

A long-term study of stable isotopes as tracers of processes governing water flow and quality in a lowland river basin: the upper Thames, UK

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Abstract: A long-term study of O, H and C stable isotopes has been undertaken on river waters across the 7000 km² upper Thames lowland river basin in the southern UK. During the period, flow conditions ranged from drought to flood. A 10-year monthly record (2003–2012) of the main River Thames showed a maximum variation of 3‰ ($\delta^{18}\text{O}$) and 20‰ ($\delta^2\text{H}$), though inter-annual average values varied little around a mean of -6.5‰ ($\delta^{18}\text{O}$) and -44‰ ($\delta^2\text{H}$). The $\delta^2\text{H}/\delta^{18}\text{O}$ slope of 5.3 suggested a degree of evaporative enrichment, consistent with derivation from local rainfall with a weighted mean of -7.2‰ ($\delta^{18}\text{O}$) and -48‰ ($\delta^2\text{H}$) for the period. A tendency towards isotopic depletion of the river with increasing flowrate was noted, but at very high flows ($>100\text{ m}^3/\text{s}$) a reversion to the mean was interpreted as the displacement of bank storage by rising groundwater levels (corroborated by measurements of specific electrical conductivity). A shorter quarterly study (October 2011 – April 2013) of isotope variations in 15 tributaries with varying geology revealed different responses to evaporation, with a high inverse correlation between $\Delta^{18}\text{O}$ and baseflow index (BFI) for most of the rivers. A comparison with aquifer waters in the basin showed that even at low flow, rivers rarely consist solely of isotopically unmodified groundwater.

Long-term monitoring (2003–2007) of carbon stable isotopes in dissolved inorganic carbon (DIC) in the Thames revealed a complex interplay between respiration, photosynthesis and evasion, but with a mean inter-annual $\delta^{13}\text{C}$ -DIC value of $-14.8 \pm 0.5\text{‰}$, exchange with atmospheric carbon could be ruled out. Quarterly monitoring of the tributaries (October 2011 – April 2013) indicated that in addition to the above factors, river flow variations and catchment characteristics were likely to affect $\delta^{13}\text{C}$ -DIC. Comparison with basin groundwaters of different alkalinity and $\delta^{13}\text{C}$ -DIC values showed that the origin of river baseflow is usually obscured.

The findings show how long-term monitoring of environmental tracers can help to improve the understanding of how lowland river catchments function.

KEY WORDS stable isotopes; baseflow index; dissolved inorganic carbon; groundwater; rainfall; river response; specific electrical conductivity

INTRODUCTION

The use of O, H and C stable isotopes applied to river catchment studies has a long pedigree (Kendall and McDonnell, 1998). An outstanding early success using $\delta^{18}\text{O}$ was the discovery

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that much so-called ‘event water’ in streams was not in fact derived from recent rainfall, but instead consisted of water displaced from soil storage (Sklash and Farvolden, 1979). Further insights from $\delta^{18}\text{O}$ and/or $\delta^2\text{H}$ included the calculation of mean water residence times, identifying flow sources and flowpaths, and recognition of evaporative fractionation (e.g. Stewart and McDonnell, 1991; Hogan and Blum, 2003; Burns and McDonnell, 1998), and the field continues to progress (McGuire and McDonnell, 2015). Many of these studies were carried out on relatively small test catchments no more than a few tens of km^2 in area and often with steep gradients and therefore hydraulic heads. In parallel with these small catchment studies, some large river systems covering a range of topographies were investigated using stable isotopes (e.g. Ramesh and Sarin, 1992; Cameron et al., 1995; Pawellek et al., 2002) but not in the same detail as the small systems for obvious logistical reasons. The same situation was largely the case for $\delta^{13}\text{C}$ in the dissolved inorganic carbon (DIC) system: small scale (e.g. Amiotte-Suchet et al., 1999) versus large scale (e.g. Aucour et al., 1999).

Since those earlier studies demonstrating the value of stable isotopes as environmental tracers, their use has become a standard technique to gain more knowledge of catchment processes (Schulte et al., 2011). Increasingly, too, mesoscale catchments are being investigated (e.g. Ogrinc et al., 2008; Speed et al., 2010; van Geldern et al., 2015). Yet the isotope records from these tend to be limited in scope and duration because of resource constraints, and therefore provide only a partial view into catchment processes. In particular, there has been little investigation of rivers on the multi-year scale (Halder et al., 2015), which has meant there is limited knowledge of how isotopic responses vary over a range of flow conditions. Long-term monitoring of the River Thames and its upper tributaries has provided an opportunity to do this in a mesoscale catchment with varied geology. Specific areas of interest were variations due to evaporation, response over drought to flood conditions, relationship to baseflow index, and river–groundwater interaction (using $\delta^{18}\text{O}$ and $\delta^2\text{H}$), and characterising the dissolved inorganic carbon baseline (using $\delta^{13}\text{C}$ -DIC). A subsidiary aim was to compare the merits of isotopic tracers against those of the simple tracer SEC (specific electrical conductivity) in a lowland river basin.

In addition to contributing to a better understanding of catchment functioning, the stable isotope baseline for the upper Thames basin established by this study is likely to inform fields such as archaeology, ecology and palaeoenvironmental studies (previous examples from the

area include Candy et al., 2007; Hughes et al., 2014; Keatings et al., 2002; Versteegh et al., 2013).

STUDY AREA AND METHODS

Study area

The study area covers about 7000 km² of the western Thames basin (Fig. 1). It extends from the perennial headwaters in the Cotswold Hills to Runnymede, some 200 km downstream of the river's source but lying above the major river water intakes (abstracting up to 50% of flow) which serve the population of Greater London. From the source to Runnymede amounts to approximately 85% of the length of the non-tidal portion of the Thames, which ends a further 30 km downstream at Teddington Weir in the SW of the Greater London area.

River gradients within the basin are generally very low: for example, the main Thames falls only some 60 m between Cricklade and Runnymede (Fig 1).

2011 Census figures indicate that the area drained by the upper Thames contains of the order of 2 M people. This, combined with a comparatively low average annual rainfall of ~690 mm/yr and an estimated potential evapotranspiration rate of ~580 mm/yr (Jolley and Wheeler, 2007), means that the area is prone to drought, thus making highly desirable any additional information relevant to water resource management.

Hydrogeology

The geology of the upper Thames basin (Fig. 1) consists of Mesozoic and Cenozoic sedimentary rocks with a regional dip towards the SE. The NW of the area is dominated by Lower, Middle and Upper Jurassic rocks, mainly oolitic limestones and clays, from which rise all the significant tributaries upstream of Wallingford. Downstream of this point, the Thames flows over Chalk strata (Upper Cretaceous) until the river runs onto the Palaeogene at Maidenhead. Between Wallingford and Runnymede the main tributaries are mostly on the southern bank and may derive wholly from the Chalk or Palaeogene, or a mixture of both.

The flow direction of rivers and streams in the upper basin is largely controlled by geological structure.

Within the upper Thames basin, the Jurassic Oolite and Cretaceous Chalk tend to be productive aquifers. The Jurassic and Palaeogene clays on the other hand have limited aquifer properties, often functioning largely as aquicludes. The consequence of this is that the rivers arising from the different strata have proportionately different inputs of groundwater. In the case of short streams fed predominantly by limestone or Chalk, e.g. the Coln and Pang, nearly all their flow consists of groundwater. At the other extreme, for clay vale rivers like the Ray and The Cut, less than half their mean flow derives from groundwater. For each of the tributaries, the groundwater contribution can be relatively quantified in terms of the Baseflow Index (BFI), which is based on hydrograph separation techniques (Marsh and Hannaford, 2008). Table 1 reports these together with mean river flows based on gauging records obtained from the UK Environment Agency (EA). Also included are a series of BFI and flow values for gauging points along the Thames.

The relationship between geology and hydrology across the Thames basin is examined in greater detail in Andrews (1962) and Bloomfield et al. (2011).

Datasets acquired

At the core of the present study is a 10-year monthly record of $\delta^{18}\text{O}$, $\delta^2\text{H}$ and a 5-year record of $\delta^{13}\text{C}$ -DIC (dissolved inorganic carbon) collected from the Thames at Wallingford, Oxfordshire, effectively the outlet point for river discharge from the predominantly Jurassic strata (mainly limestones and clays) of the upper part of the upper Thames basin (Fig. 1). This is supplemented by a quarterly record of $\delta^{18}\text{O}$, $\delta^2\text{H}$ and $\delta^{13}\text{C}$ -DIC variations at various points along a 175 km length of the river and from 15 tributaries, carried out over the course of a 18-month period which proceeded from drought to flood conditions. The data are completed by a 1-year monthly $\delta^{18}\text{O}$, $\delta^2\text{H}$ record from two sites covering the reach where the Thames crosses the Chalk (a source of groundwater discharge to the river), an 18-month record of $\delta^{18}\text{O}$, $\delta^2\text{H}$ and $\delta^{13}\text{C}$ -DIC from the foot of the study area at Runnymede, and a 22-month record of $\delta^{18}\text{O}$, $\delta^2\text{H}$ and $\delta^{13}\text{C}$ -DIC from the River Thame, which has the lowest BFI of any of the more significant upper Thames tributaries (rivers with a mean flowrate $\geq 3 \text{ m}^3/\text{s}$, Table 1).

Any consideration of isotopes in the upper Thames basin also requires a record of the rainfall input to the catchment. Monthly precipitation samples have been collected at Wallingford for isotope analysis since 1983 (Darling and Talbot, 2003; the IAEA-WMO WISER database (<https://nucleus.iaea.org/wiser>)), and this collection continued throughout the monitoring period.

Site selection, sampling and analysis

Locations of all sampling points referred to in this study are shown on the map in Fig. 1. Sampling points were usually selected to be as close as practicable to the foot of each tributary's catchment bearing in mind that repeat visits would be necessary (hence, for example, the Cherwell was sampled upstream of the suburbs of Oxford. Proximity to a gauging point was also a consideration for rivers like the Thames, which is gauged well above its confluence with the Thames. Thames sampling sites were chosen to be roughly equidistant down the river. In all cases care was taken to collect samples from the free-flowing river rather than shallow areas or backwaters. For the long-term Thames monitoring, samples of river water were collected at Wallingford Bridge on the final day of each calendar month. Separate samples were taken in glass bottles for $\delta^{18}\text{O}$ / $\delta^2\text{H}$ (28 mL) and $\delta^{13}\text{C}$ -DIC (60 mL). Standard analytical methods were used (CO_2 equilibration for $\delta^{18}\text{O}$, zinc reduction for $\delta^2\text{H}$, acidification for $\delta^{13}\text{C}$ -DIC, followed by IRMS measurement on a VG-Optima mass spectrometer). Results are expressed in permil (‰) with respect to VSMOW (for $\delta^{18}\text{O}$ and $\delta^2\text{H}$) and VPDB (for $\delta^{13}\text{C}$ -DIC). Analytical precisions were $\pm 0.1\text{‰}$ ($\delta^{18}\text{O}$), $\pm 1\text{‰}$ ($\delta^2\text{H}$) and $\pm 0.2\text{‰}$ ($\delta^{13}\text{C}$ -DIC). Specific electrical conductivity (SEC, referenced to 25°C) and pH-alkalinity were measured in the laboratory at BGS Wallingford.

A similar analytical process was applied to the shorter set of monthly samples collected from the River Thames at Dorchester and from the Thames at Runnymede. For the set of tributary samples collected quarterly, details of sampling locations are contained in Table 1. SEC and pH-alkalinity were measured in the Wallingford laboratories of BGS and CEH respectively. O, H and C stable isotopes were determined as above at BGS Wallingford until June 2012 and at BGS Keyworth (NIGL) thereafter.

Monthly rainfall samples were collected on the final day of each calendar month from the CEH Wallingford met site. Samples were measured for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ using the analytical methods outlined above.

All the data are reported in the supplementary tables S1 to S6 (see Supporting Information).

RESULTS AND DISCUSSION

Rainfall–river relationship

The term ‘rainfall’ as used here includes precipitation falling as snow (a very low proportion of the total). Results of rainfall analysis from January 2003 to May 2013 are given in Table S1. A δ -plot (Fig. 2) for the ten years 2003–2012 shows a very wide range of compositions ($\sim 13\text{‰}$ in $\delta^{18}\text{O}$, $\sim 105\text{‰}$ in $\delta^2\text{H}$) defining a meteoric line with the form

$$\delta^2\text{H} = 7.45 \delta^{18}\text{O} + 5.87 \quad (n = 119, r^2 = 0.96) \quad (1)$$

which is, as would be expected for a temperate climate, close to the form of the Global Meteoric Water Line (GMWL) of Craig (1961):

$$\delta^2\text{H} = 8 \delta^{18}\text{O} + 10 \quad (2)$$

Values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are highly correlated. The amount-weighted mean of rainfall over the years 2003–2012 is -7.22‰ $\delta^{18}\text{O}$ and -47.9‰ $\delta^2\text{H}$, very similar to the mean for the previous 20 years (-7.25‰ and -50.0‰ respectively; Darling and Talbot, 2003). Yearly amounts ranged from 435 mm in 2011 to 797 mm in 2012, coincidentally juxtaposing two years of very different rainfall input towards the end of the long-term monitoring period at Wallingford and during the quarterly monitoring of the tributaries. Indeed the whole period 2003–2012 was notably volatile in annual rainfall amount, though the decadal mean was only $\sim 4\%$ below the 20th Century average (T.J. Marsh, pers. commun.).

The strong correlation between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ means that trends over time need be considered for one isotope only. For this study, $\delta^{18}\text{O}$ will be used ($\delta^{18}\text{O}_p$). Fig. 3a depicts inter-annual statistics which show that despite large annual ranges, mean $\delta^{18}\text{O}_p$ values vary rather little. There is an inverse correlation with rainfall amount ($r^2 = 0.52$).

Figure 3b shows the seasonal rainfall statistics. The mean values show the expected cyclic structure typical of annual rainfall over much of the world (Rozanski et al., 1993), though the isotopic enrichment of the summer half-year is less well defined than the depletion of the winter half-year. Overall there is no correlation with rainfall amount ($r^2 = 0.00$), though this conceals a highly-developed inverse trend for the months of April-August ($r^2 = 0.92$), also noted for the previous 20 years in Darling and Talbot (2003). This presumably reflects the continuing dominance over the summer half-year of convective rainfall, which is more likely than frontal rainfall to give rise to the ‘amount effect’ on isotope ratios (Dansgaard, 1964).

