatial distribution of $\delta^{18}\text{O}_\text{P}$ and synoptic weather types, as classified through the Lamb Weather Type scheme (LWT; Jones et al. 1993; Lamb 1950) is explored in Figs. 9 (Cyclonic) and 10 (South Westerly). The majority of rainfall events during the studied period were associated with two principle weather types: Cyclonic (LWT = 20) and South Westerly (LWT = 15) (Figure S9). Under the influence of Cyclonic weather types, $\delta^{18}\text{O}_\text{P}$ exhibits a pattern of higher values in southern and south-west England contrasting with a

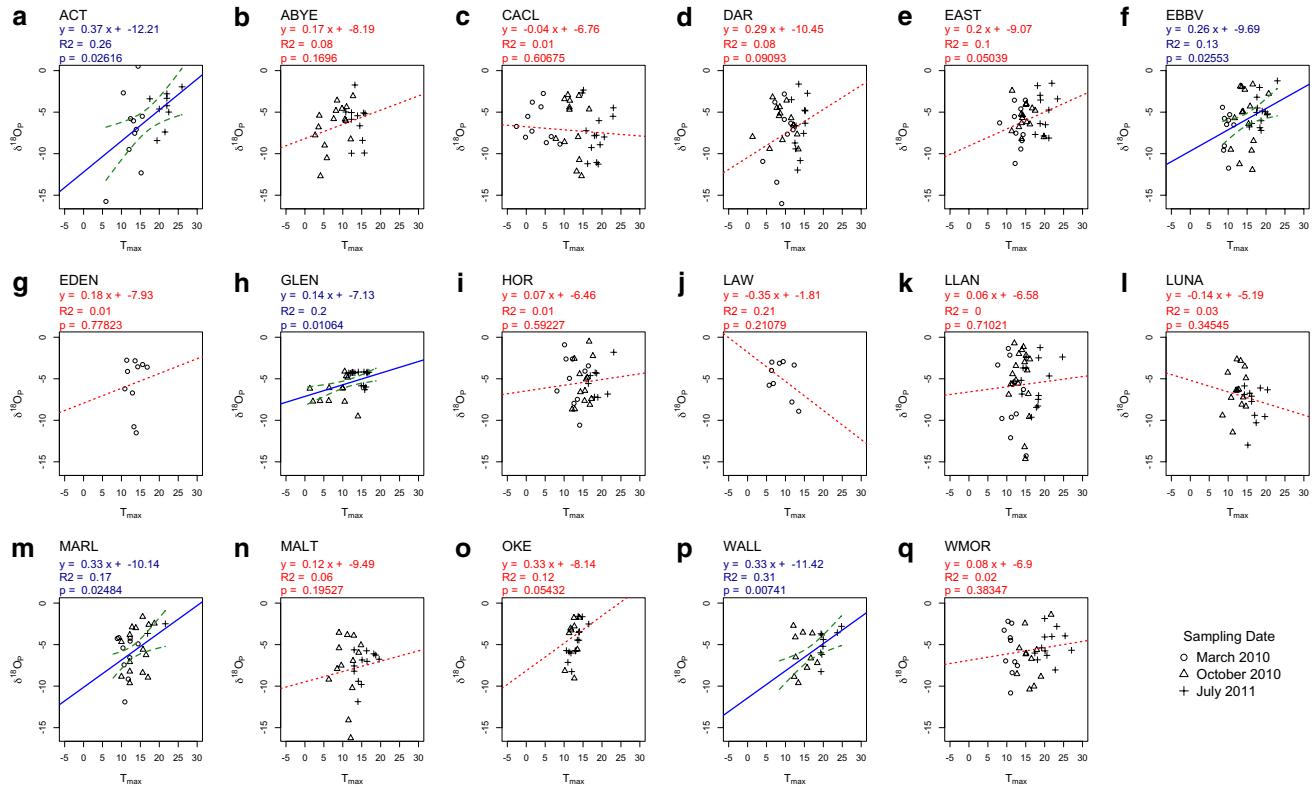


Fig. 5 Scatter plots of daily $\delta^{18}\text{O}_\text{P}$ versus daily maximum temperature (T_{max}) subset by site for all samples collected during March 2010 (open circles), October 2010 (open triangles) and July 2011 (crosses)

frequently occurring region of markedly lower $\delta^{18}\text{O}_\text{P}$ over northern England and southern Scotland (Fig. 9). Occasionally, those lower $\delta^{18}\text{O}_\text{P}$ values extend southwards along the eastern coast of England, e.g. on 8th July 2011 and 17th July 2011 (Fig. 9). Higher $\delta^{18}\text{O}_\text{P}$ values can also be observed to the far north during these weather events, e.g. on 3rd October 2010, 8th July 2011 and 18th July 2011 (Fig. 9). Under the influence of South Westerly weather (Fig. 10), a consistent spatial pattern in $\delta^{18}\text{O}_\text{P}$ is not evident and many of these days exhibit a narrow range of $\delta^{18}\text{O}_\text{P}$ (<5‰). On the 24th January 2012, $\delta^{18}\text{O}_\text{P}$ values largely exhibit a SW–NE gradient across Great Britain, except for low $\delta^{18}\text{O}_\text{P}$ at Llansadwrn (LLAN), North Wales (Fig. 10). By contrast, on 10th October 2010, the lowest $\delta^{18}\text{O}_\text{P}$ values were recorded in the south west of England and Wales. On other days (e.g. 18th March 2010; 23rd March 2010), the lowest or highest $\delta^{18}\text{O}_\text{P}$ values were recorded in northern-central England.

