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ABSTRACT

With the substantial number of lake sediment $\delta^{18}O$ records published in recent decades, a quantitative, process-based understanding of these systems can increase our understanding of past climate change. We test mass balance models of lake water $\delta^{18}O$ variability against five years of monthly monitoring data from lakes with different hydrological characteristics, in the East-Midlands region of the UK, and the local isotope composition of precipitation. These mass balance models can explain up to 74% of the measured lake water isotope variability. We investigate the sensitivity of the model to differing calculations of evaporation amount, the amount of groundwater, and to different climatic variables. We show there is only a small range of values for groundwater exchange flux that can produce suitable lake water isotope compositions and that variations in evaporation and precipitation are both required to produce recorded isotope variability in lakes with substantial evaporative water losses. We then discuss the potential for this model to be used in a long-term, palaeo-scenario. This study demonstrates how long term monitoring of a lake system can lead to the development of robust models of lake water isotope compositions. Such systematics-based explanations allow us to move from conceptual, to more quantified reconstructions of past climates and environments.

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1. Introduction

Numerous records of past oxygen isotope ($\delta^{18}O$) variability in lakes have been published over the last few decades with interpretations based on conceptual models and/or regression relationships between waters and climatic and/or hydrological variables in the present day. Few palaeostudies take a quantitative approach to $\delta^{18}O$ interpretation (but see Ricketts and Johnson, 1996; Steinman et al., 2010a,b and further examples below), and studies of modern controls on lake $\delta^{18}O$ systems tend to take a spatial approach (e.g. Kebede et al., 2002; Diefendorf and Patterson, 2005; Henderson and Shuman, 2009) or rely on intermittent sampling of one system through short time periods (e.g. Mayr et al., 2007; Kebede et al., 2009; Steinman and Abbott, 2013). Regular monitoring of lake $\delta^{18}O$ variability, producing time series which show variability at different time scales (e.g. Benson, 1994; von Grafenstein et al., 1996; Tyler et al., 2007), and that can therefore be used to test the conceptual ideas behind lake $\delta^{18}O$ interpretation, are relatively rare in the literature.

Common interpretations of past lake $\delta^{18}O$ variability, e.g. in the reviews of Talbot (1990) and Leng and Marshall (2004), suggest that records from hydrologically open systems, often with surface inflows and outflows, reflect the $\delta^{18}O$ value of precipitation (δ_P), whereas records from closed lakes, with no surface outflows and with water loss predominantly from evaporation, will reflect change in the precipitation to evaporation ratio (P:E) at the site. In addition closed lakes will have more positive absolute isotope compositions

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compared to open systems (e.g. Roberts et al., 2008), although Jones and Imbers (2010) showed that this is only true, in a relative sense, for a local geographical area, and isotope compositions will vary for lakes in the same hydrological state based on the local climate and geomorphological conditions. Roberts et al. (2008), in a conceptual model of Mediterranean lake $\delta^{18}O$ variability, suggested that open lakes would show no change in isotope composition for a regional change in water balance, as long as the isotopic value of the precipitation did not change, whereas the magnitude of response to a given shift in P:E would depend on the degree of hydrological closure of the lake system. Terminal, fully closed systems often have a reduced response, compared to more open systems of a comparable size, due to their longer residence times. Lake size has also been discussed as a key control on $\delta^{18}O$ variability (Leng and Marshall, 2004) with extremely small lakes and ponds being potentially very isotopically variable, and evaporation from large lakes having feedbacks on their own isotopic evolution (Benson and White, 1994; Gat, 1995; Gibson et al., 2016).

Where a more quantitative approach has been taken, mass balance models have been used (e.g. Ricketts and Johnson, 1996; Benson and Paillet, 2002; Steinman et al., 2010a,b). These studies suggest that different specific, although related, climatic variables such as relative humidity (Lemcke and Sturm, 1997), P:E (Jones et al., 2005) and water flux (Jones et al., 2007a) may be key to controlling $\delta^{18}O$, particularly in closed systems with a large evaporative component. However these models have rarely, if ever, been tested against long time series of lake water $\delta^{18}O$. If they are robust the models provide an important way into better interpretation of palaeolimnological $\delta^{18}O$ records. Temporally long lake isotope records are unlikely to have been controlled by the same forcings throughout their history, for example due to catchment hydrological shifts caused by landscape change or changing limnological conditions due to basin infilling. Mass balance models allow an understanding of the systematics of a given lake that can be manipulated to take account of such changes, whereas simple regression models cannot fully describe palaeo-conditions based on contemporary settings.

Here we report monthly $\delta^{18}O$ measurements of waters from three lakes in the Attenborough Nature Reserve (Nottingham, UK 52°54′03″N 1°14′05″W) monitored over a five year period. One lake (Main Pond), is hydrologically open whilst the other two (Church and Clifton Ponds), have no surface inflows or outflows and are therefore considered 'closed'. These lakes are within an area of 1 km^2, such that they respond to the same climatic forcings. The records represent the longest and most complete time series of multiple lake water $\delta^{18}O$ variability yet reported. An additional six lakes were sampled for the first two years of the project to provide a regional isotope-hydrology perspective. The full set of lakes is used here to test the hypothesis that lake size and hydrological state will control the absolute isotopic compositions of lake water and the magnitude of isotopic response to common climate forcing. Using these data, along with new data on the local isotopic composition of precipitation and atmospheric moisture and local meteorological data, we test mass balance models for the prediction of lake water $\delta^{18}O$ variability against the five year time series from the closed lake Clifton Pond.

2. Methodology

2.1. Field and laboratory methods

Water samples were taken in leak-proof plastic bottles from the surface waters (upper 3 m) of a number of lakes in the Nottingham region (Fig. 1) between October 2004 and October 2009 with varying sample intervals. In addition rainfall samples were taken from two sites, Watnall and Sutton Bonington, for the first two years of the project (Fig. 1; Jones et al., 2007b) and for the full five years from Keyworth. Meteorological data used here were obtained from an automatic station at the University of Nottingham's Sutton Bonington Campus. Comparison of meteorological data for the three sites, Watnall, Sutton Bonington and Keyworth (Supplementary Figs. 1 and 2; Jones et al., 2007b), shows that there are only small differences in values of temperature, precipitation amount and isotopic composition across the three sites.

Isotope analysis was undertaken at the NERC Isotope Geosciences Facility, British Geological Survey. For oxygen isotope analysis the waters were equilibrated with CO_2 using an Isoprep 18 device with mass spectrometry performed on a VG SIRA. For hydrogen isotope analysis, an on-line Cr reduction method was used with a EuroPyrOH-3110 system coupled to a Micromass Isoprime mass spectrometer. Isotopic ratios ($^{18}O/^{16}O$ and $^{2}H/^{1}H$) are expressed in delta units, $\delta^{18}O$ and $\delta^{2}H$ (‰, parts per mille), and defined in relation to the international standard, VSMOW (Vienna Standard Mean Ocean Water). Analytical precision was ±0.08‰ for $\delta^{18}O$ and ±1.0‰ for $\delta^{2}H$.

2.2. Mass balance models

The model development described below is based on previous work that established lake isotope mass balance theory e.g. Craig and Gordon (1965), Dincer (1968), Gat (1981), Gonfiantini (1986), Gibson et al. (2002), see also Gibson et al. (2016).