Thames-Wallingford results are reported in Table S2. On a δ -plot with the rainfall data for comparison it is apparent that the river has a restricted range but still varies by some 3‰ in $\delta^{18}\text{O}$ and 20‰ in $\delta^2\text{H}$ (Fig. 2). The data give a regression line of the form

$$\delta^2\text{H} = 5.33 \delta^{18}\text{O} - 8.92 \quad (n = 120, r^2 = 0.74) \quad (3)$$

which possesses a slope characteristic of surface water evaporation at a relative humidity of ~77% (Clark and Fritz, 1997), a value lying within the long-term mean for the Thames basin of 76–82% (Jenkins et al., 2009). There is however a tendency for the slope to vary seasonally, with the 8 out of 12 months which have good inter-annual correlations ($r^2 > 0.75$) revealing slopes ranging progressively from 5.1 in the summer to 8.0 in winter. This would be consistent with observations of seasonal changes in slope noted for other rivers (e.g. Kendall and Coplen, 2001)

The mean isotopic composition of the river water samples is -6.51‰ and -43.6‰ $\delta^2\text{H}$. This is slightly isotopically enriched compared to the rainfall weighted mean. (While rainfall is only monitored at one site, i.e. Wallingford, this lies approximately at the centre of the upper Thames basin and therefore should be reasonably representative of conditions across the study area, bearing in mind the subdued relief of the catchment.) The difference between the river and rainfall averages is further evidence for a small degree of evaporative enrichment in

the river water, particularly in the summer. In this connection it may be noted that while the Thames is free of water impoundments or low-flow augmentation, the river does have flow-limiting weir/lock combinations on average every 4.6 km, and there may also be limited interaction between the river and flooded former gravel extraction pits in its floodplain.

River flow conditions

Stable isotopes As with rainfall, the good overall $\delta^{18}\text{O}$ – $\delta^2\text{H}$ correlation for river water allows the use of a single isotope, in this case ‘ $\delta^{18}\text{O}_r$ ’, when considering processes other than evaporation. Examination of the Thames-Wallingford data in Table S2 shows that the inter-annual mean values vary little, with $\delta^{18}\text{O}_r$ in a narrow band of $\pm 0.3\text{‰}$ about a value of -6.5‰ (Fig. 3c). However, overall ranges can vary by a factor of two, from 1.3‰ in 2007 and 2012 to 2.6‰ in 2003 (values typical of mid-latitude rivers irrespective of catchment size or river length: Halder et al., 2015). Seasonally, mean values show the river reaching a maximum depletion in February and December, and maximum enrichment in August (Fig. 3d). The slightly less-depleted value for January mimics exactly the shape of the rainfall isotope curve of Fig. 3b. This may imply a time of response of the river to rainfall over the winter half-year of <1 month, but displacement of floodplain storage (discussed further below) complicates this interpretation and it is probably safer to say that no clear response time can be deduced from comparison of the seasonal curves. This is not surprising for a mixed-BFI lowland river basin whose transit time (the mean travel time of water from entry to discharge) would be expected to be of the order of a decade by comparison with data from tritium-based studies compiled in McGuire and McDonnell (2006) and Stewart et al. (2010). Regrettably there is no tritium record for the Thames to test this.

Study of the data in Tables S1 and S2 suggests that river flow tends to vary inversely with $\delta^{18}\text{O}_r$ ($r^2 = 0.70$). Flow was at its lowest in the autumn of 2003, and the Thames at Wallingford most isotopically enriched. Although similar low flows occurred in 2005, 2010 and especially 2011, $\delta^{18}\text{O}_r$ never again became so enriched. A comparison of the Day’s Weir and Thame flow data (obtained courtesy of the EA) shows that the Thame reached a particularly high percentage ($>20\%$) of the combined flow in the autumn of 2003; its relatively low BFI implies a greater potential for summer-early autumn evaporative

enrichment. Perhaps the most notable flow events in the period 2003–2012 were the single flood peak of July 2007 (summer flooding on the Thames is rare) and the multiple flow peaks of winter 2012–13 following unusually high amounts of rainfall from April 2012 onwards (September excepted). In the case of the July 2007 flood, there was no obvious response of the river isotope composition, presumably because the monthly weighted mean rainfall of -6.0‰ was similar to the summer river isotope composition. For the multiple floods of winter 2012–13, rainfall only became more isotopically depleted than the river ‘envelope’ in December 2012, with a value of -8.5‰ . This, combined with a January 2013 rainfall mean of -9.0‰ was presumably responsible for a river composition of -7.9‰ at the end of January 2013. While this was depleted relative to most monthly river values, it was just exceeded by the value of -8.0‰ recorded in February 2010. Therefore it seems that flooding events are not necessarily or generally associated with highly anomalous isotope compositions. However, this would have to be tested by event-scale monitoring.

Delta-plots for the 15 tributaries sampled (see Fig. 1 and Tables 1 and S3) are shown in Fig. 4, all to the same scale. Also included on each plot is the Wallingford meteoric line as described above in eqn (1). Most data points fall on or near to this line, any significant deviations from it occurring with more isotopically enriched samples (e.g. the Cole, Cherwell and Ray), suggesting that evaporative fractionation is responsible. The proportion of river water lost to evaporation would not have to be large to cause the levels of isotopic enrichment observed. For example, in the case of the greatest enrichment found, in the Cole, Cherwell and Ray in October 2011 (Fig. 5, Table S3), and using the approach of Skrzypek et al. (2015), a fractional loss of 9% (based on $\delta^{18}\text{O}$) or 12% (based on $\delta^2\text{H}$) can be calculated. However, this assumes that the water starts evaporating with a composition equivalent to weighted mean rainfall and is not replenished thereafter, so these figures are indicative only.

Otherwise, the rivers show differing amounts of variation (Fig. 4). The Wye has the tightest distribution, varying little beyond measurement error, while the Ray has the greatest range at 2.1‰ in $\delta^{18}\text{O}$ and 14‰ in $\delta^2\text{H}$. When values of $\delta^{18}\text{O}$ from each tributary and Wallingford rainfall (Tables S1 and S4) are compared over the quarterly sampling period it is clear that there is damping of $\delta^{18}\text{O}_r$ in relation to $\delta^{18}\text{O}_p$. However, this varies considerably, with the Wye showing the most damping and the Ray the least. In cases where the degree of damping is lower, it is possible to see tendencies towards winter depletion and summer enrichment (Fig. 5). Some of the latter may be due to evaporation, as mentioned above, but probably

also to summer rainfall which is typically enriched (Fig. 3b). The lower-BFI rivers reach their most depleted compositions by April 2013, which follows the most sustained period of months (7) with rainfall more negative than the Thames mean of -6.5% . Conversely, plots of $\delta^{18}\text{O}_r$ versus flowrate (Fig. 5) shows the immunity of high-BFI rivers even to particularly wet periods such as summer 2011 to winter 2012/13.

Specific electrical conductivity SEC data for Thames-Wallingford 2003–2012 are included in Table S2. SEC varies by a factor of two, from a low of $470\ \mu\text{S}/\text{cm}$ to a high of $980\ \mu\text{S}/\text{cm}$, with a mean of $718\ \mu\text{S}/\text{cm}$. When plotted against flow, SEC shows variable behaviour (Fig. 6a). While there is a general decrease with rise in flow rate up to $\sim 100\ \text{m}^3/\text{s}$, above this there is a return to higher values. There appears to be a 'January trend' where SEC barely changes with flow (Fig. 6a). O and H isotopes, here represented by $\delta^{18}\text{O}_r$ show very similar trends (Fig. 6b). As shown in Fig. 3d, January is normally the month of peak flow in the river, and indeed six of the eight months with mean flows $>100\ \text{m}^3/\text{s}$ (ultra-high flows, UHF) occur in January, the other two being the consecutive months November and December 2012, a notably wet period.

As suggested by a comparison between Figs 6a and b, there is a positive correlation ($r^2 = 0.25$) between SEC and $\delta^{18}\text{O}_r$ reflecting the tendency of lower-flow waters to be enriched in dissolved solids as well as isotopes owing to a combination of evaporation and proportionally greater inputs from non-rain-related sources such as baseflow and point-source inputs from sewage treatment works. Therefore the two parameters are to some extent proxies for each other. The main departure from this appears to be under UHF conditions where large amounts of isotopically-depleted rainfall have recently fallen, most notably November–December 2012 (Figs 6a and b, Tables S1 and S2).

The relative consistency of $\delta^{18}\text{O}_r$ and especially SEC values at UHF suggests that neither are attributable to direct runoff from high rainfall; if anything this would be expected to lower SEC, while consideration of the rainfall isotope record (Table S1) for each UHF month and the two preceding it give $\delta^{18}\text{O}_p$ weighted means ranging from -4.8 to -9.6% , i.e. far more variable than the observed $\delta^{18}\text{O}_r$ values. Clearly UHF conditions are mobilising stored water, which is presumably being displaced by rising groundwater levels. SEC and $\delta^{18}\text{O}$ compositions close to river averages ($718\ \mu\text{S}/\text{cm}$ and -6.5%) suggest the involvement of bank storage rather than groundwater itself, which tends to have lower conductivity and a

more depleted isotope composition (see further below). Given that alluvial deposits in the catchment above Wallingford cover some 500 km², conservative estimates of thickness (2 m) and porosity (10%) would give a storage volume of 100 Mm³, easily sufficient to contribute a significant amount to the river under appropriate conditions. Most of the displaced water is likely to be coming from gravels, which have a porosity of up to 50%.

The above interpretation would appear to be the reverse of what is generally understood by the term ‘bank storage’, whereby river water invades alluvial sediments at high flow and drains back to the river at lower flow (e.g. Chen and Chen, 2003). In reality, a normal bank storage regime may be the case for much of the Thames through most of the year, with the anomaly only occurring during situations when groundwater levels are still rising but the river falling. For example, Macdonald et al. (2012) noted that floodplain piezometer levels exceeded the river level near Oxford several times during the winter of 2009–10. A fuller examination of piezometric records from the catchment could conceivably shed more light on the processes involved, but was beyond the scope of the present paper.

A number of Thames sites at approximately 45 km intervals downstream from Cricklade (~10 km from the river head, see Fig. 1) were included in the quarterly monitoring of the tributaries. The results (Table S4) are compared in Fig. 7. Values of $\delta^{18}\text{O}$ (Fig. 7a) are at their most unstable and enriched at the beginning of the period (October 2011) when river levels were low. In particular, the value at Wallingford appears to have been affected by evaporated inflows from the more significant clay-vale rivers (Cherwell and Thame). Conversely, during the very high flow of spring 2013 the Thames values are more depleted and very uniform. SEC values are similar in some respects to the $\delta^{18}\text{O}$ values, with samples from October 2011 giving higher conductivities, and also reacting in all quarters to inputs from the Cherwell and Thame, but unlike the $\delta^{18}\text{O}$ record the very high flow of spring 2013 does not stand out (Fig.7b).

The general uniformity down the river on any particular sampling date suggests that processes such as evaporation that would otherwise progressively affect the isotopes and other parameters are being mitigated by the addition of water from downstream tributaries and baseflow.

Four sites (Wallingford, Tilehurst and Runnymede on the Thames, and Dorchester on the Thame, see Fig.1) were monitored at monthly intervals during the period between autumn 2011 and spring 2013 (Table S4) to determine what extra information might be obtainable from higher-resolution sampling.

Results for $\delta^{18}\text{O}$ are shown in Fig. 8a. The higher sampling resolution found some sizeable peaks and troughs (mainly the latter), particularly during the high-flow periods in spring 2012 and winter 2012–13. There was little difference between any of the sites, presumably reflecting the origin of rainfall during large frontal events over southern England as a whole.

The close similarity between the changes in the Thame and Thames was somewhat unexpected given their contrasting catchment areas (Thame about one-fifth that of Thames). They differ more in SEC values (Fig. 8b), but both records still show comparable patterns of peaks and troughs.

Baseflow and river–groundwater interaction

Baseflow The spread in isotope values for each river should ideally have an inverse relationship with BFI because the greater the proportion of baseflow, generally expected to have a near-constant isotopic composition, the higher the potential for damping the variable composition of recent rainfall inputs. Figure 9a shows that this is largely the case, with a high degree of correlation for all tributaries (irrespective of mean flowrate) except for the Cherwell, Cole and Ray. The isotopic evidence above (Fig. 4) shows that the BFI-related range in these three rivers has been supplemented by evaporative enrichment, thereby distorting the relationship slightly. Greater-than-normal evaporation effects might be anticipated for a river like the Ray, which flows slowly through wetlands. Although less expected for the Cherwell, which has almost twice the flow of the Ray, in this case it is probably mostly attributable to the existence of the Oxford Canal which shares water with the Cherwell at several locations above the sampling point (Neal et al., 2006), providing more scope for evaporative enrichment to affect the river. The Cherwell, Ray and Cole are also proportionally more effluent-impacted than most of the other tributaries (Bowes et al., 2014), though the limited effluent isotope data so far available from the Upper Thames suggest that discharge waters are not significantly fractionated (D C Gooddy pers. commun.).

Variations in SEC (Table S3) to some extent follow those shown by the O and H stable isotopes (Fig. 5) insofar as the Cherwell and Ray have the largest spreads. However the Cole shows only a modest range of SEC, while The Cut has one of the largest, both contrary to their isotope record. This shows that SEC is not always a proxy for stable isotopes. The reason for this is that the different tributaries have differing hydrochemical properties depending on several factors, geology probably being the most important. Since BFI is a primary function of catchment geology (Bloomfield et al., 2009) a correlation might be expected with SEC. As Fig. 9b shows, this is basically the case though there are some exceptions. The high-BFI rivers are those in Oolite or Chalk catchments, where SEC is basically controlled by calcite solubility. Thus there is little change in SEC for BFIs above 0.80. Below this, however, the river water quality data (CEH, unpublished data) show that sulphate is the dominant ion responsible for the increase in total dissolved solids and therefore SEC. In the clay-vale rivers this could be derived from SO_4 from dissolution or oxidation of the S-containing minerals typically found in clays, but more likely from fertiliser runoff. The Enborne is the only exception to the trends in Fig. 9b; although a low-BFI river it also has unusually low SEC values. The reason for this is probably catchment shape (e.g. Rinaldo et al., 1995): Fig. 1 shows that this tributary has a very narrow catchment, which means short, low-residence flow paths to the river. This in turn means that there is insufficient time for the water to reach chemical equilibrium with the soil or rocks through which it is passing. None of the other rivers considered here has a similarly-constricted catchment.

Except for the very low-flow quarterly sampling of October 2011, the simple average of SEC in the tributaries was almost identical to the simple average of SEC from the five Thames sampling points (from data in Table S3).

Relationship of surface water to groundwater This can be considered on the local and catchment scales. As an example of the former, downstream of Wallingford the Thames crosses the Chalk escarpment via the Goring Gap (Fig. 1), where modelling studies suggest that the potential for recharge of the river by groundwater exists (Jackson et al., 2006). The river accretes an average flow of $\sim 5.5 \text{ m}^3/\text{s}$ between Wallingford and Reading (Day's Lock + Wheatley compared to Reading, Table 1). The only significant tributary is the Pang, which provides $\sim 12\%$ of the increased flow (Table 1). Therefore it is likely that groundwater is contributing, since direct runoff does not occur from the Chalk. While there is some contrast

between river and groundwater isotope values, this was not great enough to show up at Tilehurst (west Reading) in Fig. 8a given that the accretion is only increasing flow by ~17%. However, SEC was consistently ~5% lower at Tilehurst (Fig. 8b), which would be in accord with the significantly lower SEC of groundwater compared to river water (see below).