4 Discussion

Daily monitoring of isotopes in rainfall, on the basis of 57 days and 17 sites, support previous observations that

square root transformed daily precipitation amount ($P^{0.5}$) is the most consistent predictor of daily $\delta^{18}\text{O}_\text{P}$ in maritime, mid-latitude regions (Baldini et al. 2010; Fischer and Baldini 2011; Fischer and Treble 2008). All data combined (including January 2012; note that regression statistics in Fig. 2a exclude January 2012) define a daily function $\delta^{18}\text{O}_{\text{P-day}} = (-0.9)P_{\text{day}}^{0.5} - 4.7$, $r^2 = 0.1$, which is very similar to the model derived by Baldini et al. (2010) based on 2 years event based monitoring of $\delta^{18}\text{O}_\text{P}$ at Dublin, Ireland (Baldini et al. 2010; Fischer and Baldini 2011) and with the relationship between daily $\delta^{18}\text{O}_\text{P}$ and $P^{0.5}$ at Wallingford, England, between November 1979–October 1980 (data reported by Darling and Talbot 2003). The $P^{0.5}$ regression coefficients derived when data are subset according to month (Fig. 3) and by site (Fig. 4) vary compared to those based on the whole dataset combined. Firstly, the regression slope varies between the 3 months studied, suggestive of a seasonally modulated relationship between $\delta^{18}\text{O}_\text{P}$ and $P^{0.5}$ as described by Fischer and Baldini (2011). Indeed, the $P^{0.5}$ coefficients obtained here (Fig. 3) are consistent with those predicted by Equation 8 in Fischer and Baldini (2011) for March and October 2010 (−1.45 and −0.97 respectively, compared to a predicted −1.30 and −1.00) but not for July 2011, where our data indicate a slope of −0.85

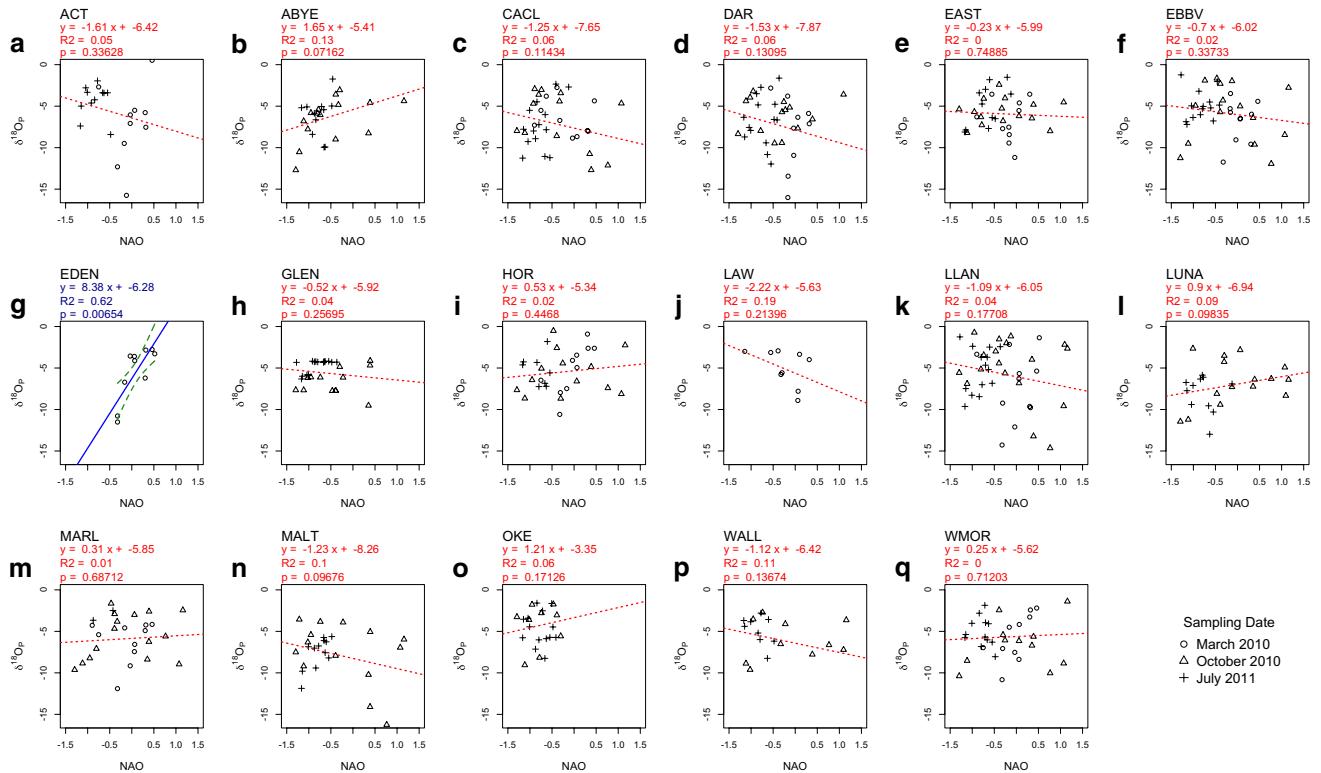


Fig. 6 Scatter plots of daily $\delta^{18}\text{O}_P$ versus North Atlantic Oscillation index (NAO) subset by site for all samples collected during March 2010 (open circles), October 2010 (open triangles) and July 2011 (crosses)

compared to a predicted -0.41 . Secondly, the $P^{0.5}$ coefficients vary spatially: steeper negative slope coefficients and higher r^2 values are generally observed in northern England and Scotland compared to larger slope coefficients and less frequent significant relationships at sites in southern England (Fig. 7). One exception to this rule—Acton (ACT)—is located in the English west midlands in the rain shadow of the Welsh mountains (Fig. 7a). We will discuss potential reasons for the variable $\delta^{18}\text{O}_P - P^{0.5}$ relationship at the end of this section.