The water mass and isotopic mass balance of a well-mixed lake, assuming constant density of water, is given respectively as:

$$\frac{dV}{dt} = P + Qi - E - Qo \tag{1}$$

$$\frac{d}{dt}(V\delta_L) = P\delta_P + Qi\delta_P - E\delta_E - Qo\delta_L \tag{2}$$

where V is the lake volume, t, time, P, precipitation on the lake surface per unit time, E is evaporation from the lake surface per unit time and Q_0 and Q_i are obtained as $Q_x = S_x + G_x$, where S_0 and G_0 and S_i and G_i are the surface and groundwater outflows and inflows respectively, and are measured in the same units as P and E. δ_P, δ_E and δ_L are the isotope values of the precipitation, evaporation and lake waters respectively. The δ notation is the common notation for isotope ratios where it represents the ratio of two stable isotopes, in the case of water either ^{18}O:^{16}O ($\delta^{18}O$) or ^{2}H:^{1}H ($\delta^{2}H$ or δD), relative to a standard, VSMOW for water.

All lakes sampled in this study are shallow (Table 1), well mixed systems, such that use of the equations above is valid.

δ_E is difficult to measure and is therefore usually calculated (e.g. Steinman et al., 2010a,b) using equations based on the evaporation model of Craig and Gordon (1965) such that

$$\delta_E = \frac{\alpha^*\delta_L - h\delta_A - \varepsilon}{1 - h + 0.001\varepsilon_k} \tag{3}$$

where α^* is the equilibrium isotopic fractionation factor dependent on the temperature at the evaporating surface and for oxygen

$$\frac{1}{\alpha^*} = \exp\left(1137T_L^{-2} - 0.4256T_L^{-1} - 2.0667 \times 10^{-3}\right) \tag{4}$$

and for hydrogen

$$\frac{1}{\alpha^*} = \exp\left(24844T_L^{-2} - 76.248T_L^{-1} - 52.61 \times 10^{-3}\right) \tag{5}$$

where T_L is the temperature of the lake surface water in degrees

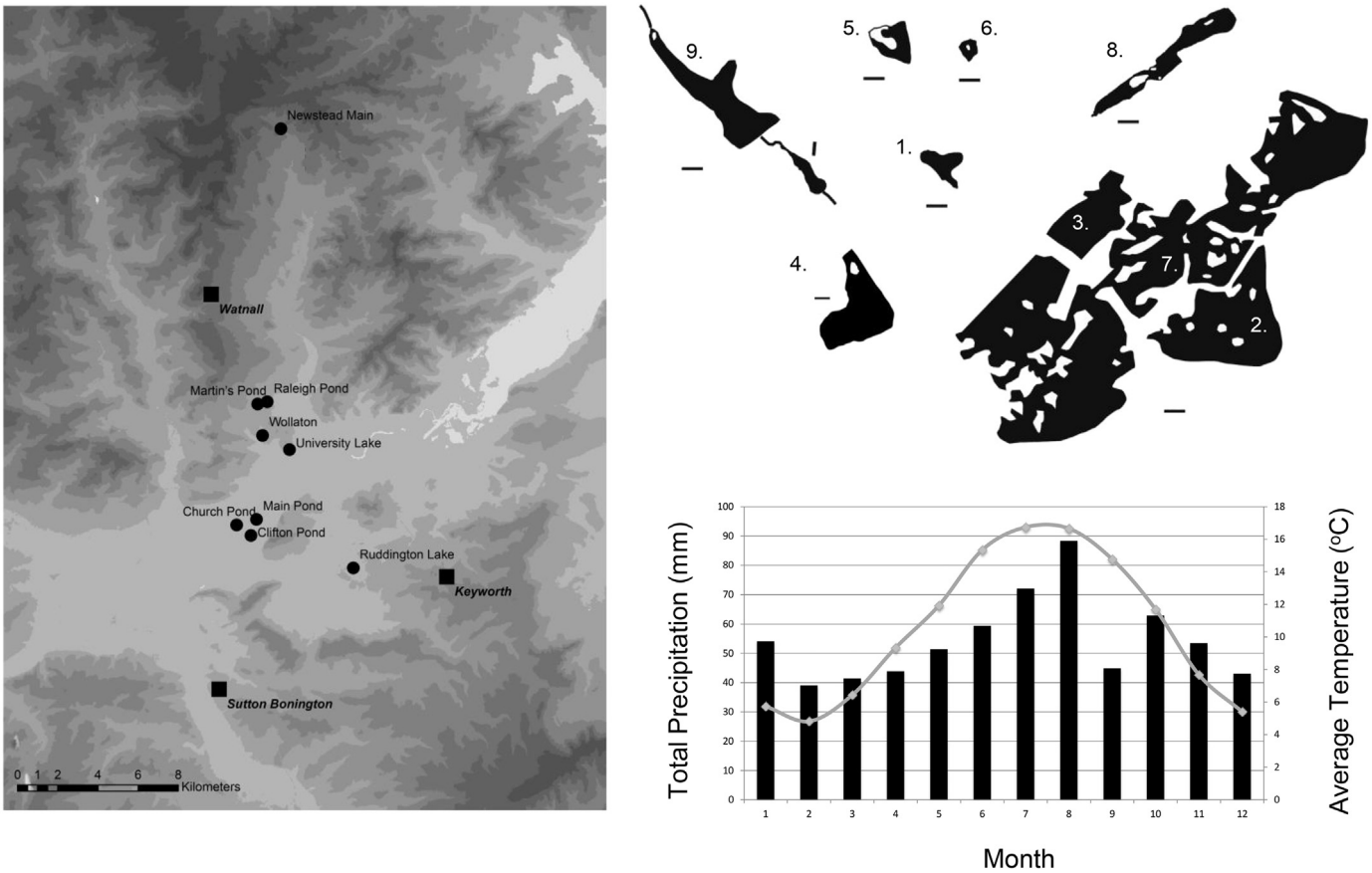

Fig. 1. Relative locations of lakes (circles; see Table 1) and precipitation samples sites (squares) used in this study. Relative lake sizes are shown as are the average monthly temperature and precipitation values from Sutton Bonington through the study period.

Table 1
Summary of physical lake characteristics and lake water oxygen isotope data for multiple lakes in the Nottingham region October 2004–July 2006. For 'Surface Inflow' and 'Surface Outflow' N = no, Y = Yes, S = seasonal.

Site number	Lake	Area (m^2)	Dmax (m)	Surface inflow	Surface outflow	Average $\delta^{18}O$ (‰)	$\delta^{18}O$ stdev (‰)	Average $\delta^{18}O$ (‰)	$\delta^{18}O$ stdev (‰)
1	Ruddington Lake	18,200	2.0	N	N	−0.5	1.0		
2	Clifton Pond[a]	185,600	3.3	N	N	−1.6	0.6	−1.5	0.6
3	Church Pond[a]	95,800	5.2	N	N	−1.6	0.7	−1.6	0.6
4	Wollaton[a]	82,700	2.4	Y	S	−3.0	1.1	−2.7	1.2
5	Martin's Pond[a]	13,800	1.1	Y	S	−5.9	1.5	−5.5	1.4
6	Raleigh Pond[a]	5900	Unknown	Y	N	−5.9	0.5	−5.8	0.6
7	Main Pond[a]	241,200	5.0	Y	Y	−6.2	0.9	−6.3	0.9
8	University Lake	57,900	1.4	Y	Y	−6.5	1.3		
9	Newstead Main	95,800	2.6	Y	Y	−7.5	0.5		

[a] These higher resolution data sets were resampled to the same resolution, ~60 days, as the other data sets for this analysis to compare like with like. Shaded boxes show average $\delta^{18}O$ values and range for the full data sets.