On the catchment scale, BFI values (Table 1) indicate that even rivers with large areas of low-permeability cover in their catchments like the Ray and The Cut have a baseflow component approaching 50% of mean flow, while the Coln and the Pang consist of little else. This raises the question of the extent to which groundwater isotopic signals are preserved in the various rivers of the catchment. The following groundwater quality studies carried out in the upper Thames region allow a comparison: Alexander and Andrews (1984), Bearcock and Smedley (2010), Cobbing et al. (2004), Darling et al. (2012), Edmunds et al. (1987), Jackson et al. (2006) and Neumann et al. (2003).

A co-plot of groundwater $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values (inset to Fig. 10) shows that they are well-correlated and tend to follow the Wallingford meteoric water line. Most results cluster in the range -7.0 to -7.5‰ $\delta^{18}\text{O}$, which is distributed around the 2003–2012 Wallingford rainfall weighted mean of -7.22‰ , and conforms with the view of Darling et al. (2003) that no significant seasonal isotopic selection occurs during the groundwater recharge process in the region. Figure 10a shows the distribution of groundwater $\delta^{18}\text{O}$ across the catchment. There is evidence for a slight isotopic enrichment from north to south, consistent with the latitudinal distribution of rainfall isotopes in southern England as proposed by Darling et al. (2003).

A simple comparison with river baseflow compositions is however not straightforward. For the quarterly sampling of October 2011, which followed a prolonged dry spell, the rivers would have been sustained largely by baseflow. However, all rivers with the exception of the Wye contained water more enriched than -7‰ $\delta^{18}\text{O}$, some much more so. This is likely to have been due to isotopic enrichment caused by evaporative fractionation, as mentioned earlier. Study of Fig. 5 suggests that the quarterly sampling most representative of baseflow conditions was probably April 2012, following a dry winter but prior to the anomalously wet summer and even wetter winter of 2012–13. On this basis, a comparison of Fig. 10a with Fig. 4 shows that only a few short limestone or chalk streams (Coln, Pang and Wye) have a composition largely unaffected by evaporation. The Kennet, while slightly enriched by comparison, is probably also mostly unaffected since it is likely to be mainly sustained by

slightly isotopically heavier groundwater in the south of the region (Fig. 10a). Most of the largest enrichments were seen in the clay-vale rivers Loddon, Thame, Ray and The Cut. Clearly, except for short, high-BFI rivers, it is unsafe to regard samples taken at any particular time of the year as having the same isotope value as the groundwater contributing the baseflow.

The net effect on the main Thames is that the river is nearly always isotopically enriched compared to groundwater in the region even in the winter, though this is minor compared to late summer–early autumn. As noted earlier in connection with Fig. 7, there is rather little change down the river for individual quarterly samplings, suggesting that increasing downstream enrichment due to progressive evaporation is cancelled out by inflow derived from tributaries and baseflow.

In terms of SEC, under the presumed near-baseflow conditions of the April 2012 sampling, the tributaries averaged 669 $\mu\text{S}/\text{cm}$ and the Thames 692 $\mu\text{S}/\text{cm}$ (from data in Table S3). This is ~15% higher than the average groundwater value of ~600 $\mu\text{S}/\text{cm}$ (data from sources cited above) and would be consistent with the effects of evaporation on baseflow, though effluent inputs with higher SEC (of the order of 1000 $\mu\text{S}/\text{cm}$) will also contribute (on average 10% of MDF at Wallingford).

However, a caveat to consider with regard to both $\delta^{18}\text{O}$ and SEC is that aquifer groundwater as sampled from boreholes is not necessarily the only contributor to baseflow. This is really an inclusive term for all forms of ‘slow’ drainage to a river (e.g. Ward and Robinson, 2000), which may include delayed drainage from the shallow subsurface which by-passes the underlying aquifer. It is conceivable, particularly for the clay-vale rivers, that this slower-moving but shallow drainage might have undergone a certain amount of isotopic modification before reaching the river (a possibility raised in connection with US rivers by Kendall and Coplen, 2001). However, testing this (presumably by shallow drilling and sampling) was beyond the resources of the present study.

Figures 8a and 8b show no evidence of consistent differences in $\delta^{18}\text{O}$ or SEC between ‘Jurassic’ Thames as sampled at Wallingford, and ‘Cretaceous + Palaeogene’ Thames as sampled at Runnymede. While the record of the latter would of course be superimposed on

the former, they do contribute approximately equal flow volumes according to the long-term gauge records (Day's Lock + Wheatley compared to Bray, Table 1).

Dissolved inorganic carbon

The source of most dissolved inorganic carbon (DIC) in the natural waters of lowland Britain is the dissolution by soil-produced CO₂ of carbonate minerals in the soil and bedrock of the catchment. Soil CO₂ with $\delta^{13}\text{C}$ of $\sim -27\text{‰}$ (Darling and Goody, 2007) reacts with carbonate minerals with $\delta^{13}\text{C}$ typically $\sim 0\text{‰}$ (Evans et al., 1979) to produce initial $\delta^{13}\text{C}$ -DIC values in the range -13 to -14‰ . Once waters are exposed to the atmosphere, the DIC budget is governed by three basic processes: degassing, oxidation of organic matter, and photosynthesis (e.g. Jarvie et al., 1997). These processes have varying isotopic effects.

Exposure to air generally results in degassing (evasion) of CO₂ owing to its low atmospheric partial pressure compared to the $p\text{CO}_2$ of most river waters (e.g. Hotchkiss et al., 2015). Loss of CO₂ raises pH, which tends to reduce DIC concentration while enriching $\delta^{13}\text{C}$ -DIC. Oxidation of organic matter, by microbial respiration in the soil and river channel, may contribute surplus CO₂ (i.e. in excess of that taken up by mineral dissolution) with a value of $\sim -27\text{‰}$. This tends to make $\delta^{13}\text{C}$ -DIC values more negative than the theoretical simple dissolution value, while raising DIC concentration. Photosynthesis has a similar effect to outgassing, so cannot easily be resolved from outgassing on the basis of $\delta^{13}\text{C}$ -DIC and alkalinity alone. Isotopic exchange with the atmosphere would raise $\delta^{13}\text{C}$ -DIC values towards $\sim 0\text{‰}$ (e.g. Kanduč et al, 2007) but this can be ruled out for the rivers of the upper Thames basin which all have relatively high alkalinities.

Results for the Thames at Wallingford during the period 2003–2007 are reported in Table S5, together with pH and alkalinity. There is little variation in $\delta^{13}\text{C}$ when the data are considered on an inter-annual basis, with average values lying within $\pm 0.5\text{‰}$ about a mean of -14.8‰ . Inter-quartile ranges also remain similar. There is similar consistency in pH and alkalinity. Seasonal statistics on the other hand reveal some seasonal fluctuations in $\delta^{13}\text{C}$ -DIC, alkalinity and $p\text{CO}_2$ (Fig. 11a-c). The carbon isotope composition of the river at any one time is the result of interaction between the three processes outlined above superimposed on any groundwater or effluent contribution. Values of $\delta^{13}\text{C}$ -DIC are poorly correlated with alkalinity, indicating that no single process predominates, and consistent with the observation

that most aquatic systems show a fluctuating respiration-photosynthesis balance (e.g. Wang and Veizer, 2000). However, given that $\log p\text{CO}_2$ values in the range -2.2 to -2.8 are an order of magnitude above atmospheric CO_2 (~ -3.4 for the period), it appears that evasion must be a relatively constant factor, though with a somewhat greater potential in the period May–September. Perhaps surprising is that the relatively large inter-quartile ranges in alkalinity (and to a lesser extent $p\text{CO}_2$) from August to December are not reflected by $\delta^{13}\text{C}$ -DIC.

At this point it must be noted that the main River Thames and at least some of its tributaries are in a far from natural state; there is for example considerable recycling of river water in the Oxford, Reading and other urbanised areas through abstraction for public supply and subsequent return of effluent, not necessarily within the same sub-catchment. For this reason alone it would be difficult to predict what effect effluent might have on dissolved inorganic carbon isotopes at any particular location. However it is also the case that the effects on $\delta^{13}\text{C}$ -DIC of urban effluents can be variable: mineralisation of organic carbon would tend to lower $\delta^{13}\text{C}$ -DIC (Barth et al, 2003), but compounds such as detergents could raise it (Shin et al., 2015). On the other hand, Wachniew (2006) found no change in $\delta^{13}\text{C}$ -DIC in the River Vistula flowing through Warsaw (pop. 1.7 M) despite half that city's sewage effluent remaining untreated. Furthermore, on a much smaller scale, Morrissey et al. (2012) found little or no evidence of change in macroinvertebrate $\delta^{13}\text{C}$ below effluent outfalls in UK urban streams. It seems probable therefore that the Thames at Wallingford has not been significantly impacted (at least in isotopic terms) by effluent-derived DIC.

Plots of tributary $\delta^{13}\text{C}$ -DIC and alkalinity (Table S6) against time are shown in Fig. 12. In most cases minimum $\delta^{13}\text{C}$ -DIC values are seen for the two October samplings, presumably due to a temporary dominance in respiration (supported by a general rise in $p\text{CO}_2$ compared to April 2012), and possibly the effects of a proportionately higher contribution of sewage effluent, though the Morrissey et al. (2012) study suggests not. Highest $\delta^{13}\text{C}$ -DIC values are generally seen for the April 2012 sampling, consistent with photosynthesis, which peaks in the spring (Neal et al., 1998), but are not replicated in the April 2013 sampling, when $\delta^{13}\text{C}$ falls. River flows had by then recently been so high (Fig. 5) that the usual seasonal processes may have been to some extent overridden by an abnormally high influx of soil water (see e.g. Griffiths et al., 2007), charged with isotopically-depleted soil-zone CO_2 . The concurrent universal fall in alkalinity would be indicative of such a dilution effect.

For the main Thames, most $\delta^{13}\text{C}$ -DIC series tend to vary rather little between the sampling sites though there is a certain amount of seasonal displacement with little apparent pattern (Fig. 7c). The October 2012 series however shows one large variation and significant displacement from the other quarters, though the cause remains unknown. Alkalinity also shows seasonal displacement, but with more longitudinal consistency, falling universally between Sonning and Runnymede (Fig 7d). After an initial fall between Hannington and Swinford, which would be typical of a baseflow-influenced upper watercourse (e.g. Kanduč et al., 2007), $p\text{CO}_2$ values generally rise slightly along the river irrespective of the season/flow conditions so probably not related to the slight increase in BFI between Day's Lock and Bray (Table 1). Given the variety of processes controlling dissolved CO_2 (Neal et al., 1998) this consistency is perhaps surprising, but it does suggest that the potential for evasion exists along the river throughout the year (Fig. 7e).

As with $\delta^{18}\text{O}$, the magnitude of changes in $\delta^{13}\text{C}$ -DIC and alkalinity might be expected to be linked to BFIs. A comparison of Tables 1 and S5 shows that to some extent this is the case, with low-BFI rivers like the Cole (0.53) and the Ray (0.49) showing significantly larger changes in $\delta^{13}\text{C}$ -DIC and alkalinity than high-BFI rivers like the Coln (0.95) and the Windrush (0.87). However, there are exceptions like the chalk streams Kennet, Pang and Wye (0.87 to 0.94) which have relatively large fluctuations in $\delta^{13}\text{C}$ -DIC, and intermediate-BFI rivers like the Evenlode (0.71) and the Loddon (0.69) which show less change. It is therefore likely that in addition to fluctuations in the respiration-photosynthesis-evasion balance, variations in $\delta^{13}\text{C}$ -DIC between the rivers are due to a complex interaction between river length, catchment geology and anthropogenic factors, and consequently difficult to unravel.

Figure 10b shows the distribution of groundwater $\delta^{13}\text{C}$ -DIC values. Samples from the Jurassic and Cretaceous parts of the basin fall in the range -12 to -16‰ , while those from the Palaeogene lie in the range -17.5 to -19‰ (though there are many fewer samples from the Palaeogene because it generally makes a poor aquifer). As outlined earlier, $\delta^{13}\text{C}$ -DIC values in groundwater are the consequence of soil CO_2 reacting with rock carbonate combined with further modification by various processes. An initial $\delta^{13}\text{C}$ -DIC value of $\sim -13\text{‰}$ can be made more positive by further dissolution-precipitation reactions, and more negative by further equilibration with soil-derived CO_2 (i.e. closed- and open-system conditions respectively).

The $\delta^{13}\text{C}$ -DIC values in Fig. 10b show that most if not all of the groundwaters are evolving under open-system conditions, though there is a difference in the extent of this between the Oolite or Chalk waters compared with the Palaeogene. Limestone and chalk groundwater alkalinities as HCO_3 are invariably >220 mg/L but the Palaeogene waters, from what are basically sandstone aquifer units, are all <150 mg/L (data from sources used for Fig. 10). They are therefore much less buffered against re-equilibration with soil-derived CO_2 , and consequently more depleted in ^{13}C .

The Cut, Enborne and Loddon all have low alkalinities compared to the other tributaries (Table S6), reflecting their origins on the Palaeogene strata. This difference however does not extend to their $\delta^{13}\text{C}$ -DIC values, which cannot be distinguished from the other rivers. The three basic processes acting on surface waters outlined earlier (respiration, photosynthesis and evasion) are clearly very effective in overprinting the $\delta^{13}\text{C}$ values of baseflow contributions.

CONCLUSIONS

The aim of this study has been to investigate the processes operating in a mesoscale lowland river basin using environmental tracers (stable isotopes and specific electrical conductivity) on temporal and areal scales rarely attempted previously. It has been achieved over a period which included both drought and flood conditions. The results should therefore be highly representative of the behaviour of similar temperate-zone catchments under the likely range of present climatic conditions.

Insights obtained included the following:

Based on $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data, the upper Thames and most of its tributaries showed evidence of evaporative enrichment compared to rainfall in the area. The extent of this varied seasonally. Calculations suggested that relatively low amounts of evaporation would achieve the observed enrichments.

While the Thames varied within a range of 3‰ in $\delta^{18}\text{O}$ and 20‰ in $\delta^2\text{H}$, little information about the response time of the various water compartments in the basin could be extracted

from the isotope data. However, $\delta^{18}\text{O}$ and specific electrical conductivity (SEC) showed strong evidence for a release of bank-stored water under highest river flow conditions, in apparent contravention of the normal bank storage process.

For most tributaries, baseflow index was revealed to be highly correlated with the magnitude of $\delta^{18}\text{O}$ change from drought to flood conditions. Despite this, comparison with previously-obtained hydrogeochemical data suggests that rivers even at low flow rarely consist wholly of unfractionated groundwater.

In terms of tracing groundwater inputs to rivers, SEC is likely to be a more sensitive indicator than O or H stable isotopes because of the greater contrast between river and groundwater. However, on a local scale when river water may be invading superficial sediments owing to pumping or other effects, isotopes may provide confirmation (e.g. Jackson et al., 2006).

The results of $\delta^{13}\text{C}$ -DIC, pH and alkalinity measurements showed that while the river system as a whole probably always has evasion potential, thus counteracting any tendency towards isotopic equilibration with atmospheric CO_2 , there is a complex interaction between respiration, photosynthesis and degassing and catchment factors which is difficult to unravel. Indeed, these processes proved to be very effective at masking the origin of individual rivers' baseflow components.