The relationship between air temperature and daily $\delta^{18}\text{O}_P$ is less convincing. A weak yet significant correlation is observed between daily $\delta^{18}\text{O}_P$ and daily maximum air temperature (T_{\max}) based on all samples (Fig. 2b). At first glance, this apparent temperature effect appears to support previous observations, based on global compilations of monthly data (e.g. Araguas-Araguas et al. 2000; Dansgaard 1964; Rozanski et al. 1992, 1993). Furthermore, a temperature effect has some theoretical grounding, since changes in temperature affect the vapour-liquid fractionation factor during condensation (Dansgaard 1964; Merlivat 1978; Merlivat and Nief 1967). However, it should be noted that although this relationship is deemed significant on the basis of the p statistic, an r^2 of

0.02 indicates that T_{\max} explains just 2 % of the variance in $\delta^{18}\text{O}_P$, thus the importance of this relationship should be interpreted with caution. Furthermore, the relationship between T_{\max} and $\delta^{18}\text{O}_P$ does not consistently hold when samples are subset according to month or site, with only the July 2011 monthly subset and 5 out of 17 site-specific analyses producing a regression with $p < 0.001$ (Figs. 3, 5 and 7). As is the case with $P^{0.5}$, the occurrence of significant relationships with T_{\max} varies spatially, with predominantly southern and central sites exhibiting T_{\max} effects (Fig. 7c, d). One of those sites is Wallingford (WALL), for which Darling and Talbot (2003) observed significant positive correlations between daily average air temperature and daily $\delta^{18}\text{O}_P$ for winter (DJF) and autumn (OSN) precipitation (sampled between November 1979–October 1980). The coefficients of those 1979–1980 models are similar to those derived for July 2011 (Fig. 3f). However, Darling and Talbot (2003) did not observe a significant relationship with temperature during summer precipitation at Wallingford, further highlighting the inconsistency of temperature-based regression with daily $\delta^{18}\text{O}_P$. Three sites along the southern English coast exhibit no significant relationship between $\delta^{18}\text{O}_P$ and T_{\max} , whilst another site, Glenmore Lodge in Scotland, does (Fig. 7c,

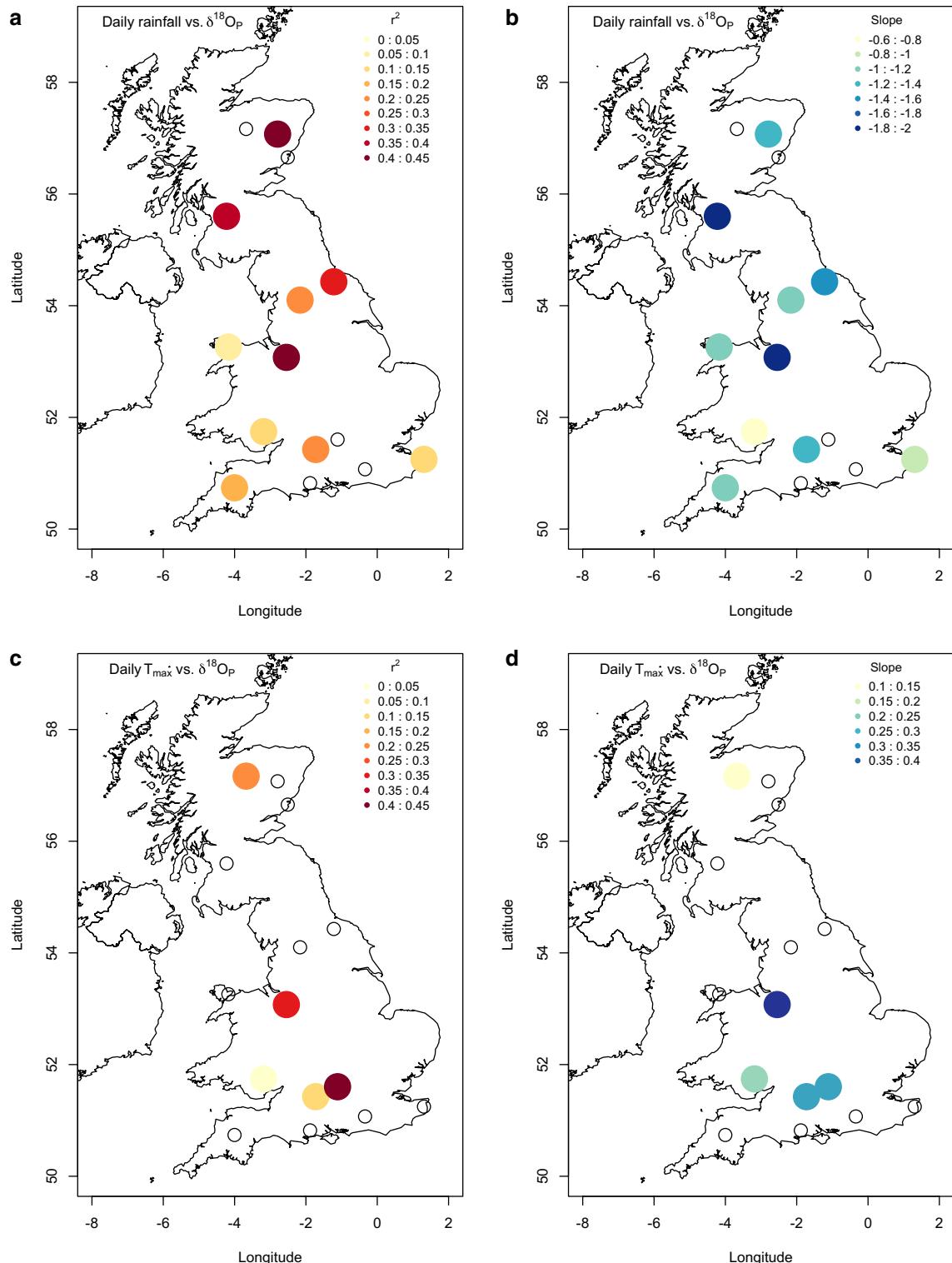
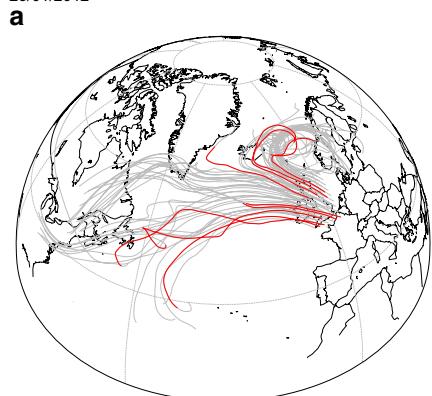