Kelvin (Majoube, 1971). h is the relative humidity normalised to the saturation vapour pressure at the temperature of the air water interface and ε_k is the kinetic fraction factor; for $\delta^{18}O$ ϵ_k has been shown to approximate $14.2\ (1-h)$ and $12.5\ (1-h)$ for δ^2H (Gonfiantini, 1986). δ_A is the isotopic value of the air vapour over the lake and $\varepsilon = \varepsilon^* + \varepsilon_k$ where $\varepsilon^* = 1000\ (1-\alpha^*)$.

Following Jones and Imbers (2010) we develop a semi-analytical equation from those above to calculate the isotopic value of lake waters (δ_L) at a given time, $t + \Delta t$, based on the value of δ_L at time t, and the inputs and outputs from the lake between t and $t + \Delta t$.

We expand the left-hand side of Eq. (2) and then substitute Eq. (1) into it:

$$\frac{d}{dt}(V\delta_L) = V\frac{d\delta_L}{dt} + \delta_L\frac{dV}{dt} = \delta_L(P + Qi - E - Qo) + V\frac{d\delta_L}{dt} \tag{6}$$

and then re-write, such that δ_L dependences are explicit. Firstly, δ_E is expressed as a function of δ_L such that

$$\delta_E = A\delta_L + C \tag{7}$$

where, for Equation 3$A = ((\alpha^*)/(1 - h + 0.001\ \varepsilon_k))$ and $C = -((h\delta_A + \varepsilon)/(1 - h + 0.001\ \varepsilon_K))$

Taking Eqs. (2) and (6) and replacing δ_E using Eq. (7) we have:

$$V\frac{d\delta_L}{dt} + \delta_L(P + Qi - E - Qo) = \delta_P(P + Qi) - E(A\delta_L + C) - Qo\delta_L \quad (8)$$

Rearranging all terms in Eq. (8) then leads to:

$$V\frac{d\delta_L}{dt} = \delta_P(P + Qi) - EC - \delta_L(P + Qi - E(1 - A)) \quad (9)$$

In order to ease the notation in the following equations, we define λ and β as: $\lambda = (P + Qi)\,\delta_P - EC$ and $\beta = P + Qi - E\,(1 - A)$ such that equation (9) can be rewritten as:

$$V\frac{d\delta_L}{dt} = \lambda - \beta\delta_L \quad (10)$$

Note that λ and β are calculated from experimental data and therefore take different values for each time step.

Equations (1) and (2) define the dynamics of a lake in a continuous form (as dt is infinitesimal), however, field measurements are usually recorded in discrete time steps e.g. $\Delta t = 1$ month, as in the case of the datasets used here. Hence, we assume that dV/dt can be adequately approximated as equal to the change of volume over 1 month and all other variables are also input to the model as rates per month.

Integrating equation (10) obtains an expression for the evolution of δ_L with time. At this stage we introduce a first approximation by assuming a constant value for V for each month; consistent with constant values of P and Qi etc. over each month. The following parameterisation for V is used:

$$\overline{V} = \frac{V_{30\,th} + V_0}{2} \quad (11)$$

where V_{30th} is the total volume on the last day of each month, and V_0 is the initial volume on the first day of the month.

Integration of Eq. (10) after considering the approximation in equation (11) results in:

$$\ln\left(\frac{\lambda - \beta\delta_{L0}}{\lambda - \beta\delta_L}\right) = \frac{\beta}{\overline{V}}\Delta t \quad (12)$$

where δ_{L0} is the initial isotopic composition (i.e. at the beginning of each month) and $\Delta t = 1$ for each monthly step of our model. Finally exponentials of both sides of Eq. (12) give an expression for δ_L:

$$\delta_L = \frac{1}{\beta}(\lambda - (\lambda - \beta\delta_{L0})\,exp\left(-\frac{\beta}{V}\right) \quad (13)$$

3. Results and discussion

3.1. Multiple sites 2004–2006

For the common time period October 2004 to September 2006 lake water isotope values were measured from lakes with a range of hydrological states (Table 1; Fig. 2) from completely closed, with no surface or discernible groundwater inflow or outflow (i.e. Ruddington Lake), to lakes which were considered completely open, as they are, in effect, wide sections of river e.g. Newstead Main Pond, Main Pond. Average $\delta^{18}O$ compositions were most positive in Ruddington Lake (−0.5‰) and in other lakes with no surface inflow or outflow (Table 1), and the most negative $\delta^{18}O$ compositions were found in the open systems (e.g. −7.5‰ for Newstead Main pond). Lakes with seasonal outflows, that are seasonally open or closed, had intermediate values, e.g. −5.8‰ for Martin's Pond. Mean values remained the same, within error, independent of the sampling interval used to calculate the mean (Table 1). Isotopic time series measured at both weekly and two-monthly intervals in the lakes showed smoothed patterns relative to the highly variable weekly δp measurements from Keyworth (Fig. 2).

The lake water $\delta^{18}O$ and $\delta^{2}H$ values define a local evaporation line (LEL) which confirms that the lakes with more positive average δ_L values are more evaporated (Fig. 3). The intercept of the LEL described by Ruddington, Wollaton and Raleigh Ponds (Fig. 3) with the Meteoric Water Line (MWL) for Keyworth over the same period should reflect the weighted average of precipitation at the

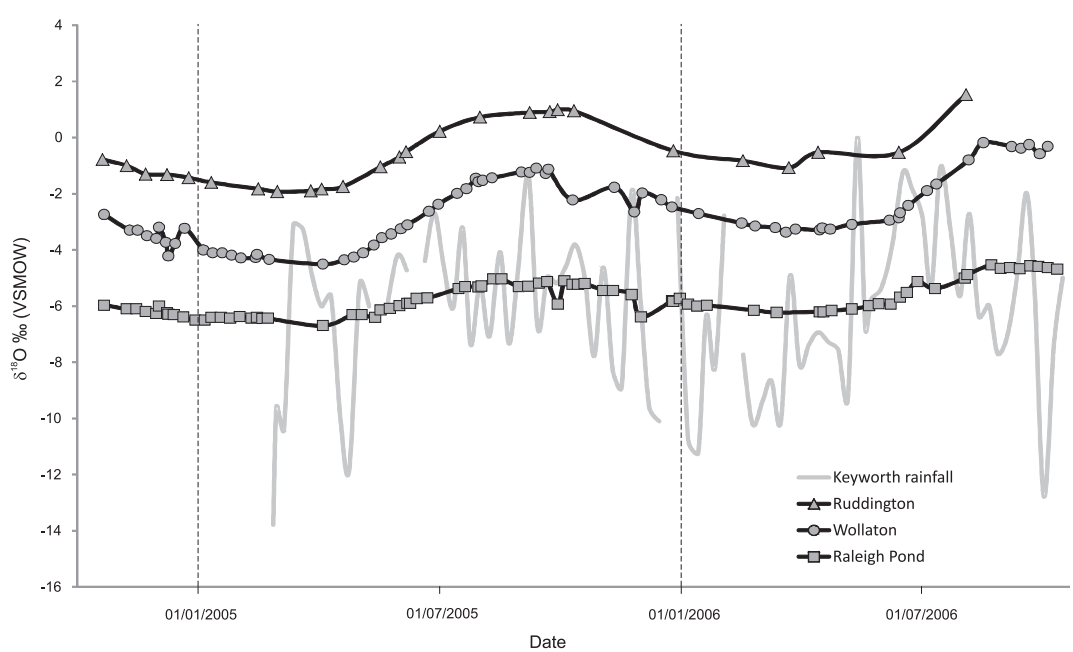

Fig. 2. Time series of lake $\delta^{18}O$ variability from Ruddington (triangles), Wollaton (circles) and Raleigh Pond (squares) compared to measured δp variability from Keyworth (grey line). Vertical dashed lines mark calendar years.