These insights will contribute to a better understanding of the functioning of a lowland river basin in a water-critical area, and demonstrate the value of long-term river monitoring using environmental tracers.

ACKNOWLEDGMENTS

The original scope of this study was greatly enhanced by the cooperation of the NERC-funded Thames Initiative research platform of the Centre for Ecology and Hydrology (CEH) in the collection of river water samples and provision of supporting data. The authors are grateful to the following: Colin Roberts and Pete Scarlett (CEH) for the quarterly sample collection; Heather Wickham (CEH) for sample organisation; Milly Lewis (BGS) for sample collection at Tilehurst; Gillian Wells (Environment Agency) for river flow data; Steph Bricker (BGS) for the geology map used in Figs 1 and 10; Andy Newell (BGS) for further geological advice; and Thames Water Utilities Ltd for information on the use of their Farmoor reservoir. Terry Marsh (CEH) is thanked for commenting on an earlier draft of the manuscript. Also thanked are two anonymous referees, whose comments helped to improve the structure and content of this paper. WGD contributes with the permission of the Executive Director, British Geological Survey (NERC).

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Table 1. Sampling locations for the Thames and tributaries in the upper river basin. Also included are values for mean flow and baseflow index, and gauging station details. Cases where the gauging point is >1 km from the sampling point are noted.

River	Sampling point	NGR		Nearest gauge	EA no.	Mean flow m ³ /s	BFI	Period	Notes
		E	N						
Coln	Whelford	417121	199200	Fairford	39110	1.99	0.95	1991-2005	~3 km D of gauge
Cole	Lynt Bridge	421057	198107	Inglesham	39090	1.20	0.53	1976-2005	
Leach	Lechlade	422700	199320	Lechlade	39042	0.75	0.79	1972-2005	
Windrush	Newbridge	440179	201858	Newbridge	39006	3.29	0.87	1996-2005	
Evenlode	Cassington Mill	444853	209919	Cassington Mill	39034	3.72	0.71	1950-2005	
Cherwell	Hampton Poyle	449912	215282	Enslow Mill	39021	3.81	0.66	1969-2005	~4 km D of gauge
Ray	Islip	452320	213730	Islip	39140	2.01	0.49	1962-2005	
Ock	Abingdon	448148	196667	Abingdon	39081	1.53	0.64	1972-2005	
Thame	Wheatley	461190	205030	Wheatley	39105	3.79	0.59	1970-2005	
Pang	Tidmarsh	463600	174700	Pangbourne	39027	0.65	0.87	1968-2005	~1.5 km U of gauge
Kennet	Woolhampton	457120	166462	Theale	39016	9.75	0.87	1995-2005	~7km U of gauge
Enborne	Brimpton	456783	164772	Brimpton	39025	1.33	0.54	1967-2005	
Loddon	Charvil	477872	176587	Twyford	39138	6.68	0.69	1965-2005	
Wye	Bourne End	489612	186580	Hedsor Mill	39023	1.01	0.94	1964-2005	
The Cut	Paley Street	487037	176290	Binfield	39052	0.39	0.46	1957-2005	~6 km D of gauge
Thames	Hannington	415407	196085	Cricklade	39040	1.44	0.67	1961-2005	~10 km D of gauge
Thames	Swinford	444307	208615	Eynsham	39008	14.8	0.67	1951-2001	
Thames	Wallingford	461045	189467	Day's Lock	39002	28.3	0.64	1938-2002	~7 km D of gauge, ~6 km D of Thame confl.
Thames	Sonning	475500	175780	Reading	39130	37.5	0.66	1992-2005	~5 km D of gauge, ~4 km D of Kennet confl.
Thames	Runnymede	500567	172352	Bray*	39009	58.2	0.70	1959-1982	~15 km D of gauge, ~14 km D of Cut confl.

NGR - National grid reference

EA no. - Environment Agency gauging station number

BFI - Baseflow index

D - downstream

U - upstream

*Not a primary gauging station owing to leakage, flows indicative only (Marsh and Hannaford, 2008)

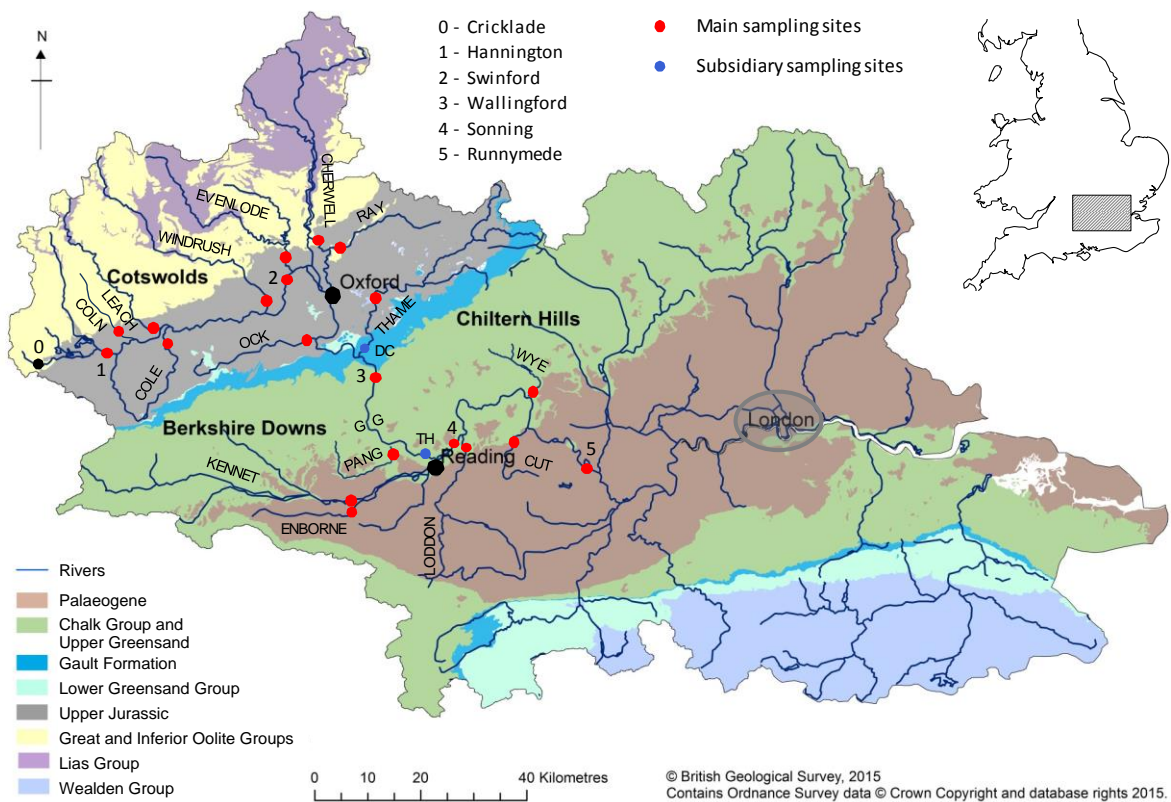


Figure 1. Map of the Thames basin with bedrock geology, river network and sampling points. Main carbonate formations shown in green or yellow. The upper Thames is defined here as the river network above Runnymede (sampling point 5). DC – Dorchester, GG – Goring gap, TH – Tilehurst.

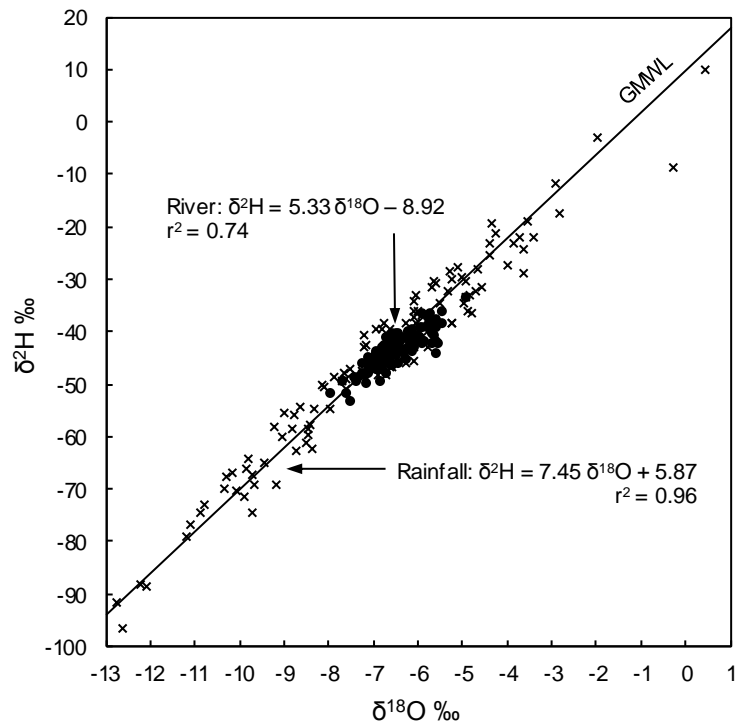


Figure 2. Delta plot of monthly cumulative rainfall and River Thames monthly spot samples collected at Wallingford for the years 2003–2012. Regression equations and correlation coefficients are shown for both data series. The global meteoric water line (GMWL) is shown for comparison.

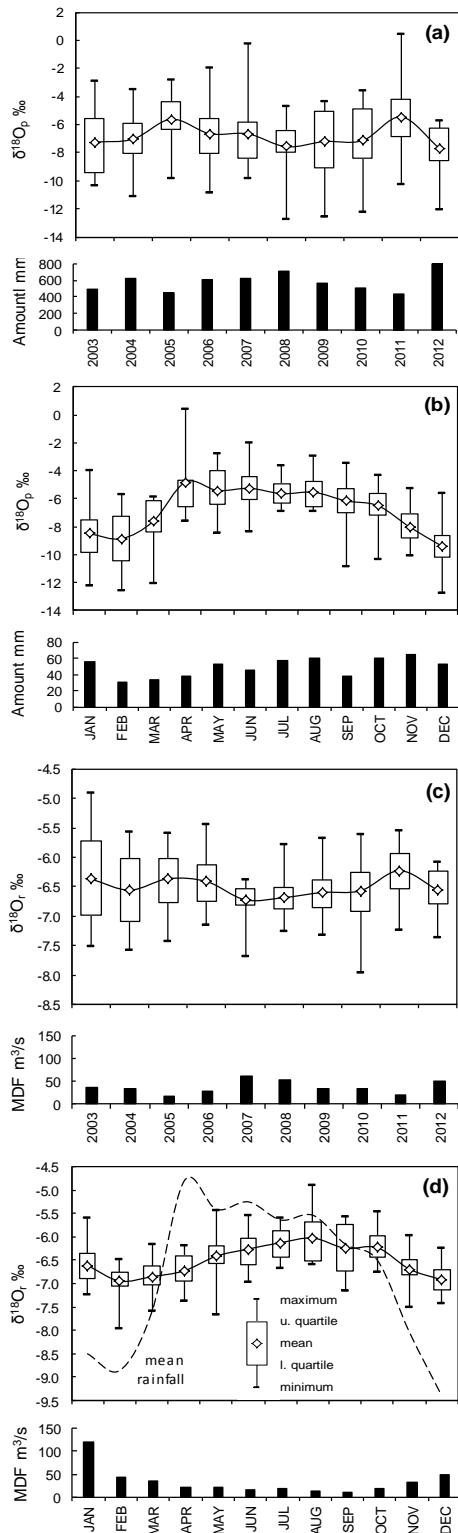


Figure 3. Box plots for $\delta^{18}\text{O}_p$ and $\delta^{18}\text{O}_r$ at Wallingford for inter-annual (a,c) and seasonal (b,d) means over the period 2003–2012. Also shown are the respective rainfall amounts (a,b), and river flows expressed in terms of mean daily flow (MDF) (c,d). The mean rainfall curve from Fig. 3b (dashed line) is also plotted on (d) for comparison.

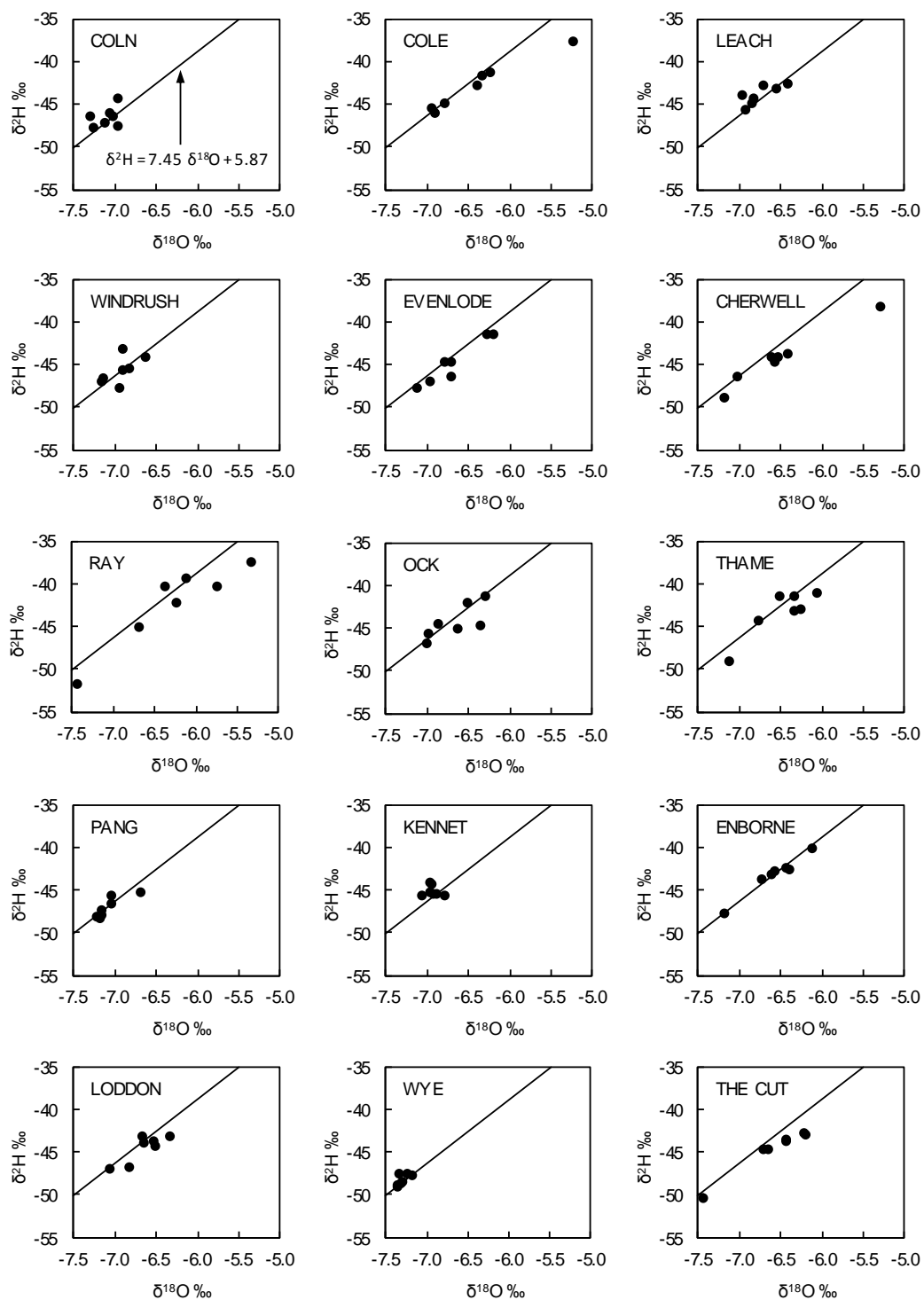


Figure 4. Delta plots of samples collected quarterly from October 2011 to April 2013 from the main tributaries in the upper Thames basin. Shown on each plot is the Wallingford meteoric line (equation shown on the plot for the Coln).