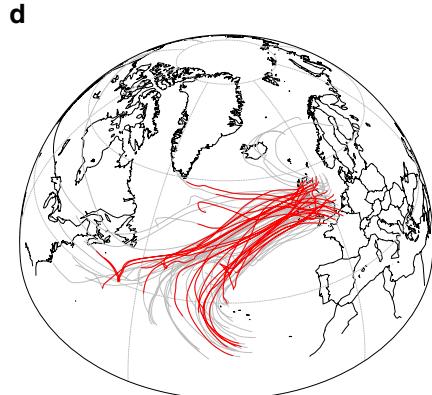
Fig. 7 Map of regression coefficients against daily rainfall amount (square root transformed, $P^{0.5}$) and daily maximum temperature (T_{\max}) for all sites in Table 1, except Edenbridge and Lawkland, for which only one month's data were collected. **a** r^2 statistic for $P^{0.5}$ ver-

sus $\delta^{18}\text{O}_\text{P}$; **b** slope for $P^{0.5}$ versus $\delta^{18}\text{O}_\text{P}$; **c** r^2 statistic for T_{\max} versus $\delta^{18}\text{O}_\text{P}$; **d** slope for T_{\max} versus $\delta^{18}\text{O}_\text{P}$. Open circles indicate the location of sites for which no significant regression was observed for the variable mapped

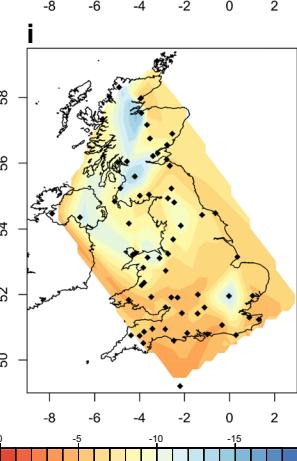
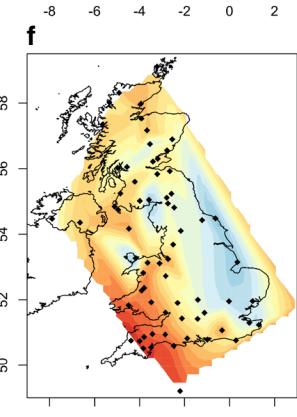
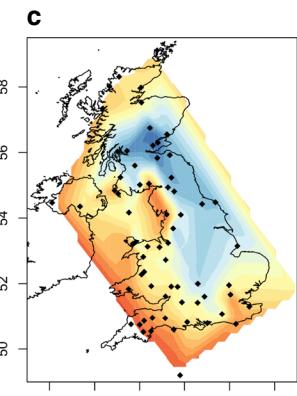
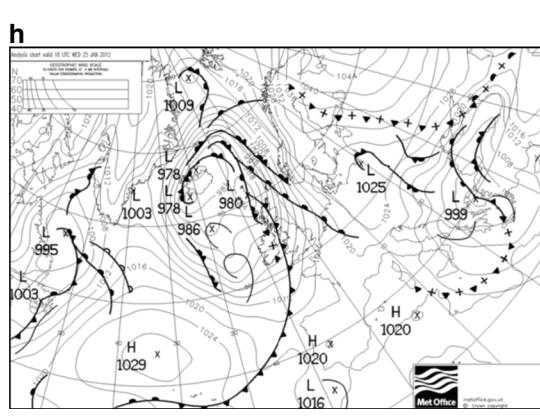
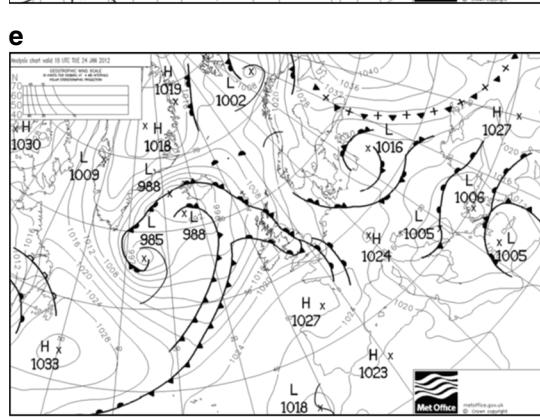
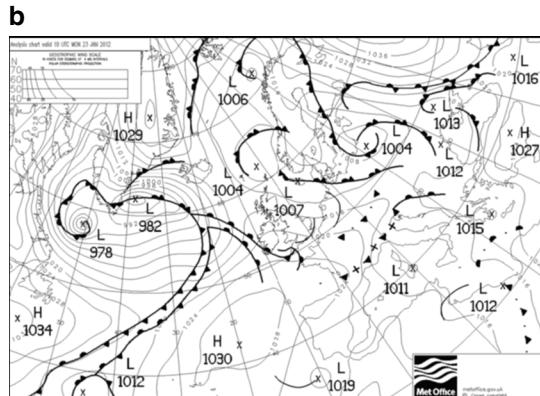
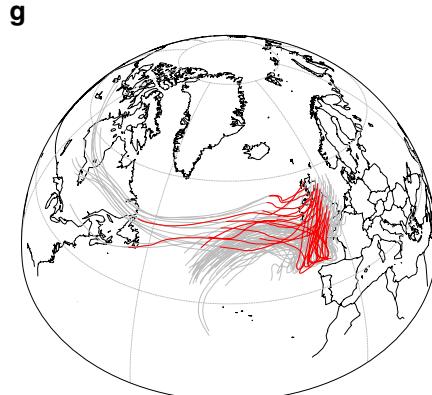
23/01/2012