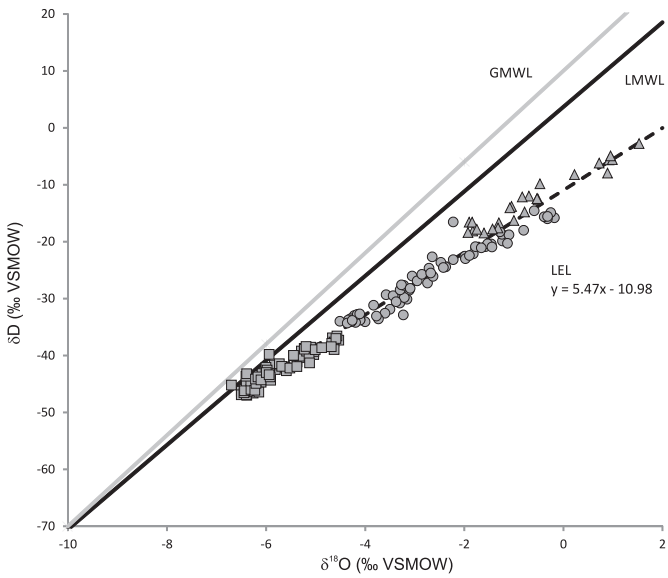

Fig. 3. $\delta^{18}O$:δD cross plot for the lake data shown in Fig. 2 (using the same symbols). The Local Meteoric Water Line (LMWL) for Keyworth, for the same time period, is shown (solid black line) alongside the Global MWL (solid grey line). The Local Evaporation Line (LEL) is also shown.

site i.e. the average isotopic composition of rain supplying the lake. The intercept of the LEL and MWL is more negative ($\delta\ ^{18}O = -7.4‰$) than the weighted average composition of precipitation, −6.6‰ for Keyworth and −7.2‰ and −6.4‰ for Watnall and Sutton Bonington respectively (Jones et al., 2007b). This suggests that winter and autumn rainfall, which have more negative isotopic values, may be more influential on lake water $\delta^{18}O$ values than annual weighted δp values. Henderson and Shuman (2009) also noted the importance of seasonality on lake inputs from their work in the western USA.

The range of lakes analysed here allow us to investigate the effect of lake size and degree of hydrological closure on mean $\delta^{18}O$ values and variability. T-tests (two-tailed heteroscedastic) show that the mean $\delta^{18}O$ values for lakes with and without inflows ($p = 0.00037$) and outflows ($p = 0.031$) are significantly different, with lakes without inflows or outflows being more positive, but their variability (standard deviation) through the period of analysis is not significantly different. There are no strong relationships between lake size and isotope value, although maximum lake depth explains 39% of the lake isotope variability ($p = 0.099$), with shallower lakes being more variable (Supplementary Fig. 3).

3.2. Attenborough lakes 2004–2009

The Attenborough Nature Reserve, a series of former gravel pits on the River Trent floodplain (Supplementary Fig. 4) is situated at the confluence of the Rivers Trent and Erewash. The lakes were left to fill naturally after gravel extraction ended in 1960 (Main Pond), 1965 (Church Pond) and 1968 (Clifton Pond). All three lakes are small (<25 ha) and shallow (maximum depth 5.2 m) with a well-mixed water column. Main Pond is an open water body, located third along a chain of interconnected lakes supplied by the River Erewash (catchment size 206 km^2). Water flows from the three interconnected lakes into the River Trent through weirs situated in the first lake and Main Pond. When the water level in the River Trent and interconnected lakes rises, the first outflow stagnates and forces the majority of inflowing water to leave the lakes through Main Pond. Church and Clifton Ponds are usually isolated from each other and all of the other lakes.

Near monthly sampling occurred at Attenborough between October 2004 and October 2009, resulting in a long time series of lake $\delta\ ^{18}O$ variability (Fig. 4). Both open and closed systems followed a seasonal pattern for the first two years, with more positive values in summer and more negative values in winter, but this pattern was not evident during the final three years of the study. Substantial negative shifts occurred in the closed lake records in the summer of 2007 and in both the closed and open systems during the winter of 2007/2008 (Fig. 4) associated with flooding events at the site. The historic meteorological record for Sutton Bonington shows that the period March 2007–March 2008 had the highest recorded total rainfall for that period since records began in 1961 (Cross et al., 2014).

4. Mass balance modelling

Based on equation (13) a model was developed to test the validity of such mass balance models through comparison to observations of lake water isotope variability from Clifton (Supplementary Data) and Church Ponds. No model was produced from Main Pond as it tracks δp. Inputs for the model are from field measurements of lake waters, lake levels and meteorological conditions or parameterisation based on our physical understanding of the hydrology of the system as described in Fig. 5 and below.

4.1. Hydrological mass balance

V: is calculated from the sum of water in and out of the lake (P + Qi − E − Qo), which is assumed to have constant surface area. Initial lake volume was based on calculations following field bathymetric surveys and lake area calculations from maps, aerial photos and ground GPS surveys. Given surface area would change with volume in reality and the actual lake is not a simple cuboid, the model lake area and volume have to be adjusted slightly from field measurements to achieve a stable system. Here we use a lake with the same initial volume as Clifton and Church Pond (250,000 m^3 and 113,000 m^3) but a slightly smaller surface area (15,0000 m^2 compared to 185600 m^2 and 90,000 m^2 compared to 95,800 m^2).
P: from measured rainfall at Sutton Bonington (Fig. 4) and lake area.
Qi: the sum of surface (Si) and Groundwater (Gi) into the system. Understanding groundwater conditions is important when attempting to model lake hydrology (e.g. Almendinger, 1993; Donovan et al., 2002). From our understanding of the groundwater systems at Attenborough (Fig. 5; Humphrey, 2011) groundwater recharges the sand and gravel aquifer and flows under a local gradient of around 0.001 towards the River Trent. An unknown contribution to baseflow from the underlying Mercia Mudstone deposits is assumed to be minimal. The groundwater levels in the sands and gravels are controlled by complex interactions between surface water bodies, dominantly the River Trent, and recharge from up-catchment. A variable thickness of silt and clay (of low permeability, k) lines the lake bottoms and restricts the connection between the lake and the groundwater. Groundwater level variations in the sands and gravels create a highly temporally variable hydraulic gradient into and out of the lake which governs the groundwater inflow and outflow.