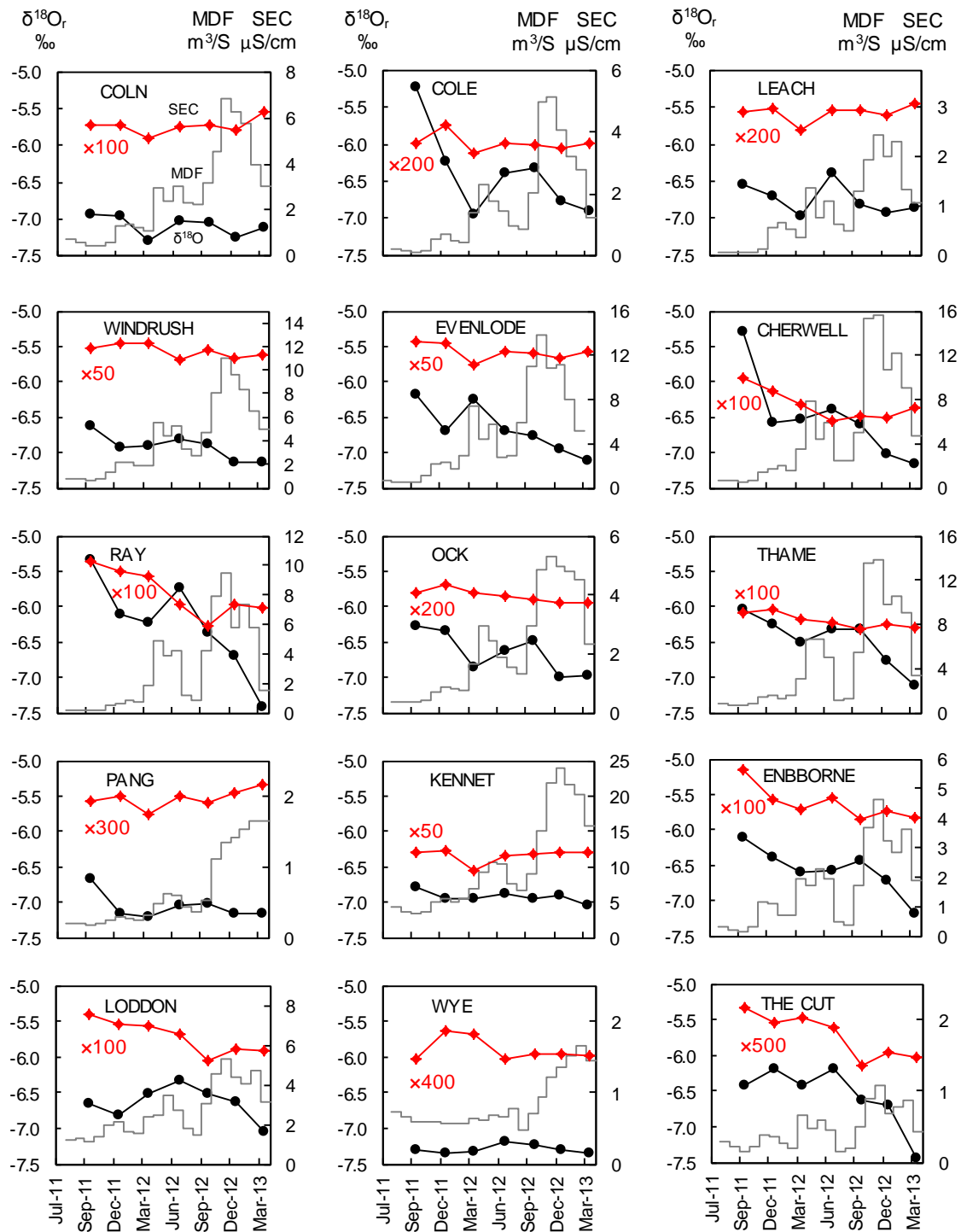


Figure 5. Values of $\delta^{18}\text{O}_r$ (in ‰) from the October 2011–April 2013 quarterly sampling of the upper Thames tributaries compared to monthly mean daily flow (MDF, in m^3/S). Quarterly values of SEC (specific electrical conductivity) are also shown (in red) for comparison, with multiplication factor to give results in $\mu\text{S}/\text{cm}$.

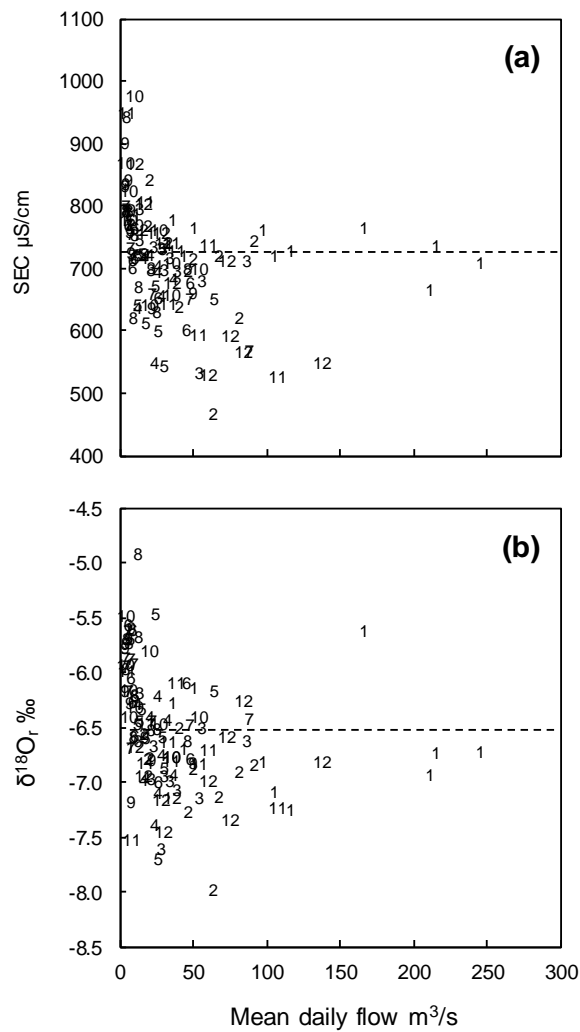


Figure 6. Plots of values from monthly spot samples from the Thames at Wallingford for (a) SEC and (b) $\delta^{18}O_r$ versus mean daily flow (MDF) averaged for the whole month. Data points are represented by the number of the month (January – 1, February – 2, etc.). Dashed lines indicate the 10-year median values.

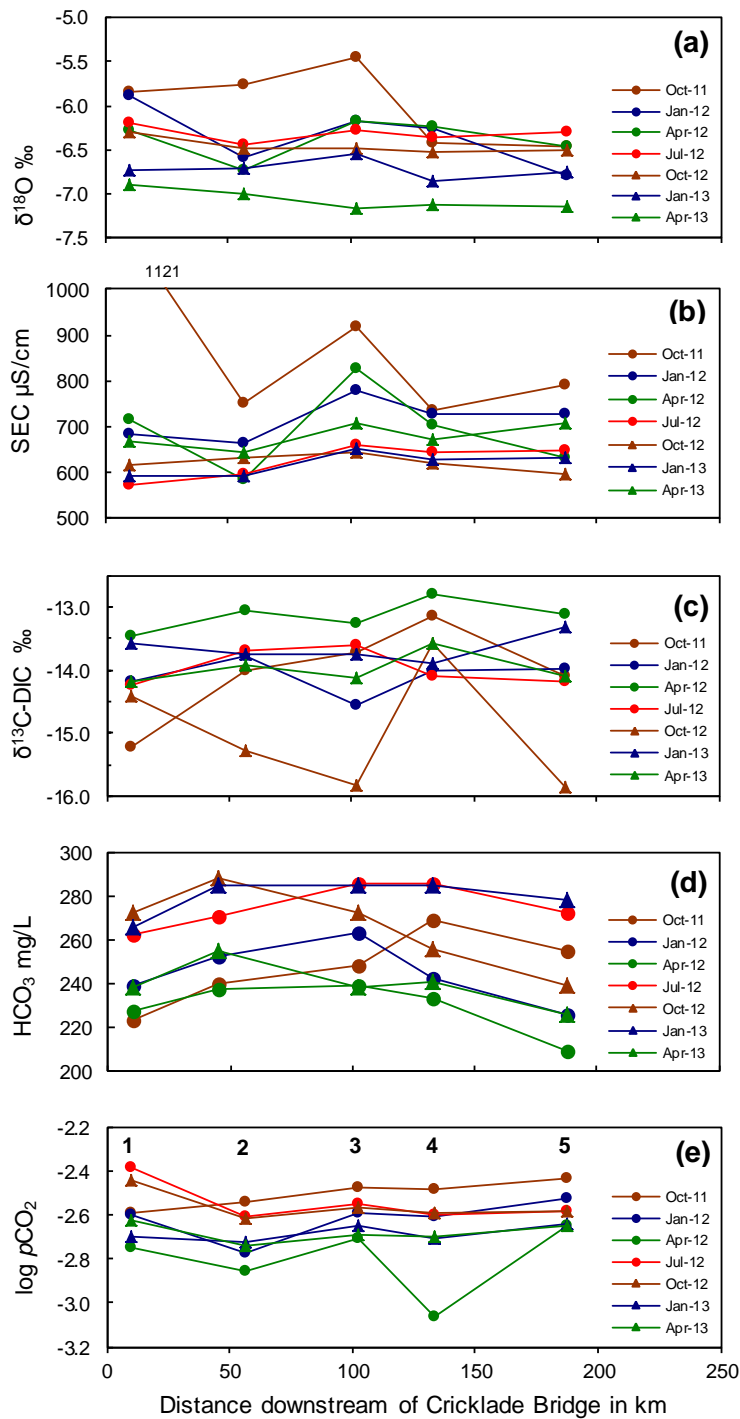


Figure 7. Plots of (a) $\delta^{18}\text{O}$, (b) $\delta^{13}\text{C-DIC}$, (c) alkalinity, (d) $p\text{CO}_2$ and (e) SEC (specific electrical conductivity) for River Thames sampling sites over the quarterly monitoring period Oct 2011 to April 2013. Sites are: 1 – Hannington, 2 – Swinford, 3 – Wallingford, 4 – Sonning, 5 – Runnymede. Refer to Figure 1 for locations.

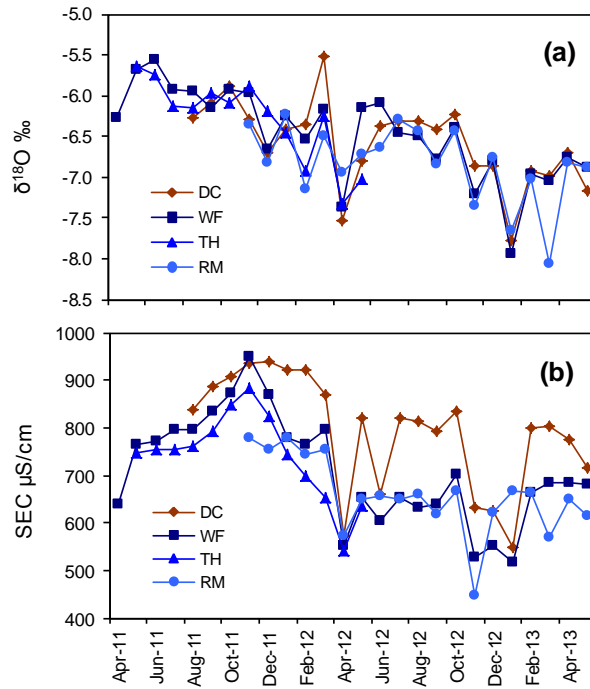


Figure 8. Comparison of monthly spot samples for (a) $\delta^{18}\text{O}$ and (b) SEC (specific electrical conductivity) from the River Thames at Dorchester (DC), and the River Thames at Wallingford (WF), Tilehurst (TH) and Runnymede (RM). Refer to Figure 1 for locations.

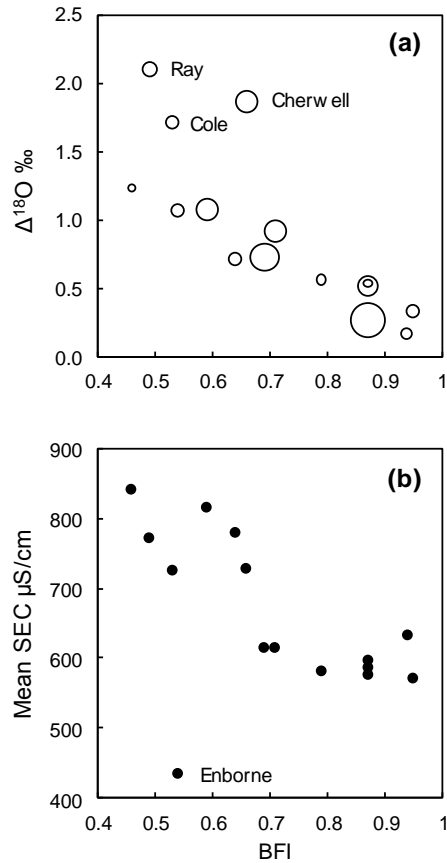


Figure 9. Plot of baseflow index (BFI, Table 1) versus (a) total range of $\delta^{18}\text{O}$ values measured in each of the upper Thames tributaries during quarterly sampling October 2011–April 2013 (symbol area proportional to mean flow in each tributary, Table 1), (b) mean specific electrical conductivity (SEC) from the quarterly sampling. Exceptions to the general trends are identified.