24/01/2012



25/01/2012



$\delta^{18}\text{O}$ Precip. (%)

Fig. 8 Weather and isotope maps for 23rd, 24th and 25th January 2012. **a, d, g** HYSPLIT 96 h back trajectories for air parcels arriving at a matrix of 63 points across the British Isles. All simulations start at 1500 m.a.s.l. Grey lines indicate all back trajectories, red lines are those whereby significant moisture uptake is estimated. The

length of the red lines indicates the distance from the initial site of moisture uptake. **b, e, h** Daily weather maps, as reported by the U.K. Met Office. **c, f, i** The spatial distribution of $\delta^{18}\text{O}_\text{P}$ based on up to 70 monitoring stations, collecting precipitation water at 9 a.m. the following day

d). It is therefore not possible to make generalisations concerning the spatial patterns in T_{\max} effects upon $\delta^{18}\text{O}_\text{P}$. One potential explanation for the correlation between T_{\max} and $\delta^{18}\text{O}_\text{P}$ when all data are combined (Fig. 2), but the absence of such a correlation when data are subset according to month (Fig. 3), is that both T_{\max} and $\delta^{18}\text{O}_\text{P}$ exhibit strong seasonal components which do not affect regressions on

sub-monthly timescales. However, although both vary seasonally, a causal relationship between T_{\max} and $\delta^{18}\text{O}_\text{P}$ is not certain and their correlation may instead relate to seasonal changes in a variety of conditions, including moisture source, trajectory, weather type and land surface feedbacks (Baldini et al. 2010; Fischer and Treble 2008; Treble et al. 2005).

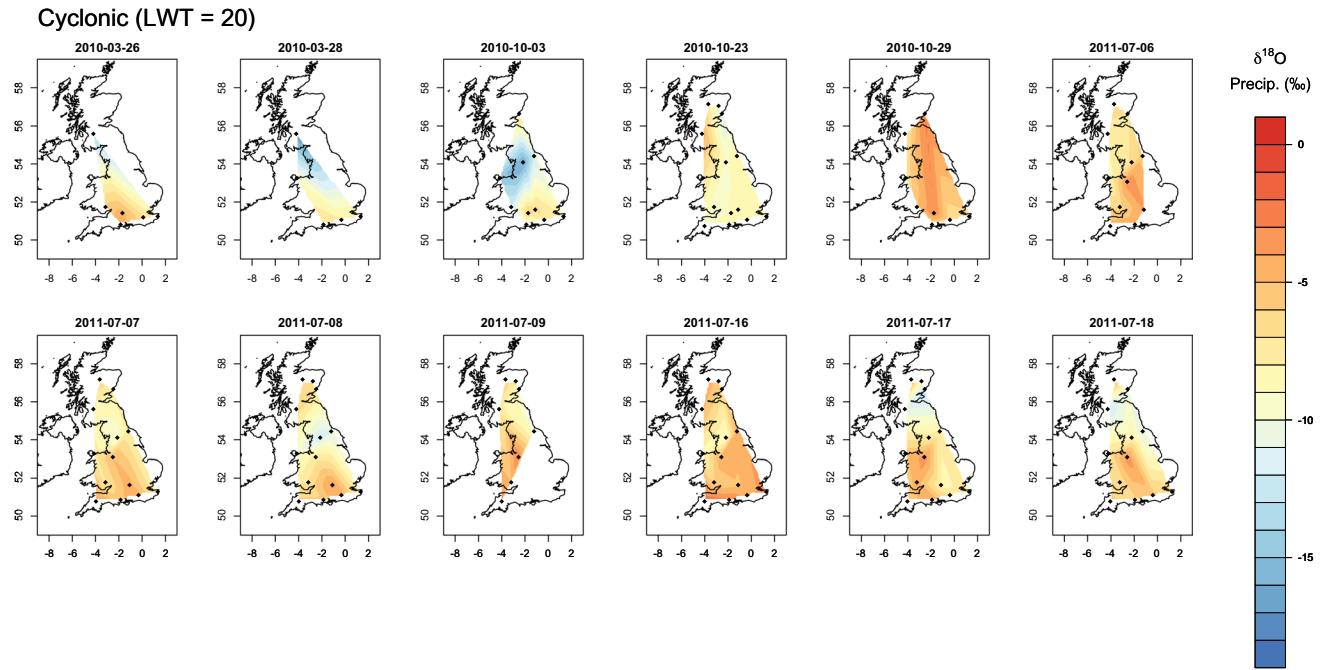


Fig. 9 Spatial pattern of $\delta^{18}\text{O}_P$ occurring on days with a cyclonic weather pattern (Lamb weather type = 20)