On a monthly basis the lake may both receive water from, and lose water to the sand and gravel deposit. Based on this conceptual model (Fig. 5) we assume that Gi is constant, and Si is zero, apart

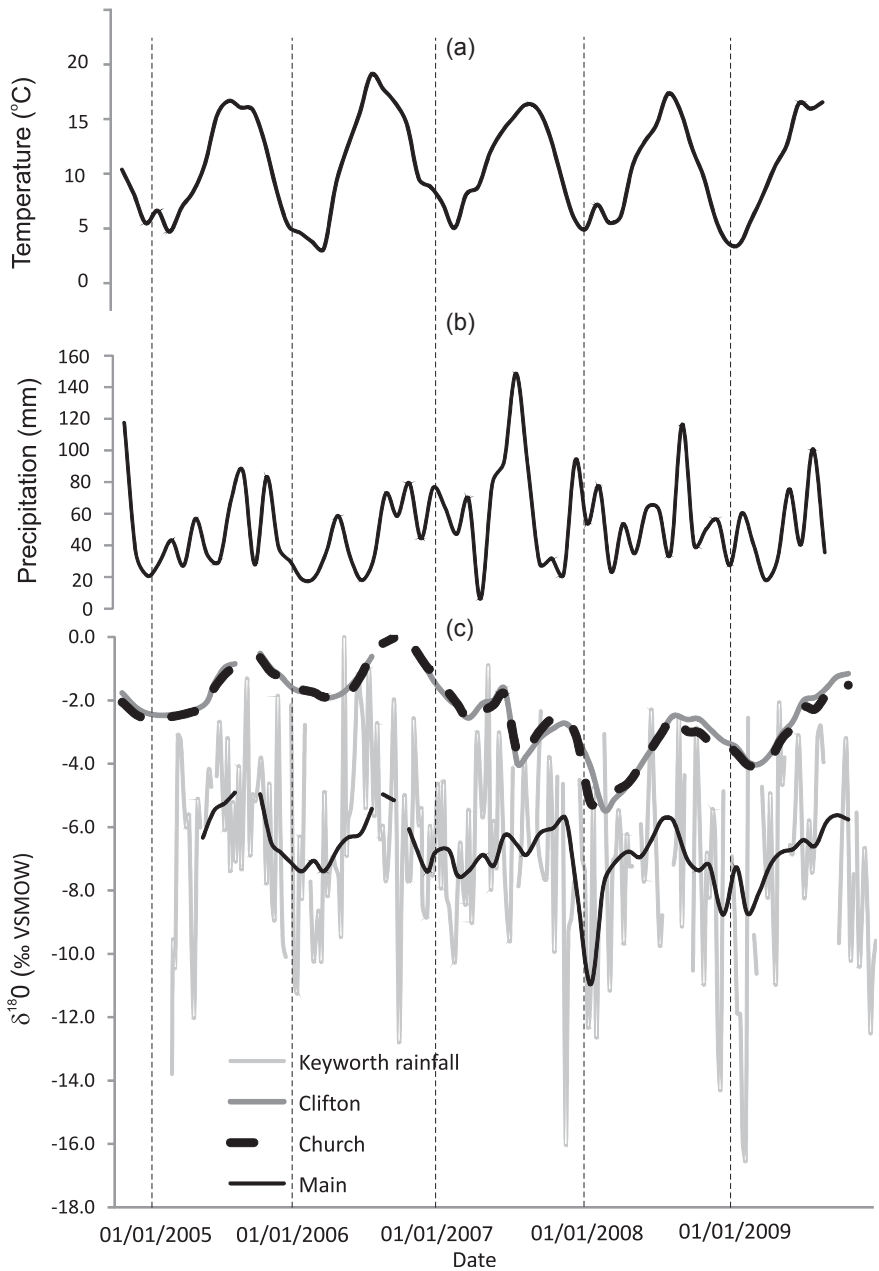

Fig. 4. Average air temperature (a) and precipitation (b) variability through the study period at Sutton Bonington (30 day means) and (c) $\delta^{18}O$ time series for Church (dashed black line) and Clifton (dark grey line) ponds and Main pond (lower black line) compared to Keyworth rainfall (lower grey line). Vertical dashed lines mark calendar years.

from during flooding events. These are defined in the model by thresholds in absolute (*thr_a*) and effective rainfall (i.e. precipitation – evaporation; *thr_ef*), such that if the thresholds are exceeded surface inflow occurs and the lake fills to maximum depth (see Supplementary Data for details).

Values for these thresholds and the amount of groundwater inflow were found by optimising the model output to the measured data using the Microsoft Excel Solver add-in, such that Gi, *thr_a* and *thr_ef* were varied until the Normalised Root Mean Square Error of a comparison between the modelled and observed δ_l values was minimised, and then values adjusted to ensure the lake volume was in steady state i.e. followed the long term trend of observed lake levels.

Qo: the sum of surface (So) and Groundwater (Go) outflow. Simple mass balance shows that Qi must be greater than Qo for lakes to exist at Attenborough as E (see below) is greater than P. Our conceptual model (Fig. 5) indicates that sub-monthly groundwater head variations drive groundwater in and out through the base of the ponds, depending on the relative head gradient between pond and aquifer, but that at monthly time steps this is likely to be more or less constant. So is known to be zero, and Go is optimised (as with *thr_a*, *thr_ef* and Gi) by tuning the model to the data (see above). In months following surface inflow, as described above, the model is balanced by removing the equivalent volume of water.

E: Evaporation is often calculated rather than measured. There are numerous methods for calculating E, based around the equations of Penman (1948), and varying on the meteorological information available for a given site. To investigate the impact of different evaporation equations on lake isotope mass balance models here we used a number of approaches in turn.

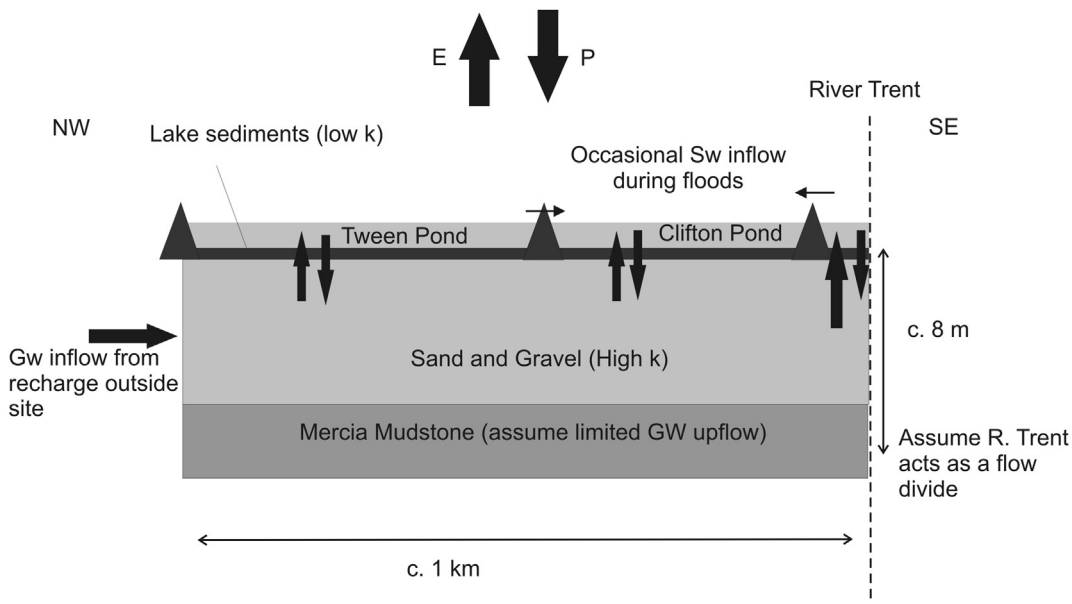

Fig. 5. Conceptual hydrogeological model of Clifton Pond (after Humphrey, 2011). k = permeability.