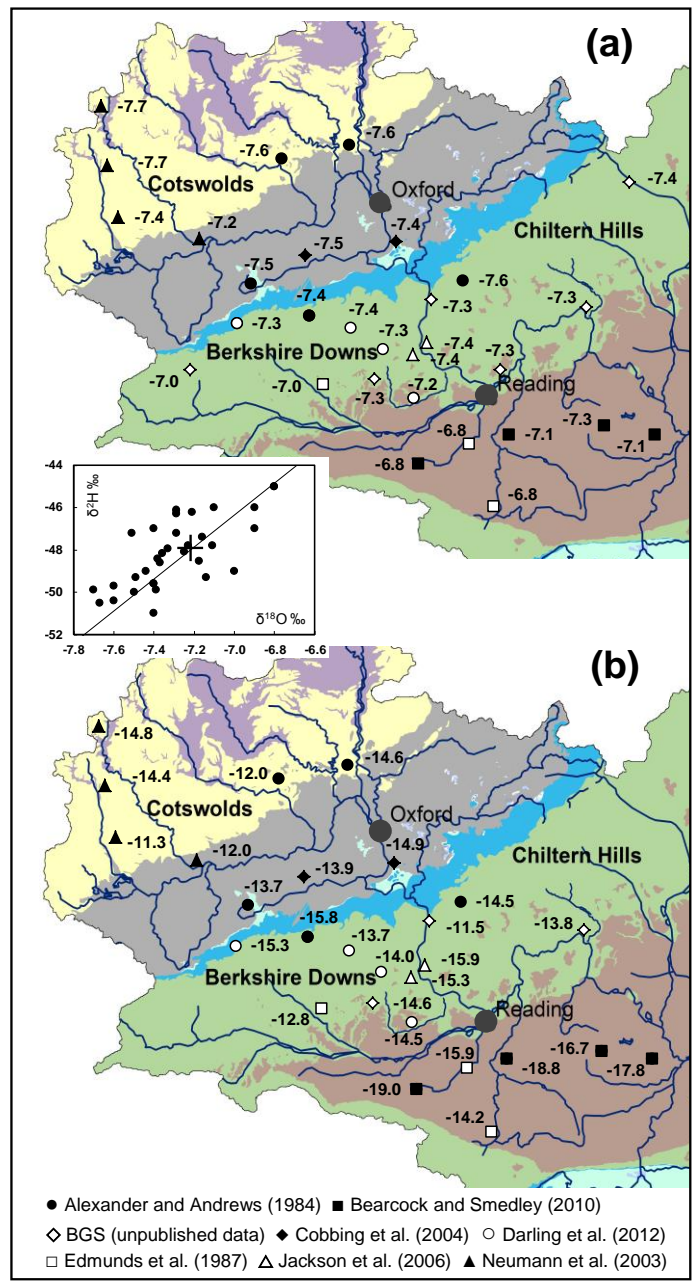


Figure 10. Maps showing regional distributions of (a) $\delta^{18}\text{O}$ and (b) $\delta^{13}\text{C}$ -DIC in groundwaters of the upper Thames basin. Data sources as indicated. Geological legend and map copyrights as for Figure 1. Inset: delta-plot of groundwater data from the same sites, shown in relation to the Wallingford meteoric line (cross indicates the 2003–2012 weighted mean values for rainfall at Wallingford).

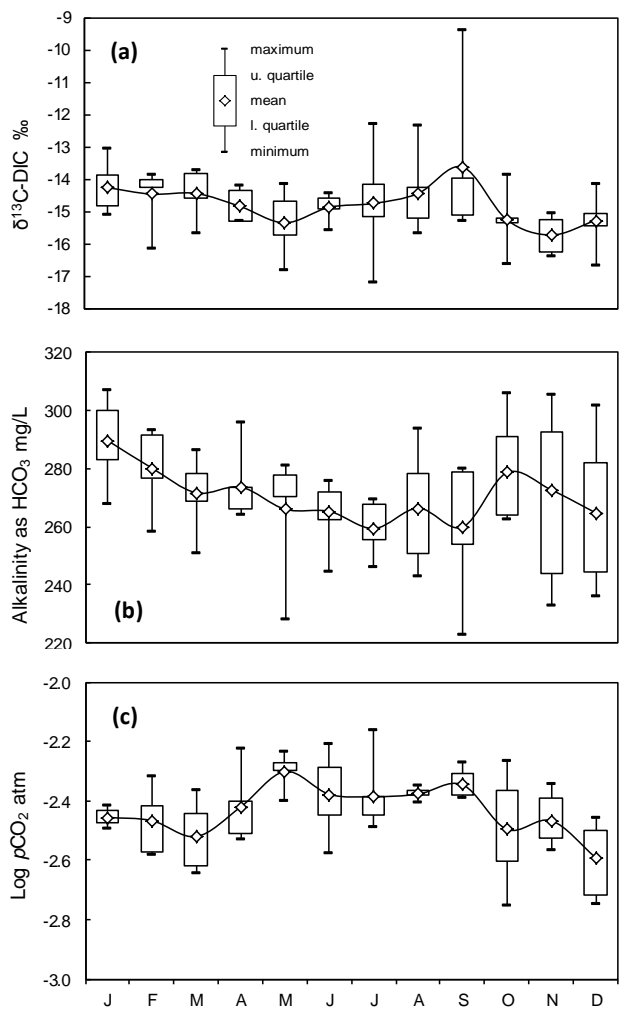


Figure 11. Box plots for monthly spot samples from the Thames at Wallingford for (a) $\delta^{13}\text{C-DIC}$, (b) alkalinity and (c) $p\text{CO}_2$, by monthly mean over the period 2003–2007.

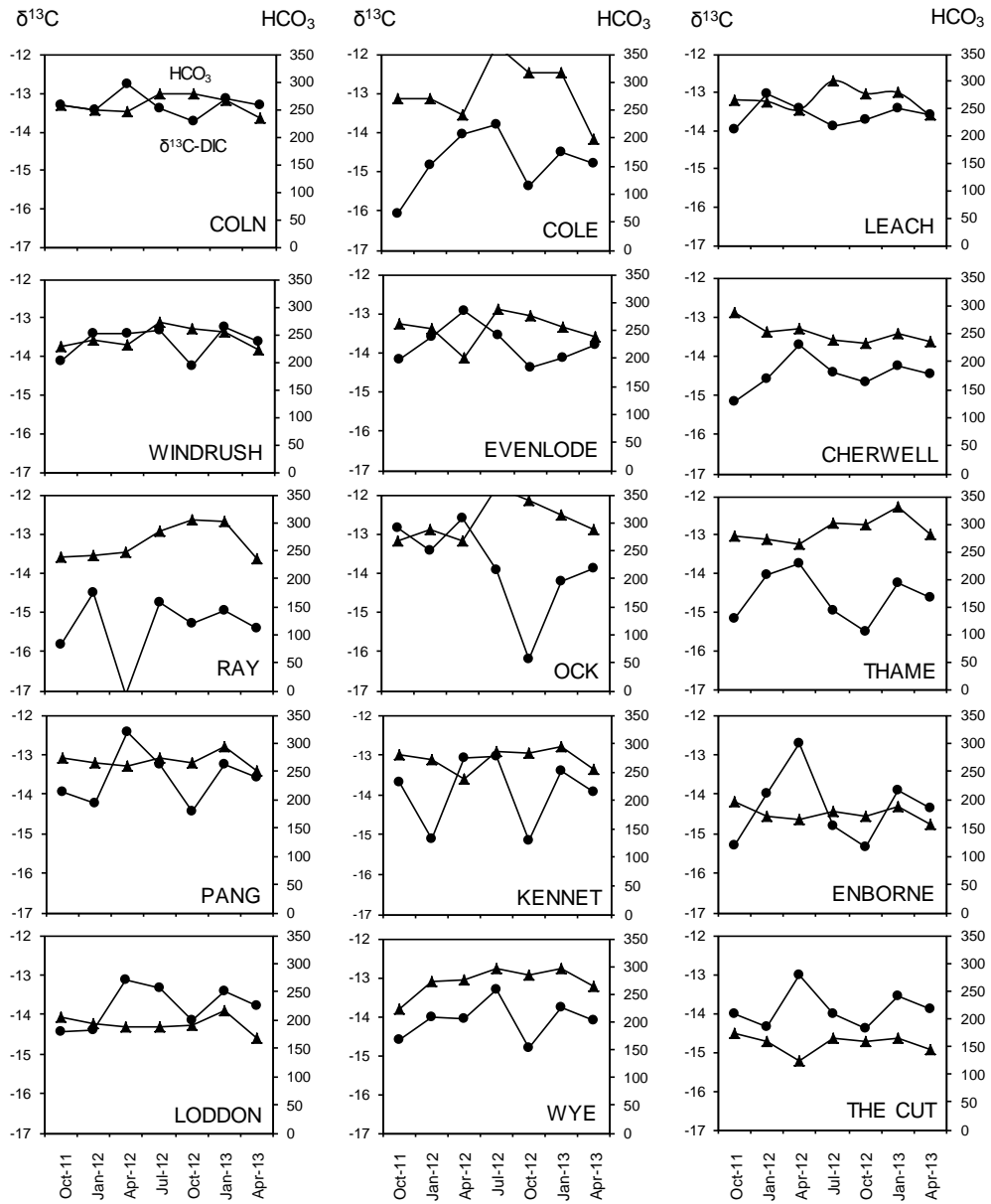


Figure 12. Values of $\delta^{13}\text{C-DIC}$ (in ‰) and alkalinity as HCO_3^- (in mg/L) from quarterly sampling of the upper Thames tributaries, October 2011–April 2013.

Table S1. Values of $\delta^{18}\text{O}$, $\delta^2\text{H}$ and amount for monthly rainfall samples collected at Wallingford between January 2003 and May 2013.

Month	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	Amount mm	Month	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	Amount mm	Month	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	Amount mm
Jan-03	-10.15	-66.8	78	Jan-07	-5.89	-37.0	69	Jan-11	-9.89	-71.3	77
Feb-03	-9.20	-58.1	32	Feb-07	-9.44	-64.9	13	Feb-11	-7.19	-48.3	38
Mar-03	-8.15	-50.1	20	Mar-07	-5.97	-41.6	41	Mar-11	-6.72	-48.2	9
Apr-03	-6.82	-39.4	33	Apr-07	-0.29	-8.6	1	Apr-11	0.42	9.8	2
May-03	-3.73	-22.0	32	May-07	-8.45	-59.6	125	May-11	-3.39	-22.1	11
Jun-03	-4.41	-25.3	48	Jun-07	-8.35	-62.2	85	Jun-11	-4.85	-32.9	42
Jul-03	-6.08	-34.1	37	Jul-07	-6.04	-38.5	97	Jul-11	-4.98	-34.4	35
Aug-03	-2.93	-11.7	10	Aug-07	-6.44	-45.7	34	Aug-11	-5.26	-38.5	64
Sep-03	-5.98	-40.5	22	Sep-07	-5.52	-34.6	34	Sep-11	-3.64	-24.2	47
Oct-03	-10.36	-69.9	36	Oct-07	-5.60	-30.6	43	Oct-11	-4.34	-19.4	22
Nov-03	-10.09	-70.2	104	Nov-07	-9.81	-64.3	54	Nov-11	-5.29	-28.6	26
Dec-03	-9.00	-55.6	42	Dec-07	-8.08	-50.5	24	Dec-11	-10.31	-67.6	62
Jan-04	-8.75	-62.7	80	Jan-08	-9.69	-69.2	76	Jan-12	-7.38	-48.2	33
Feb-04	-5.67	-31.6	29	Feb-08	-6.51	-43.3	15	Feb-12	-11.18	-78.9	15
Mar-04	-8.42	-57.7	46	Mar-08	-6.62	-39.6	68	Mar-12	-12.10	-88.5	21
Apr-04	-7.60	-49.2	67	Apr-08	-7.61	-50.9	45	Apr-12	-5.76	-40.0	111
May-04	-5.33	-32.3	49	May-08	-6.27	-38.5	78	May-12	-6.50	-41.8	45
Jun-04	-6.10	-37.3	22	Jun-08	-7.68	-49.3	65	Jun-12	-6.05	-40.7	118
Jul-04	-6.95	-46.1	133	Jul-08	-6.05	-33.2	71	Jul-12	-6.28	-46.1	87
Aug-04	-3.52	-18.8	22	Aug-08	-4.72	-32.3	70	Aug-12	-6.11	-43.0	68
Sep-04	-7.15	-42.6	101	Sep-08	-7.12	-46.9	62	Sep-12	-7.25	-47.4	27
Oct-04	-6.76	-38.3	30	Oct-08	-7.22	-42.9	44	Oct-12	-6.26	-41.2	97
Nov-04	-11.09	-76.9	40	Nov-08	-8.64	-54.5	78	Nov-12	-8.82	-58.7	79
Dec-04	-3.97	-27.3	15	Dec-08	-12.76	-91.8	34	Dec-12	-8.52	-61.2	96
Jan-05	-7.53	-47.2	16	Jan-09	-9.19	-69.1	46	Jan-13	-8.95	-61.3	54
Feb-05	-6.10	-45.4	39	Feb-09	-12.62	-96.4	56	Feb-13	-11.78	-85.8	36
Mar-05	-4.77	-36.6	45	Mar-09	-9.72	-74.6	18	Mar-13	-10.43	-73.7	87
Apr-05	-2.81	-17.4	21	Apr-09	-5.79	-42.8	28	Apr-13	-8.03	-58.5	20
May-05	-3.87	-23.1	31	May-09	-5.10	-27.6	36	May-13	-7.60	-51.6	57
Jun-05	-6.90	-48.3	40	Jun-09	-4.38	-23.0	26				
Jul-05	-4.55	-31.6	36	Jul-09	-6.59	-46.9	79				
Aug-05	-5.23	-29.8	53	Aug-09	-4.92	-33.6	34				
Sep-05	-5.78	-37.6	50	Sep-09	-5.76	-38.0	11				
Oct-05	-5.99	-36.0	43	Oct-09	-5.00	-29.5	52				
Nov-05	-9.83	-66.3	66	Nov-09	-8.33	-54.7	107				
Dec-05	-7.89	-48.8	17	Dec-09	-9.04	-59.9	72				
Jan-06	-8.46	-58.6	34	Jan-10	-12.22	-88.2	63				
Feb-06	-5.89	-39.1	31	Feb-10	-10.79	-73.1	58				
Mar-06	-5.25	-38.2	18	Mar-10	-6.35	-44.2	36				
Apr-06	-7.65	-47.9	105	Apr-10	-4.64	-28.2	23				
May-06	-1.99	-2.8	7	May-10	-4.92	-30.2	28				
Jun-06	-4.26	-21.1	46	Jun-10	-4.88	-36.1	16				
Jul-06	-6.92	-39.6	45	Jul-10	-3.61	-28.7	19				
Aug-06	-10.89	-74.4	52	Aug-10	-6.62	-46.9	110				
Sep-06	-6.10	-36.2	114	Sep-10	-6.66	-46.1	42				
Oct-06	-8.77	-55.7	69	Oct-10	-7.22	-40.7	42				
Nov-06	-5.65	-30.2	71	Nov-10	-7.97	-54.6	46				
Dec-06				Dec-10	-9.71	-67.1	22				

Table S2. Values of $\delta^{18}\text{O}$, $\delta^2\text{H}$, temperature and specific electrical conductivity for end-of-month spot samples collected from the River Thames at Wallingford 2003–2012. Also included is mean daily flow for the whole month calculated from flows measured by the Environment Agency at Day’s Lock (Thames, Stn. 39002) and Wheatley (Thame, Stn. 39105).