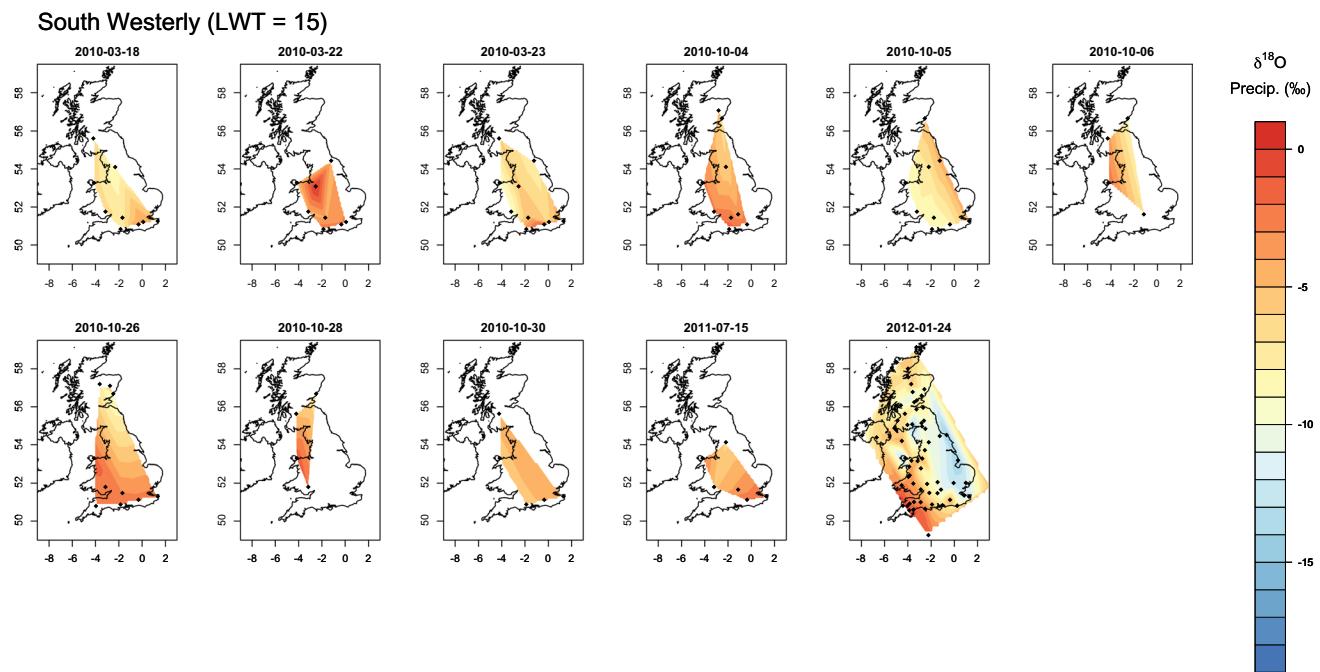


Fig. 10 Spatial pattern of $\delta^{18}\text{O}_P$ occurring on days with a South Westerly weather pattern (Lamb Weather Type = 15)

Changes in the North Atlantic Oscillation (NAO) (Hurrell 1995) would be expected to influence $\delta^{18}\text{O}_P$ as it reflects the position of the westerly jet as a function of air pressure differentials across the North Atlantic, resulting in changes to the source and trajectory of weather systems

and water vapour travelling to the British Isles. However, we observe no significant regression between $\delta^{18}\text{O}_P$ and NAO, either when all data are combined or when data are subset according to month (Figs. 2c; 3g–i). It should be noted that our data do not comprehensively represent

winter (DJF) conditions in the British Isles, the season when NAO is considered to have its largest effect upon $\delta^{18}\text{O}_\text{P}$ (Baldini et al. 2008; Fischer and Baldini 2011). Except for January 2012, for which 3 days sampling is insufficient to examine the role of temporal changes in the NAO, the closest month to winter sampled in this study is March 2010, whereby three sites exhibit significant correlations between NAO and $\delta^{18}\text{O}_\text{P}$: Horsham, West Moors and Edenbridge (for which March 2010 are the only samples collected) (Fig. 6; Figure S1). Otherwise, none of the other sites, or months examined, exhibit significant effects of the NAO upon British $\delta^{18}\text{O}_\text{P}$. A generally weak effect of the NAO would contrast with the conclusions of previous studies that the NAO has a significant, positive relationship with winter $\delta^{18}\text{O}_\text{P}$ (Baldini et al. 2008; Fischer and Baldini 2011). However, the limited coverage of winter rainfall through this study precludes further comment on the effect of NAO upon $\delta^{18}\text{O}_\text{P}$ and further sampling of daily winter rainfall across a spatial gradient is required to fully address this uncertainty.