Valiantzas (2006) describe simplified versions of the Penman (1948) equation:

$$E = 0.051(1-a)Rs\sqrt{(T+9.5)} - 0.188(T+13)((Rs/Ra) - 0.194) \times (1 - 0.00014(0.7Tmax + 0.3Tmin + 46)^2 \sqrt{(RH/100)}) + (0.049(Tmax + 16.3)(1 - (RH/100)(au + 0.536u) \quad (14)$$

where a, the albedo (0.08 for open water), Rs is the incoming solar radiation ($MJ/m^2/d$) and Ra is extraterrestrial solar radiation ($MJ/m^2/d$) calculated based on the latitude and Julian day at the site. au, is a wind speed coefficient and has a value of 1 and u is wind speed at 2 m height (m/s).

If wind speed data are unavailable Valiantzas (2006) gives the following equation as an estimate of Penman Evaporation:

$$E = 0.047Rs\sqrt{(T+9.5)} - 2.4(Rs/Ra)^2 + 0.09(T+20)(1 - (RH/100)) \quad (15)$$

Linacre (1992) describe a formula for calculating E when solar radiation data are not available such that:

$$E(mm/day) = \left[0.015 + 4 \times 10^{-4}\, T_a + 10^{-6} z\right] \times [480\,(T_a + 0.006z)/(84 - A) - 40 + 2.3\,u\,(T_a - T_d)] \quad (16)$$

where T_a is air temperature (°C), z = altitude (m), A = latitude, T_d = dew point temperature = 0.52 $T_{a\,min}$ + 0.60 $T_{a\,max}$ − 0.009 $(T_{a\,max})^2$−2 °C.

4.2. Isotope mass balance

δp: taken from the measured values from Keyworth (Fig. 4).

δ_A: the isotope value of atmospheric water was also measured at Keyworth between January 2006 and June 2009. The relationship between these values and values of δp (Supplementary Fig. 5) were used for values of δ_A in the model such that: for $\delta^{18}O$ $\delta_A = 0.30\delta p - 12.89$ and for δ^2H $\delta_A = 0.23\delta p - 97.7$.

δ_{Qi}: Following our groundwater investigations (summarised in Fig. 5), which include isotopic measurements of groundwater that show similar values to those from Main Pond and the River Trent (Humphrey, 2011) we assume that isotopic values of groundwater express the long term average rainwater composition due to diffusion/dispersion except in locations where strong groundwater–surfacewater exchange is occurring. δ_{GWi} is taken as the long term average of δp through the study period here, with surface input, when occurring, taken as the value of δp for that month.

δ_{Qo}: is the isotopic value of the lake water (δl) in that month.

δ_E: to check that Equation (3) gives sensible values for δ_E in the Nottingham region a theoretical regional end member 'index' lake was investigated (e.g. Gibson et al., 2016).

Lakes in a constant climatic and geomorphological setting will approach a steady state, such that

$$\frac{d}{dt}(V\delta_L) = 0 \quad (17)$$

$$\frac{d}{dt}V = 0 \quad (18)$$

Two end member scenarios then exist and for terminal, closed systems ($Q_o = 0$) the mass balance will approach

$$P\delta_P + Q_i\delta_P = E\delta_E \quad (19)$$

where δ_E therefore equals δ_P, and via equation (3) we can then calculate end member values for δ_L for lakes in the Nottingham region, taking average conditions for the first 2 years of this study (2005 and 2006).

To allow this we need a value of lake water temperature, compared to air temperature such that values of h, α_{eq} etc. can be calculated. To do this measured lake temperatures for Clifton Pond were compared to air temperatures from Sutton Bonington (Supplementary Fig. 6). As observed elsewhere (e.g. Jones et al., 2005) lake water temperatures are generally warmer than

average air temperatures, especially in the spring and summer months.

Calculated values of δ_E for such a terminal lake system lie on the Nottingham LEL, at the most enriched end of the range of isotope values from Ruddington Lake (Supplementary Fig. 7), as would be expected as this is a lined pond, protected from any groundwater influence.

4.3. Model performance and sensitivity tests

Taking our model parameters as above, in the first instance using Clifton Pond and Equation (14) for calculating evaporation, and optimising the values of Gi, Go, *thr_a* and *thr_ef* by comparing model output to measured data, a model is produced that explains 71% of the variability in measured lake water isotope variability (Fig. 6). The physical plausibility of the model has been additionally checked by comparing measured to modelled lake level (Fig. 6). The optimised values of Gi, Go and thresholds of P and effective P vary depending on the equation used for the calculation of E (Table 2) but are all of a similar magnitude and the resulting models explain approximately the same degree of the data variability.

A very similar output is seen for the Church Pond Model (Supplementary Fig. 8). δ_L values from Church Pond and Clifton Pond are very similar (Fig. 4) despite their different sizes (Table 1). The Church Pond model, when optimized to the data, has precipitation threshold values the same as for Clifton Pond, but the values of groundwater inflow and outflow are smaller than in the nearby larger lake (18,500 and 16,700 m^3/month respectively), as would be expected. This is the only difference required in the model to produce the same lake water isotope values for two adjacent lakes of different size. Given the similarities in the models we continue discussion using only the Clifton Pond model.

We can test the sensitivity of the model to investigate the dominant controls on the lake isotope system. This is particularly important for the optimised values of Gi and Go. If the groundwater values are both reduced or increased the mean value and standard deviation of the modelled lake waters changes, with mean values and lake variability decreasing as groundwater values increase (Table 3). If either Gi or Go is reduced and the other increased the model quickly breaks down i.e. lake level values increase or decrease beyond the possible thresholds of the lake. This shows that for a given lake, in a given climate setting, there is only a narrow window of Gi and Go values that can successfully produce a lake model with water isotope values that would be found in measured field experiments.

Table 2
Values of optimum Qi and Qo factors (giving the best fit with recorded δ_l data) for different calculations of E (see section 4.1 for details). These values when Area = 15,000 m^2 and Vo = 250,000 m^3.

Parameter	E from Eq. (13)	E from Eq. (14)	E from Eq. (15)
Gi (m^3/month)	30,764	27,892	39,223
Go (m^3/month)	28,067	26,188	34,037
P threshold (mm)	120	120	120
P-E threshold (mm)	70	70	50
Data explained (%)	71	74	73

To observe model sensitivity to other variables the model was run using Equation (14) for evaporation and holding E, P, T, H and δ_P constant respectively, using the average values of these parameters through the period October 2005 to September 2009 i.e. four annual cycles (Fig. 7). When T and H were held constant they were also held constant in the calculation for E. The sensitivity analysis shows that the δ_L model for Clifton Pond requires both changing evaporation and precipitation to produce the variability observed from field measurements; as would be expected from an evaporating lake basin. When P is constant most of the intra-annual variability is maintained, whereas the longer term trends in the data are more apparent in a model where E is constant but P varies. This sensitivity analysis also suggests that in such evaporating lakes, relatively short term variability in δ_P around the long term average has little impact on values of δ_l, although changes in long term average values of δ_P offset the long term average δ_l values with otherwise similar trends (Supplementary Fig. 9).