Month	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	Temp °C	SEC μS/cm	MDF m ³ /s	Month	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	Temp °C	SEC μS/cm	MDF m ³ /s
Jan-2003	-6.71	-47.8		711	245	Jan-2008	-6.92	-45.0	8.8	668	211
Feb-2003	-6.86	-49.3		717	50.4	Feb-2008	-7.25	-46.1	7.7	698	47.1
Mar-2003	-7.05	-45.6		697	39.3	Mar-2008	-6.49	-40.4	9.1	681	56.4
Apr-2003	-6.96	-45.6		719	16.6	Apr-2008	-6.74	-45.7	11.5	658	29.0
May-2003	-6.43	-43.0		748	13.9	May-2008	-6.85	-45.9	14.8	546	30.7
Jun-2003	-6.03	-40.8		779	8.0	Jun-2008	-6.77	-42.4	17.7	679	48.4
Jul-2003	-5.61	-41.7		791	6.1	Jul-2008	-6.43	-40.1	20.7	661	22.5
Aug-2003	-4.91	-33.5		943	5.0	Aug-2008	-6.51	-41.9	17.9	699	21.8
Sep-2003	-5.76	-37.3		902	4.0	Sep-2008	-6.81	-43.0	13.5	663	50.3
Oct-2003	-5.47	-38.2		980	4.0	Oct-2008	-5.79	-39.3	8.4	643	20.2
Nov-2003	-7.51	-53.2		790	7.9	Nov-2008	-6.69	-45.8	5.7	739	60.3
Dec-2003	-7.14	-48.0		759	28.1	Dec-2008	-6.97	-45.0	2.4	532	60.0
Jan-2004	-7.07	-46.7		722	105	Jan-2009	-6.80	-46.2	3.0	764	97.8
Feb-2004	-7.12	-44.9		721	67.9	Feb-2009	-6.83	-44.4	8.3	745	91.9
Mar-2004	-7.59	-51.5		734	28.6	Mar-2009	-6.97	-44.9	9.3	719	34.7
Apr-2004	-7.08	-45.3		706	26.4	Apr-2009	-6.94	-44.2	14.3	724	18.4
May-2004	-6.57	-43.9		733	29.6	May-2009	-6.45	-43.0	18.6	644	12.5
Jun-2004	-6.20	-41.7		766	10.6	Jun-2009	-6.56	-44.3	21.5	718	10.6
Jul-2004	-5.86	-41.6		757	8.1	Jul-2009	-6.67	-44.2	18.1	734	7.9
Aug-2004	-5.66	-40.5		673	13.3	Aug-2009	-6.19	-42.6	17.2	755	10.6
Sep-2004	-5.58	-39.3		795	8.2	Sep-2009	-5.68	-40.2	14.6	843	6.2
Oct-2004	-6.75	-45.9		659	35.1	Oct-2009	-6.14	-42.4	10.5	779	5.9
Nov-2004	-6.08	-41.6		730	38.3	Nov-2009	-6.62	-45.5	7.3	646	32.6
Dec-2004	-7.13	-46.1		679	35.6	Dec-2009	-7.33	-48.6	2.4	594	74.9
Jan-2005	-6.13	-42.0		766	50.8	Jan-2010	-5.61	-43.9	3.2	766	167
Feb-2005	-6.76	-45.4		843	20.7	Feb-2010	-7.96	-51.7	6.3	469	63.9
Mar-2005	-6.95	-43.6		702	21.8	Mar-2010	-7.13	-46.3	8.7	535	54.5
Apr-2005	-6.42	-41.9		740	32.9	Apr-2010	-6.92	-45.5	15.0	685	37.2
May-2005	-6.32	-41.0		725	15.5	May-2010	-6.58	-46.3	16.5	615	18.3
Jun-2005	-5.60	-37.5		702	9.2	Jun-2010	-6.25	-45.2	21.7	716	9.2
Jul-2005	-6.15	-39.6	18.9	771	6.8	Jul-2010	-5.85	-41.9	21.1	801	4.6
Aug-2005	-5.68	-39.3	19.8	794	5.1	Aug-2010	-6.57	-43.5	16.2	623	9.6
Sep-2005	-5.72	-36.3	15.0	837	4.4	Sep-2010	-6.26	-43.4	14.2	759	7.1
Oct-2005	-6.39	-43.3	14.4	825	6.2	Oct-2010	-6.30	-44.0	10.5	771	9.9
Nov-2005	-6.81	-44.8	4.6	808	17.2	Nov-2010	-6.44	-46.1	1.4	758	17.6
Dec-2005	-7.44	-48.8	4.1	742	29.6	Dec-2010	-6.93	-47.1	3.8	805	16.0
Jan-2006	-6.68	-42.8	3.4	722	43.8	Jan-2011	-7.24	-47.9	3.0	730	117
Feb-2006	-6.77	-42.9	5.1	769	19.6	Feb-2011	-6.49	-44.4		640	40.8
Mar-2006	-6.65	-44.1	10.0	736	23.4	Mar-2011	-6.93	-46.4		700	30.8
Apr-2006	-6.20	-41.7	12.7	696	26.2	Apr-2011	-6.27	-43.3	16.7	638	12.7
May-2006	-5.45	-36.1	14.2	674	24.9	May-2011	-5.68	-42.3	16.0	764	8.0
Jun-2006	-6.61	-42.1	20.0	723	12.9	Jun-2011	-5.55	-42.2	19.6	771	6.4
Jul-2006	-5.91	-36.5	23.2	724	10.2	Jul-2011	-5.93	-42.2	21.1	797	4.8
Aug-2006	-5.72	-38.5	18.3	794	6.8	Aug-2011	-5.95	-41.0	16.5	795	4.4
Sep-2006	-7.16	-49.7	17.2	726	8.1	Sep-2011	-6.15	-40.1	19.4	834	4.0
Oct-2006	-6.75	-45.6	11.7	710	35.1	Oct-2011	-5.92	-39.0	13.2	871	3.8
Nov-2006	-6.82	-46.2	8.5	596	53.5	Nov-2011	-5.97	-39.3	8.9	950	4.5
Dec-2006	-6.24	-40.0	5.7	568	83.9	Dec-2011	-6.66	-44.1	8.9	869	10.2
Jan-2007	-6.72	-40.9	10.1	738	215	Jan-2012	-6.26	-43.4	5.2	780	36.4
Feb-2007	-6.89	-47.0	8.2	623	81.8	Feb-2012	-6.54	-44.1	9.3	763	17.0
Mar-2007	-6.61	-42.7	9.4	713	86.8	Mar-2012	-6.17	-42.5	12.8	796	13.9
Apr-2007	-6.39	-41.6	16.1	724	21.0	Apr-2012	-7.37	-49.3	9.3	550	24.2
May-2007	-7.68	-49.5	13.9	602	26.6	May-2012	-6.15	-43.6	19.5	653	64.8
Jun-2007	-6.98	-46.9	16.6	654	26.7	Jun-2012	-6.08	-42.8	17.0	604	46.0
Jul-2007	-6.41	-41.3	18.2	570	88.6	Jul-2012	-6.46	-43.3	17.2	653	48.1
Aug-2007	-6.61	-41.8	16.7	701	46.6	Aug-2012	-6.50	-44.2	16.2	633	25.8
Sep-2007	-6.57	-42.8	12.8	725	17.5	Sep-2012	-6.78	-47.0	12.5	638	22.2
Oct-2007	-6.45	-41.1	11.5	764	26.6	Oct-2012	-6.39	-43.3	8.8	700	53.8
Nov-2007	-6.79	-45.4	8.1	742	34.8	Nov-2012	-7.22	-48.1	3.8	528	107
Dec-2007	-6.57	-40.2	7.2	714	72.6	Dec-2012	-6.80	-45.4	8.1	551	138

SEC - specific electrical conductivity

MDF - mean daily flow

Table S3. Values of $\delta^{18}\text{O}$, $\delta^2\text{H}$, temperature and specific electrical conductivity (SEC) for river water samples collected from the upper Thames basin on the dates indicated from sites shown on the map in Fig. 1. Samples collected along the Thames are prefixed by T-.

River	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	Temp °C	SEC $\mu\text{S}/\text{cm}$	River	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	Temp °C	SEC $\mu\text{S}/\text{cm}$
17-18 Oct 2011					17-18 Oct 2011 (contd.)				
Coln	-6.95	-44.4	10.2	570	Kennet	-6.78	-45.8	10.3	605
Cole	-5.23	-37.7	10.1	731	Enborne	-6.11	-40.2	10.2	561
Leach	-6.54	-43.3	10.4	579	Loddon	-6.66	-43.2	11.6	753
Windrush	-6.63	-44.2	10.3	591	Wye	-7.30	-48.8	12.3	589
Evenlode	-6.19	-41.6	10.1	663	The Cut	-6.43	-43.6	13.1	1085
Cherwell	-5.29	-38.4	10.7	991	T-Hannington	-5.84	-39.1	11.8	1121
Ray	-5.33	-37.6	10.6	1026	T-Swinford	-5.76	-39.9	12.3	751
Ock	-6.28	-41.4	10.7	811	T-Wallingford	-5.45	-39.0	13.9	918
Thame	-6.04	-41.2	10.8	906	T-Sonning	-6.43	-43.6	13.6	734
Pang	-6.67	-45.3	9.1	575	T-Runnymede	-6.47	-45.4	14.3	790
16 Jan 2012					16 Jan 2012 (contd.)				
Coln	-6.96	-47.6	6.1	573	Kennet	-6.94	-44.4	3.2	619
Cole	-6.23	-41.4	1.9	847	Enborne	-6.39	-42.7	2.2	465
Leach	-6.69	-42.9	5.7	595	Loddon	-6.81	-46.9	3.8	704
Windrush	-6.93	-47.8	2.7	611	Wye	-7.34	-49.1	7.7	742
Evenlode	-6.70	-46.5	3.1	655	The Cut	-6.20	-42.9	4.8	973
Cherwell	-6.57	-44.9	2.7	877	T-Hannington	-5.89	-40.1	4.9	683
Ray	-6.10	-39.4	2.3	962	T-Swinford	-6.58	-44.8	4.2	663
Ock	-6.34	-44.9	2.6	870	T-Wallingford	-6.17	-43.0	5.5	778
Thame	-6.24	-43.0	2.4	929	T-Sonning	-6.26	-42.2	5.3	726
Pang	-7.17	-48.4	3.4	602	T-Runnymede	-6.80	-44.8	6.3	726
16 Apr 2012					16 Apr 2012 (contd.)				
Coln	-7.29	-46.5	11.2	509	Kennet	-6.95	-44.3	10.5	477
Cole	-6.94	-45.6	10.1	663	Enborne	-6.61	-43.2	7.9	431
Leach	-6.96	-44.0	9.6	509	Loddon	-6.51	-44.5	10.0	693
Windrush	-6.90	-43.3	9.8	615	Wye	-7.32	-47.6	9.3	725
Evenlode	-6.26	-41.6	9.8	553	The Cut	-6.42	-43.8	9.3	1009
Cherwell	-6.52	-44.2	9.6	750	T-Hannington	-6.27	-42.0	10.1	714
Ray	-6.22	-42.3	8.6	928	T-Swinford	-6.73	-42.1	10.3	583
Ock	-6.85	-44.6	10.1	810	T-Wallingford	-6.18	-42.6	11.0	828
Thame	-6.51	-41.6	9.3	849	T-Sonning	-6.24	-41.6	10.8	704
Pang	-7.21	-48.3	9.3	519	T-Runnymede	-6.46	-43.7	11.0	632
23-24 Jul 2012					23-24 Jul 2012 (contd.)				
Coln	-7.02	-46.6	15.1	563	Kennet	-6.88	-45.5	17.8	576
Cole	-6.39	-42.9	18.8	732	Enborne	-6.57	-42.8	15.8	466
Leach	-6.39	-42.7	15.5	588	Loddon	-6.32	-43.2	18.0	657
Windrush	-6.81	-45.6	17.4	540	Wye	-7.18	-47.9	15.4	588
Evenlode	-6.70	-44.8	17.1	618	The Cut	-6.19	-43.0	18.3	944
Cherwell	-6.40	-43.8	18.4	611	T-Hannington	-6.19	-42.0	18.8	571
Ray	-5.73	-40.4	17.8	729	T-Swinford	-6.45	-43.9	18.1	595
Ock	-6.62	-45.1	17.9	787	T-Wallingford	-6.27	-42.2	18.5	658
Thame	-6.32	-43.2	18.0	816	T-Sonning	-6.36	-42.8	18.0	642
Pang	-7.04	-46.7	15.8	600	T-Runnymede	-6.30	-42.3	18.8	649
22-23 Oct 2012					22-23 Oct 2012 (contd.)				
Coln	-7.06	-46.1	11.2	570	Kennet	-6.95	-45.4	12.0	585
Cole	-6.33	-41.7	12.1	711	Enborne	-6.43	-42.6	12.1	393
Leach	-6.82	-44.3	11.5	588	Loddon	-6.52	-43.8	12.9	524
Windrush	-6.89	-45.7	11.5	582	Wye	-7.23	-47.6	12.8	613
Evenlode	-6.77	-44.9	11.5	613	The Cut	-6.64	-44.7	13.7	682
Cherwell	-6.61	-44.3	11.6	652	T-Hannington	-6.29	-42.3	12.2	616
Ray	-6.36	-40.4	12.3	589	T-Swinford	-6.48	-44.1	11.8	631
Ock	-6.49	-42.1	12.3	763	T-Wallingford	-6.48	-42.8	12.1	644
Thame	-6.32	-41.5	12.2	754	T-Sonning	-6.52	-41.4	12.1	619
Pang	-7.03	-45.8	12.0	574	T-Runnymede	-6.51	-42.8	12.3	597
14 Jan 2013					14 Jan 2013 (contd.)				
Coln	-7.25	-47.9	7.2	548	Kennet	-6.92	-45.6	6.0	598
Cole	-6.77	-45.0	5.6	699	Enborne	-6.72	-43.9	5.3	421
Leach	-6.92	-45.7	7.2	569	Loddon	-6.63	-44.0	5.7	575
Windrush	-7.15	-47.0	5.6	548	Wye	-7.30	-48.6	7.4	616
Evenlode	-6.96	-47.0	5.5	586	The Cut	-6.70	-44.9	5.5	774
Cherwell	-7.02	-46.5	4.2	638	T-Hannington	-6.73	-45.1	5.5	592
Ray	-6.69	-45.1	4.1	731	T-Swinford	-6.72	-45.7	4.9	590
Ock	-7.00	-46.9	5.4	740	T-Wallingford	-5.55	-42.1	5.0	650
Thame	-6.76	-44.4	4.2	793	T-Sonning	-6.87	-45.2	5.4	628
Pang	-7.16	-47.5	6.0	611	T-Runnymede	-6.76	-45.3	5.9	630
15 Apr 2013					15 Apr 2013 (contd.)				
Coln	-7.12	-47.3	12.3	627	Kennet	-7.05	-45.7	12.1	606
Cole	-6.89	-46.2	11.8	722	Enborne	-7.18	-47.8	10.8	399
Leach	-6.85	-45.0	11.1	616	Loddon	-7.05	-47.1	12.1	568
Windrush	-7.13	-46.7	11.5	566	Wye	-7.35	-49.0	10.8	608
Evenlode	-7.11	-47.8	10.5	620	The Cut	-7.43	-50.6	11.8	738
Cherwell	-7.16	-49.0	11.1	731	T-Hannington	-6.90	-45.8	11.4	666
Ray	-7.43	-51.9	10.7	716	T-Swinford	-7.01	-46.5	11.2	644
Ock	-6.97	-45.7	11.8	746	T-Wallingford	-7.16	-48.8	11.2	707
Thame	-7.12	-49.3	11.3	773	T-Sonning	-7.13	-47.8	11.0	670
Pang	-7.16	-48.0	12.0	649	T-Runnymede	-7.14	-47.9	11.0	708

Table S4. Results of end-of-month sampling of the River Thames at Dorchester (DC) and the River Thames at Wallingford (WF), Tilehurst (TH) and Runnymede (RM). Refer to Fig. 1 for locations.