The spatial and temporal variability in $P^{0.5}$ and T_{\max} coefficients indicates that models derived from individual sites cannot be unilaterally applied, even within relatively small geographical areas such as the British Isles. However, those variable coefficients do provide potential insights into the mechanisms behind the relationship between $\delta^{18}\text{O}_\text{P}$, $P^{0.5}$ and T_{\max} . Rayleigh distillation is a commonly cited simple model for isotope fractionation during water condensation within a cloud (Dansgaard 1964). As a finite parcel of moisture condenses, Rayleigh fractionation predicts that the initial stages of condensation will be associated with relatively little change in $\delta^{18}\text{O}_\text{P}$. For example, condensation of the initial 50 % of vapour is predicted to equate to an $\sim 8\text{‰}$ decrease in $\delta^{18}\text{O}_\text{P}$. By contrast, condensation of the final 20 % of vapour within a parcel is predicted to impart an isotopic depletion of $>30\text{‰}$ (Dansgaard 1964). The degree of rainout from a vapour parcel is therefore likely to be a simple, first order mechanism which results in an inverse correlation between $\delta^{18}\text{O}_\text{P}$ and rainfall amount. In reality, a pure Rayleigh distillation is unlikely to occur within a cloud, due to the resupply of moisture from evapotranspiration and mixing between vapour parcels. Furthermore, a wide range of factors introduce complexity, from changes in the isotopic composition of the initial vapour parcel (reflecting the conditions at its origin and subsequent mixing and phase changes during transit) to the subsequent modification of raindrop $\delta^{18}\text{O}$ due to evaporation and equilibrium exchange with ambient vapour (Celle-Jeanton et al. 2004; Gedzelman and Arnold 1994). Nevertheless, some degree of Rayleigh fractionation of atmospheric vapour remains a viable explanation for some of the observed relationships between $\delta^{18}\text{O}_\text{P}$ and precipitation amount, whereby weather events associated with a high amount of

precipitation become progressively isotopically depleted. The rainout effect is non-linear and likely to result in heterogeneous spatial and temporal patterns. In particular, because rainout occurs as a function of progressive cooling (e.g. due to convective or orographic uplift of a vapour parcel), $\delta^{18}\text{O}_\text{P}$ at a low altitude, coastal sites that more frequently encounter vapour parcels in the initial stages of moisture depletion is less likely to exhibit a marked sensitivity to rainfall amount. By contrast, inland sites encounter vapour parcels that have undergone a larger degree of prior cooling and rainout, meaning that subsequent condensation and precipitation should exhibit steeper isotope effects. For the maritime climate of the British Isles, this pattern of progressive rainout may provide one explanation for the spatial and temporal variability in the relationship between $\delta^{18}\text{O}_\text{P}$ and rainfall amount, whereby $\delta^{18}\text{O}_\text{P}$ is more sensitive to rainout effects in northern Britain, downstream of the direction of the prevailing weather [Fig. 7, e.g. Aboyne (126 m) and Darvel (217 m)]. By contrast, southern, low elevation sites are less likely to be susceptible to rainout effects and therefore may exhibit correlations with other variables, including temperature and changes in oceanic moisture source. This pattern is partially observed when comparing the slope of the daily $P^{0.5}$ versus $\delta^{18}\text{O}_\text{P}$ regression against latitude and altitude (Supplementary Information, Figures S10a and S10b). Overall, these plots suggest a negative association between slope and both latitude and altitude, but there are notable exceptions. One exception is Acton, which exhibits a relatively steep slope despite sitting at a low altitude and latitude. Acton lies in the rain shadow of the Welsh mountains, and is therefore likely to receive moisture that has undergone significant cooling and depletion prior to precipitation at the site. By contrast, the three northernmost sites (Lunan Valley, Aboyne and Glenmore Lodge) all exhibit relatively small slopes, which probably relates to their receipt of moisture from north easterly weather systems off the North Sea, resulting in relatively little prior rainout despite their high latitude. The mechanisms described above are also supported to some extent by the inverse correlations between monthly mean $\delta^{18}\text{O}_\text{P}$ and latitude (Figure S10c and Figure S5) although a similar relationship is not observed with altitude (Figure S10d). It is important to recognise that due to the temporal migration of weather trajectories, spatial patterns in $\delta^{18}\text{O}_\text{P}$ and associated correlations with climate variables are unlikely to remain constant in time. A more detailed elucidation of the mechanisms behind isotope fractionation in daily British rainfall could be achieved using isotope enabled climate models, validated or trained against spatially resolved data such as those presented here (e.g. Langebroek et al. 2011; Risi et al. 2010). Such an analysis is beyond the scope of this paper but would represent a valuable direction for future research.

4.1 Spatial patterns in daily $\delta^{18}\text{O}_\text{P}$ relate to weather types

Analysis of $\delta^{18}\text{O}_\text{P}$ from a highly resolved spatial context provides a means of further deciphering the controls over $\delta^{18}\text{O}_\text{P}$. This is particularly apparent for the 3 days in January 2012 for which 70 sites provided $\delta^{18}\text{O}_\text{P}$ data (Fig. 8). On 23rd January 2012, the passage of an occluded front, with low pressure centres to the east and north west of the British Isles resulted in a complex weather pattern (Fig. 8b). The majority of atmospheric flow approached the British Isles from the southwest, accounting for the gradient of decreasing $\delta^{18}\text{O}_\text{P}$ along that trajectory in southern England and Wales (Fig. 8a). However, the markedly low $\delta^{18}\text{O}_\text{P}$ values measured from central Scotland relate to northerly winds travelling along a trough which developed to the north west of Scotland and brought air masses from near Iceland to the British Isles (Fig. 8b). On the 24th January, 2012, the previous day's complex weather had passed, and eastern England and Scotland experienced South Westerly weather characterised by a warm front passing perpendicular to the east coast, leading to a characteristic east–west $\delta^{18}\text{O}_\text{P}$ gradient suggestive of progressive rainout (Fig. 8d–f). On 25th January 2012, a further cold front arrived in north western Scotland and England and Northern Ireland resulting in moderate isotopic depletion of rainfall in the west, and limited precipitation in the south east (Fig. 8g–i).