Also of interest is the substantial change in the model output when temperature and relative humidity are held constant. In these cases the model requires resetting in terms of the ground and

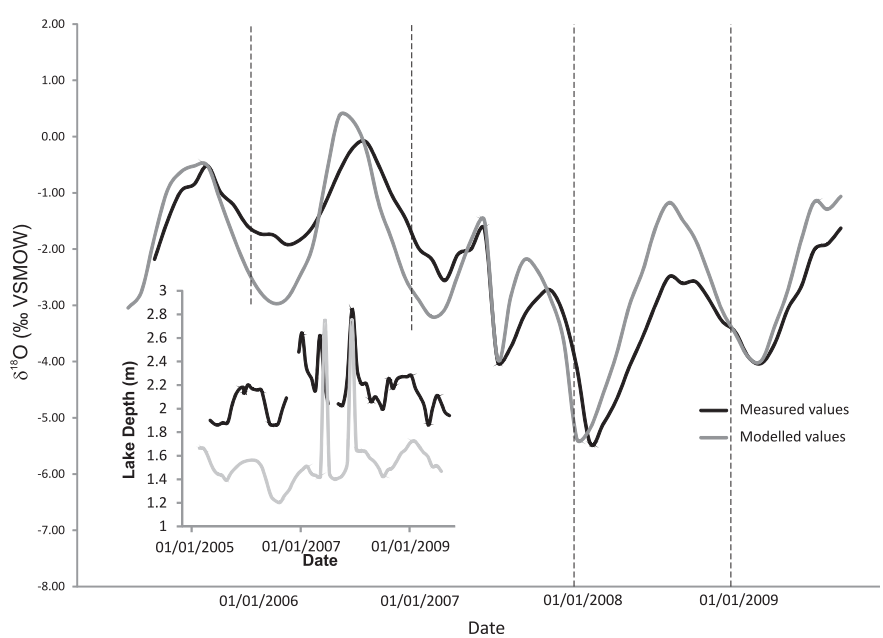

Fig. 6. Data (black line) model (grey lines) comparison for Clifton Pond. Vertical dashed lines mark calendar years. The insert shows a comparison of the modelled (grey line) and measured (black line) lake level.

Table 3
Impact of varying groundwater values in the Clifton Pond model on lake water isotope values (mean ± 1 standard deviation).

Best fit model	GWi and GWo +10%	GWi and GWo +20%	GWi and GWo −10%	GWi and GWo −20%
−2.29 ± 1.26	−2.47 ± 1.23	−2.62 ± 1.20	−2.10 ± 1.30	−1.89 ± 1.35

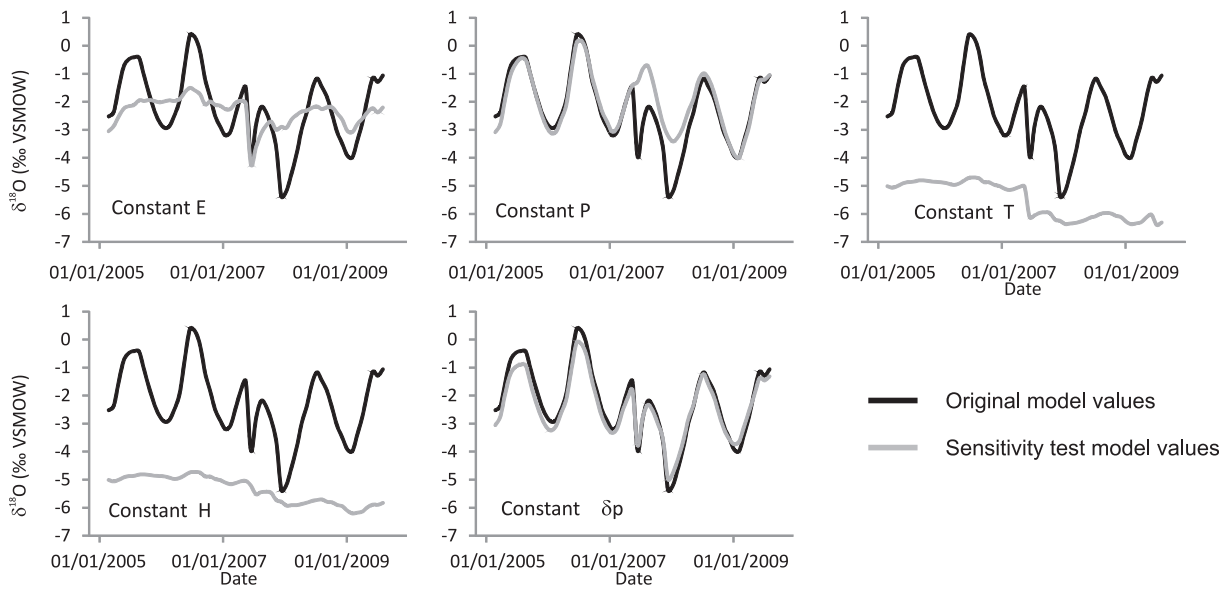

Fig. 7. Sensitivity tests of the mass balance model showing model response if different controls are held constant at mean values through the five year model run (grey line) compared to the original model (black line).

surface water constants; otherwise the lake increases in volume such that the model fails i.e. evaporation is too low. This highlights the importance of seasonal differences in evaporation relative to precipitation in keeping Clifton Pond in its current hydrological 'steady state'. The similar shape of the model curve from constant T and H, compared to constant E, also highlights the importance of these 2 parameters in controlling evaporation in the model (Supplementary Fig. 10). The issues of seasonality must therefore be carefully considered if running models with longer time steps e.g. annual.

4.4. Modelling the past

If such models are to be used to help interpret palaeoenvironmental records then ideally they need to be based on as few unknowns as possible. For closed lakes where δ_L compositions

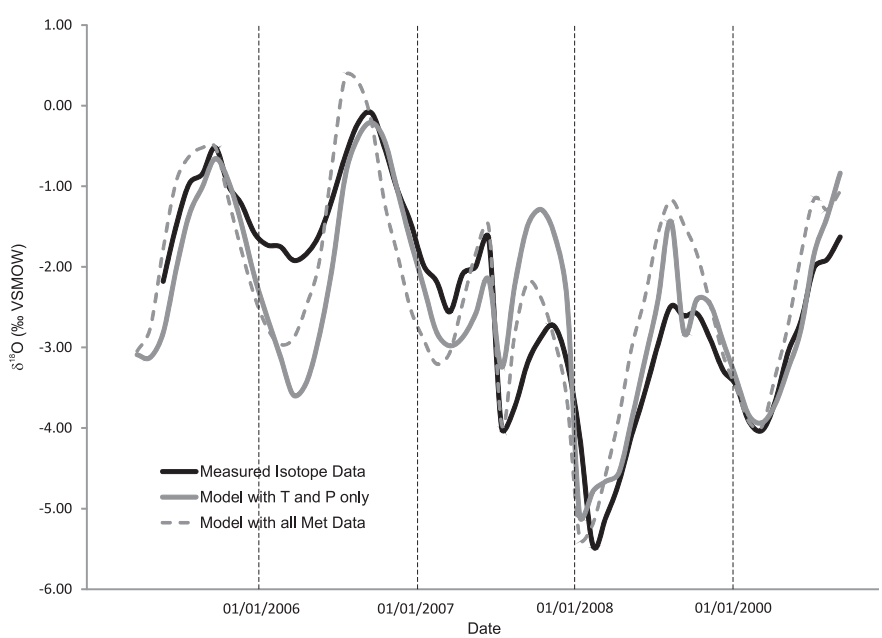

Fig. 8. Data (black line) model (solid grey lines) comparison using T and P as the only independent variables to force the model. Model output using all measured variables (i.e. as in Fig. 6) is shown for reference (dashed grey line).

rely on the balance between inputs and outputs the minimum number of required unknowns in the system is likely to be two, a precipitation-related and evaporation-related variable as suggested by previous modelling work on closed systems (e.g. Jones et al., 2005) and our sensitivity analysis above.