Month	$\delta^{18}\text{O} \text{‰}$				$\delta^2\text{H} \text{‰}$				$\delta^{13}\text{C}\text{-DIC} \text{‰}$				SEC mS/cm				Temp °C			
	DC	WF	TH	RM	DC	WF	TH	RM	DC	WF	TH	RM	DC	WF	TH	RM	DC	WF	TH	RM
Apr-11	-	-6.27	-	-	-	-43.3	-	-	-13.5	-	-	-	-	638	-	-	16.7	-	-	
May-11	-	-5.68	-5.65	-	-	-42.3	-42.9	-	-13.5	-	-	-	-	764	746	-	16.0	-	-	
Jun-11	-	-5.55	-5.74	-	-	-42.2	-41.3	-	-13.8	-	-	-	-	771	755	-	19.6	-	-	
Jul-11	-	-5.93	-6.12	-	-	-42.2	-42.4	-	-14.2	-	-	-	-	797	754	-	21.1	-	-	
Aug-11	-6.28	-5.95	-6.15	-	-43.2	-41.0	-40.1	-	-15.6	-13.8	-	-	837	795	761	-	15.2	16.5	-	
Sep-11	-6.08	-6.15	-5.96	-	-41.7	-40.1	-39.1	-	-15.4	-14.3	-	-	886	834	791	-	15.2	19.4	-	
Oct-11	-5.89	-5.92	-6.08	-	-41.6	-39.0	-40.5	-	-15.5	-14.8	-	-	907	871	849	-	11.3	13.2	-	
Nov-11	-6.29	-5.97	-5.89	-6.35	-41.6	-39.3	-40.1	-40.4	-14.5	-14.2	-	-14.4	935	950	883	780	7.1	8.9	-	8.9
Dec-11	-6.70	-6.66	-6.19	-6.82	-46.1	-44.1	-41.7	-43.7	-14.1	-14.4	-	-14.2	940	869	824	755	8.8	8.9	-	8.1
Jan-12	-6.41	-6.26	-6.46	-6.24	-45.0	-43.4	-44.8	-44.4	-14.7	-14.2	-	-14.2	920	780	745	779	3.9	5.2	-	6.4
Feb-12	-6.35	-6.54	-6.93	-7.15	-46.3	-44.1	-45.9	-46.5	-13.4	-13.0	-	-13.3	920	763	697	743	9.3	9.3	-	9.2
Mar-12	-5.52	-6.17	-6.26	-6.50	-43.5	-42.5	-43.9	-45.2	-13.8	-13.9	-	-12.7	868	796	653	756	10.8	12.8	-	12.5
Apr-12	-7.54	-7.37	-7.32	-6.94	-49.7	-49.3	-48.0	-47.2	-16.9	-16.3	-	-15.1	574	550	542	572	10.6	9.3	-	11.3
May-12	-6.80	-6.15	-7.02	-6.71	-46.4	-43.6	-47.1	-43.2	-14.6	-13.7	-	-13.5	820	653	636	649	19.0	19.5	-	20.5
Jun-12	-6.38	-6.08	-	-6.63	-43.2	-42.8	-	-44.0	-16.3	-15.6	-	-14.7	661	604	656	656	16.0	17.0	-	17.4
Jul-12	-6.31	-6.46	-	-6.30	-43.5	-43.3	-	-42.3	-16.2	-13.3	-	-14.2	820	653	649	649	17.1	17.2	-	18.8
Aug-12	-6.32	-6.50	-	-6.43	-43.3	-44.2	-	-43.5	-14.5	-13.8	-	-15.0	813	633	659	659	17.6	16.2	-	18.1
Sep-12	-6.41	-6.78	-	-6.84	-42.9	-47.0	-	-45.8	-14.8	-14.5	-	-14.9	791	638	617	617	11.6	12.5	-	13.5
Oct-12	-6.24	-6.39	-	-6.43	-42.4	-43.3	-	-43.4	-15.6	-14.0	-	-15.0	834	700	666	666	8.6	8.8	-	10.5
Nov-12	-6.87	-7.22	-	-7.35	-45.4	-48.1	-	-49.8	-16.1	-15.3	-	-15.6	633	528	447	447	4.3	3.8	-	8.5
Dec-12	-6.87	-6.80	-	-6.76	-45.3	-45.4	-	-45.4	-16.4	-15.2	-	-15.0	624	551	623	623	8.7	8.1	-	8.6
Jan-13	-7.78	-7.94	-	-7.65	-52.3	-53.2	-	-51.2	-16.5	-16.1	-	-15.5	549	517	667	667	8.6	8.3	-	5.6
Feb-13	-6.92	-6.96	-	-7.02	-45.5	-46.9	-	-46.1	-16.2	-14.2	-	-14.4	800	662	663	663	5.4	5.0	-	5.6
Mar-13	-6.98	-7.05	-	-8.06	-45.9	-47.5	-	-56.2	-14.3	-14.5	-	-15.6	803	686	570	570	4.8	5.2	-	6.3
Apr-13	-6.69	-6.77	-	-6.82	-44.3	-45.2	-	-46.0	-13.1	-13.6	-	-12.9	776	684	651	651	11.0	11.7	-	-
May-13	-7.16	-6.89	-	-6.88	-47.9	-46.4	-	-46.4	-14.5	-13.7	-	-12.7	716	680	613	613	11.5	12.9	-	-

Table S5. Values of $\delta^{13}\text{C-DIC}$, pH and alkalinity as HCO_3 for end-of-month spot samples collected from the River Thames at Wallingford, 2003–2007.

Month	$\delta^{13}\text{C-DIC}$ ‰	pH	Alkalinity mg/L	Month	$\delta^{13}\text{C-DIC}$ ‰	pH	Alkalinity mg/L
Jan-2003	-15.1	7.80	291	Jul-2005	-15.0	7.87	268
Feb-2003	-14.0	7.83	291	Aug-2005	-14.2	7.81	267
Mar-2003	-13.8	7.90	274	Sep-2005	-15.1	7.75	254
Apr-2003	-14.3	7.77	264	Oct-2005	-15.4	7.76	264
May-2003	-14.2	7.63	271	Nov-2005	-16.4	7.95	289
Jun-2003	-14.8	7.61	263	Dec-2005	-15.5	7.87	282
Jul-2003	-14.2	7.84	256	Jan-2006	-13.1	7.80	283
Aug-2003	-12.4	7.81	278	Feb-2006	-14.3	7.94	277
Sep-2003	-14.0	7.73	280	Mar-2006	-14.4	7.82	269
Oct-2003	-13.9	7.98	270	Apr-2006	-14.2	7.90	269
Nov-2003	-15.7	7.70	233	May-2006	-15.7	7.82	281
Dec-2003	-15.1	8.03	244	Jun-2006	-14.6	7.81	272
Jan-2004	-14.4	7.85	268	Jul-2006	-15.2	7.80	246
Feb-2004	-14.1	7.79	281	Aug-2006	-14.8	7.73	243
Mar-2004	-13.7	8.02	279	Sep-2006	-15.3	7.61	223
Apr-2004	-15.3	7.60	266	Oct-2006	-15.2	7.91	291
May-2004	-14.7	7.70	278	Nov-2006	-16.3	7.67	244
Jun-2004	-14.5	7.99	272	Dec-2006	-16.7	7.76	236
Jul-2004	-17.2	7.90	269	Jan-2007	-13.9	7.90	300
Aug-2004	-15.7	7.80	251	Feb-2007	-16.2	7.67	258
Sep-2004	-14.4	7.78	264	Mar-2007	-15.7	8.02	286
Oct-2004	-16.6	7.64	263	Apr-2007	-15.1	7.99	274
Nov-2004	-15.3	7.91	293	May-2007	-16.9	7.60	228
Dec-2004	-15.1	7.87	260	Jun-2007	-14.9	7.87	276
Jan-2005	-14.9	7.88	307	Jul-2007	-12.3	7.57	259
Feb-2005	-13.9	7.97	293	Aug-2007	-15.2	7.83	294
Mar-2005	-14.6	7.70	251	Sep-2007	-9.4	7.80	279
Apr-2005	-15.3	7.85	296	Oct-2007	-15.2	8.19	306
May-2005	-15.4	7.25	273	Nov-2007	-15.1	7.95	306
Jun-2005	-15.6	7.65	244	Dec-2007	-14.2	8.16	302

DIC - dissolved inorganic carbon

Table S6. Values of $\delta^{13}\text{C-DIC}$, pH and alkalinity as HCO_3 for river water samples collected from the upper Thames basin on the dates indicated from sites shown on the map in Fig. 1. Samples collected along the Thames are prefixed by T-

River	$\delta^{13}\text{C-DIC}$ ‰	pH	Alkalinity mg/L	River	$\delta^{13}\text{C-DIC}$ ‰	pH	Alkalinity mg/L
17-18 Oct 2011				17-18 Oct 2011 (contd.)			
Coln	-13.3	8.03	258	Kennet	-13.7	7.87	281
Cole	-16.1	7.88	270	Enborne	-15.3	7.68	197
Leach	-14.0	7.90	266	Loddon	-14.4	7.82	205
Windrush	-14.1	7.91	227	Wye	-14.6	8.16	224
Evenlode	-14.2	7.86	262	The Cut	-14.0	7.46	175
Cherwell	-15.2	7.78	287	T-Hannington	-15.2	7.90	223
Ray	-15.8	7.31	239	T-Swinford	-14.0	7.89	242
Ock	-12.9	7.98	268	T-Wallingford	-13.7	7.84	248
Thame	-15.2	7.71	277	T-Sonning	-13.1	7.88	269
Pang	-14.0	7.88	273	T-Runnymede	-14.1	7.81	255
16 Jan 2012				16 Jan 2012 (contd.)			
Coln	-13.4	7.99	252	Kennet	-15.1	7.96	272
Cole	-14.8	8.02	270	Enborne	-14.0	7.71	171
Leach	-13.1	8.02	263	Loddon	-14.4	7.75	193
Windrush	-13.4	8.10	241	Wye	-14.0	7.99	273
Evenlode	-13.6	8.00	253	The Cut	-14.4	7.54	158
Cherwell	-14.6	7.93	252	T-Hannington	-14.2	7.92	239
Ray	-14.5	7.81	242	T-Swinford	-13.8	8.11	262
Ock	-13.4	8.03	288	T-Wallingford	-14.6	7.94	263
Thame	-14.0	7.94	271	T-Sonning	-14.0	7.92	242
Pang	-14.3	7.94	266	T-Runnymede	-14.0	7.83	226
16 Apr 2012				16 Apr 2012 (contd.)			
Coln	-12.7	8.08	248	Kennet	-13.1	7.68	239
Cole	-14.1	8.05	242	Enborne	-12.7	8.16	164
Leach	-13.4	7.78	249	Loddon	-13.1	8.12	187
Windrush	-13.4	8.02	232	Wye	-14.1	8.10	277
Evenlode	-12.9	7.95	201	The Cut	-13.0	7.72	125
Cherwell	-13.7	7.89	260	T-Hannington	-13.5	8.05	227
Ray	-17.1	7.72	247	T-Swinford	-13.1	8.18	238
Ock	-12.6	8.37	268	T-Wallingford	-13.3	8.04	239
Thame	-13.8	8.05	262	T-Sonning	-12.8	8.38	233
Pang	-12.4	7.78	258	T-Runnymede	-13.1	7.92	209
23-24 Jul 2012				23-24 Jul 2012 (contd.)			
Coln	-13.4	7.93	258	Kennet	-13.0	8.17	281
Cole	-13.8	7.96	298	Enborne	-14.8	7.87	205
Leach	-13.9	7.88	282	Loddon	-13.3	7.94	220
Windrush	-13.3	8.04	249	Wye	-13.3	8.18	286
Evenlode	-13.6	7.80	279	The Cut	-14.0	7.76	191
Cherwell	-14.4	7.78	251	T-Hannington	-14.2	7.80	262
Ray	-14.7	7.49	316	T-Swinford	-13.7	7.97	236
Ock	-13.9	7.99	302	T-Wallingford	-13.6	8.00	286
Thame	-15.0	7.67	346	T-Sonning	-14.1	8.05	286
Pang	-13.2	8.02	286	T-Runnymede	-14.2	8.01	272
22-23 Oct 2012				22-23 Oct 2012 (contd.)			
Coln	-13.7	7.95	270	Kennet	-15.2	8.06	310
Cole	-15.4	7.92	314	Enborne	-15.4	7.76	164
Leach	-13.7	8.05	285	Loddon	-14.2	7.72	192
Windrush	-14.2	8.11	265	Wye	-14.8	8.04	286
Evenlode	-14.4	8.02	281	The Cut	-14.4	7.70	161
Cherwell	-14.7	7.96	297	T-Hannington	-14.4	7.84	272
Ray	-15.3	7.48	155	T-Swinford	-15.3	8.03	286
Ock	-16.2	7.89	346	T-Wallingford	-15.8	7.94	272
Thame	-15.5	7.80	300	T-Sonning	-13.6	7.96	256
Pang	-14.5	7.88	284	T-Runnymede	-15.9	7.92	239
14 Jan 2013				14 Jan 2013 (contd.)			
Coln	-13.2	8.04	267	Kennet	-13.4	8.05	295
Cole	-14.5	8.12	316	Enborne	-13.9	7.93	187
Leach	-13.4	8.07	280	Loddon	-13.4	7.91	217
Windrush	-13.3	8.12	254	Wye	-13.8	7.98	295
Evenlode	-14.1	8.08	256	The Cut	-13.5	7.71	165
Cherwell	-14.3	8.03	249	T-Hannington	-13.6	8.05	266
Ray	-15.0	7.83	301	T-Swinford	-13.8	8.09	280
Ock	-14.2	8.12	314	T-Wallingford	-13.8	8.03	285
Thame	-14.3	8.05	330	T-Sonning	-13.9	8.08	285
Pang	-13.2	7.94	293	T-Runnymede	-13.3	8.01	278
15 Apr 2013				15 Apr 2013 (contd.)			
Coln	-13.4	8.04	237	Kennet	-14.3	8.14	255
Cole	-14.9	8.14	197	Enborne	-14.6	7.91	157
Leach	-13.6	7.72	237	Loddon	-13.8	7.73	169
Windrush	-13.7	8.03	221	Wye	-14.3	8.05	263
Evenlode	-14.3	7.99	240	The Cut	-14.0	7.76	145
Cherwell	-14.5	8.03	237	T-Hannington	-14.0	7.96	238
Ray	-15.1	7.68	237	T-Swinford	-14.5	8.10	254
Ock	-15.2	8.20	287	T-Wallingford	-14.8	8.08	241
Thame	-14.9	7.88	281	T-Sonning	-13.7	8.03	238
Pang	-13.8	8.00	252	T-Runnymede	-14.6	7.96	226