The coherency of daily $\delta^{18}\text{O}_\text{P}$ patterns for the British Isles under different weather-types highlights significant potential for developing an isotope-based synoptic typology, which could then be applied to palaeoclimate research. To do so rigorously would require a much more detailed study, however the data obtained to date highlight some encouraging patterns. The rainfall events sampled through this study predominantly occurred during two common weather types: Cyclonic and South Westerly weather types (according to the Lamb Weather Type scheme). Although it is not possible to make conclusive statements on the way these weather types are manifest in daily $\delta^{18}\text{O}_\text{P}$ over the British Isles, there is evidence to suggest that the rotational flow associated with Cyclonic weather types is manifest in a progressive south-north $\delta^{18}\text{O}_\text{P}$ gradient, which curves around a region of maximum isotopic depletion (lowest $\delta^{18}\text{O}_\text{P}$), representative of the epicentre of the cyclonic vortex (Fig. 9). The patterns associated with Cyclonic weather types in the British Isles are similar, if smaller, to those related to cyclonic precipitation in the eastern United States, including storm precipitation (Good et al. 2014; Lawrence and Gedzelman 1996). By contrast we are not yet able to make generalisations concerning the spatial $\delta^{18}\text{O}_\text{P}$ patterns associated with South Westerly weather types, for which the data to date exhibit less coherent patterns in space (Fig. 10). These varying isotopic spatial gradients

associated with South Westerly weather types may reflect complex or heterogeneous rainfall patterns across the country and associated fractionation processes. Within this context, complexities arise owing to variability in the direction of flow and the interaction between numerous air parcels. For example, our data to date are insufficient to identify and evaluate the effect of frontal rainfall upon $\delta^{18}\text{O}_\text{P}$, however it is expected that the passage of, and interaction between, warm and cold fronts would cause significant intra- and inter-daily variability in $\delta^{18}\text{O}_\text{P}$ due to localised changes in air pressure, the altitude of precipitation formation and air temperature (Celle-Jeanton et al. 2001, 2004). Furthermore, a number of weather types are only sporadically captured in our dataset (Figure S9) and future research should therefore attempt to undertake a more detailed and prolonged monitoring project in order to develop a synoptic typology of $\delta^{18}\text{O}_\text{P}$ for the British Isles.

5 Conclusion

Daily monitoring of the oxygen isotope composition of rainfall from multiple sites across the British Isles reveals a relationship between rainfall amount (square root transformed; $P^{0.5}$) and $\delta^{18}\text{O}_\text{P}$, which emerges when all data are combined and when the data are subset according to month or site. By contrast, daily maximum air temperature (T_{\max}) exerts a weaker and less consistent relationship and daily NAO exhibits limited influence, although winter conditions are not extensively sampled in our data. The $P^{0.5}$ and T_{\max} regression coefficients and r^2 vary seasonally, in support of previous observations from Dublin, Ireland (Fischer and Baldini 2011). They also vary spatially, with a greater influence of temperature in southern sites, and greater influence of precipitation amount at northern sites. We propose a simple explanation that these spatio-temporal patterns in regression coefficients reflect the non-linear influence of Rayleigh fractionation and rainout upon $\delta^{18}\text{O}_\text{P}$ as a vapour parcel becomes progressively depleted. Future research involving the integration of climate models with highly resolved data such as ours should be directed at testing this interpretation. By mapping the distribution of daily $\delta^{18}\text{O}_\text{P}$ across the British Isles, we are able to observe patterns that may be characteristic of some weather types, namely Cyclonic weather types under the Lamb classification scheme. These observations are a step towards an improved mechanistic understanding of the climate controls over $\delta^{18}\text{O}_\text{P}$ and a synoptic typology, which will aid attempts to reconstruct past changes in dominant weather patterns.

Acknowledgments This research is heavily indebted to the voluntary weather monitors affiliated with the U.K. Met Office and the Climate Observers Link, whose enthusiasm and diligence in collecting

daily rainfall samples was central to the conduct of this study—thank you. In particular we thank Sarah Dunn, Ruth Brookshaw, Mike Cinderrey, Mike Chalton, John Walker, Jane Corey, David King, Kirsty Murfitt, Richard Griffith, Margaret Airy, Donald Perkins, Malham Tarn FSC Field Centre Staff, Eric Gilbert, Roland Bol, George Darling and Martin Rowley. We thank Joseph Bailey for assistance in producing one of the figures and Bronwyn Dixon for her advice on HYSPLIT modelling. The research was supported by the U.K. Natural Environment Research Council (NERC) through a Fellowship (NE/F014708/1) to JJT. MJ thanks the School of Geography, Planning and Environmental Management at the University of Queensland for a Visiting Fellowship during which some of this manuscript was written. Three anonymous reviewers and the editor Jean Claude Duplessy are thanked for their insightful comments on an earlier draft of this manuscript.

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