The Clifton Pond model was run using only two climate variables, average temperature and precipitation, such that other variables (relative humidity, δ_P, minimum and maximum temperatures) were calculated from their relationships with average temperature and precipitation amount through the 5 year sampling period. E was calculated using Equation (16) with a constant windspeed from the average value through the study period. The resulting lake isotope model (Fig. 8), with optimum Gi and Go values of 37,158 and 33,081 m^3/month respectively and *thr_a* = 105 and *thr_ef* = 50, explains 67% of the measured lake water isotope variability, highlighting both the seasonal and longer term patterns in the data with a performance almost as strong as the model run using the full suite of measured meteorological variables (Fig. 6).

To test the model's ability to produce long (>100 years) time series we forced this latter model, requiring only temperature and precipitation to run, with the Central England Temperature (CET) and England and Wales precipitation (EWP) series from the Hadley Centre (Parker et al., 1992; Alexander and Jones, 2001), between 1766 and the present. It was necessary to vary the ground and surface water parameters, such that a hydrologically stable lake was produced with isotopic variability similar to that observed at Clifton and the other lakes in the Nottingham region through this study (Fig. 9). Over the period of the model, average monthly precipitation was greater than average monthly evaporation such that groundwater outflows (33,081 m^3/month) had to be greater than groundwater inflows (32,058 m^3/month) to balance the model. Precipitation thresholds were also changed to keep the model in a steady enough state (*thr_a* = 120 mm and *thr_ef* = 100 mm) and surface inflows were set not to fill the lake, only to add additional water. Interestingly the model output shows that intra-annual lake

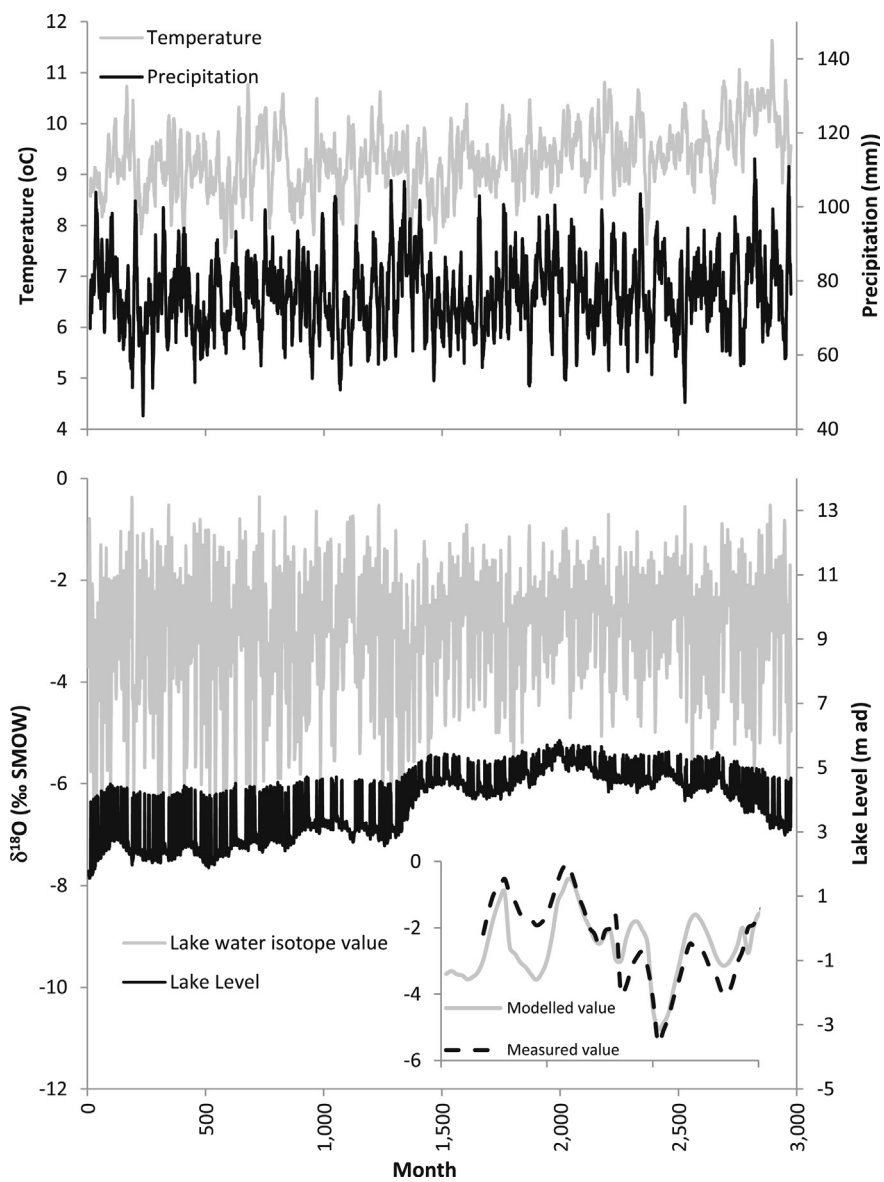

Fig. 9. Lower Panel: δ_L variability in a model lake, based on Clifton Pond, forced using the Hadley Centre CET and EWP datasets (grey line) between 1766 and 2013; the depth of the model lake is also shown (black line). The inset compares model lake isotope variability (grey line) with the measured variability in δ_L in Clifton Pond (dashed black line) over the sampling period 2004–2009. Upper Panel: 12 month running mean through the CET and EWP monthly data used to force the lake isotope model.

variability increases with lower lake levels in the model (Fig. 9) following the relationship observed from the modern Nottingham lakes (Supplementary Fig. 3) and previous modelling studies (Steinman et al., 2010a,b). Overall, as would be expected from an evaporating lake system, lake levels rise as temperatures fall, with a resulting shift to more negative lake water isotope compositions.

An identical lake to Clifton would not be expected, as the CET and EWP data sets are not centred on Nottingham, comparison of CET and EWP to temperature and precipitation data from Sutton Bonington through the monitoring period shows temperatures to be similar ($SB = [0.95 \times CET] + 0.7$; $r^2 = 0.9$) and Sutton Bonington to have generally less precipitation than the EWP ($SB = [0.44 \times EWP] + 18.0$; $r^2 = 0.25$). However, these data do show that it is possible to develop a lake model that can produce monthly δ_L time series over long time periods, allowing us to further analyse past records of long-term lake isotope variability; this will form the basis for future work.

5. Conclusions

The use of the long monitoring data has shown that hydrologically open lake systems (when $\delta^{18}O$ and δ^2H lie on the MWL) closely track rainfall isotope variability and that closed or intermittently closed systems, with substantial evaporation loss, can be successfully modelled using a mass balance approach, given two independent climate variables (i.e. P and E) and a quantified understanding of the local hydrology.

All lakes sampled in this study are shallow, well mixed systems and therefore need relatively simple mass balance models to explain them. Deeper, stratified systems, or large systems with significant surface inflow may have spatial variability in their δ_L systems which require more complex modelling, as would systems with a significantly older groundwater component. However, the success of the models in predicting the δ_L compositions in the Nottingham lakes highlights the potential for this type of approach in a range of applications such as improving understanding of groundwater–surface water interactions and in the interpretation of proxy records of past environmental change.

Key to the success of the model is the monitoring of the lakes and a sound conceptual understanding of their hydrological controls, allowing known–unknowns in the model to be robustly parameterised. The mass balance equations provide a good basis for a quantitative assessment of most small lake sites. However, without accompanying monitoring a full understanding of how, for example, groundwater or flooding impacts the model is difficult to achieve. Where this is possible such systematics based interpretations of lake isotope variability will allow us to move from conceptual, to more robust interpretations of past climate and environmental variability.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.quascirev.2015.09.012.

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