

---

## The O & H stable isotopic composition of fresh waters in the British Isles. 2. Surface waters and groundwater

W.G. Darling<sup>1</sup>, A.H. Bath<sup>2</sup> and J.C. Talbot<sup>1</sup>

<sup>1</sup>British Geological Survey, Wallingford, OX10 8BB, UK

<sup>2</sup>Intellisci Ltd, Loughborough, LE12 6SZ, UK

Email for corresponding author: wgd@bgs.ac.uk

---

### Abstract

The utility of stable isotopes as tracers of the water molecule has a long pedigree. The study reported here is part of an attempt to establish a comprehensive isotopic 'baseline' for the British Isles as background data for a range of applications. Part 1 of this study (Darling and Talbot, 2003) considered the isotopic composition of rainfall in Britain and Ireland. The present paper is concerned with the composition of surface waters and groundwater. In isotopic terms, surface waters (other than some upland streams) are poorly characterised in the British Isles; their potential variability has yet to be widely used as an aid in hydrological research. In what may be the first study of a major British river, a monthly isotopic record of the upper River Thames during 1998 was obtained. This shows high damping of the isotopic variation compared to that in rainfall over most of the year, though significant fluctuations were seen for the autumn months. Smaller rivers such as the Stour and Darent show a more subdued response to the balance between runoff and baseflow. The relationship between the isotopic composition of rainfall and groundwater is also considered. From a limited database, it appears that whereas Chalk groundwater is a representative mixture of weighted average annual rainfall, for Triassic sandstone groundwater there is a seasonal selection of rainfall biased towards isotopically-depleted winter recharge. This may be primarily the result of physical differences between the infiltration characteristics of rock types, though other factors (vegetation, glacial history) could be involved. In the main, however, groundwaters appear to be representative of bulk rainfall within an error band of 0.5‰  $\delta^{18}\text{O}$ . Contour maps of the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  content of recent groundwaters in the British Isles show a fundamental SW-NE depletion effect modified by topography. The range of measured values, while much smaller than those for rainfall, still covers some 4‰ for  $\delta^{18}\text{O}$  and 30‰ for  $\delta^2\text{H}$ . Over lowland areas the 'altitude effect' is of little significance, but in upland areas is consistent with a range of  $-0.2$  to  $-0.3$ ‰ per 100 m increase in altitude. Groundwaters dating from the late Pleistocene are usually modified in  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  owing to the effects of climate change on the isotopic composition of rainfall and thus of recharge. Contour maps of isotopic variability prior to 10 ka BP, based on the relatively limited information available from the British Isles, allow a first comparison between groundwaters now and at the end of the last Ice Age. The position of the British Isles in the context of the stable isotope systematics of NW Europe is reviewed briefly.

**Keywords:** Stable isotopes, surface waters, groundwater, British Isles

### Introduction

Away from coastal influences, surface waters and groundwaters are derived exclusively from precipitation. Part 1 of this study (Darling and Talbot, 2003) focused on the isotopic composition of rainfall in Great Britain and Ireland. The present paper considers mainly the recharge process and the pattern of groundwater isotope values resulting from the climate of the British Isles. In addition, the isotopic variability of surface waters is considered briefly, though fewer data are available.

Oxygen and hydrogen stable isotope ratios ( $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/^1\text{H}$  ratios of the water molecule) are by their nature

excellent tracers of the physical processes affecting water. A knowledge of 'baseline' isotopic compositions in the waters of a region creates a starting point for isotope-based applications ranging from the local, e.g. fingerprinting sources of water leakage (Butler and Verhagen, 1997; Maréchal and Etcheverry, 2003), to the regional, e.g. groundwater resource and quality studies (Smith *et al.*, 1976; Rauert *et al.*, 1993), the archaeological (Iacumin *et al.*, 1997; White *et al.*, 1998), the environmental (Andrews *et al.*, 1997; Iacumin and Longinelli, 2002), the quasi-forensic (Keenlyside *et al.*, 1997) and ultimately as part of the global mosaic which aids the understanding of climatic processes

(Rozanski *et al.*, 1993; Hoffmann *et al.*, 2000). In contrast to some areas of Europe, such as Germany and Italy (Förstel and Hütten, 1983; Longinelli and Selmo, 2003), the stable isotopic variations of waters in the British Isles have hitherto not been summarised in any systematic way. However, the compilation of isotopic datasets by the British Geological Survey (BGS) over the past 25 years combined with (relatively scarce) published studies by other researchers makes it possible for the present paper to attempt a synthesis. Although there are rather few data for Ireland in comparison to Great Britain, enough have been obtained to permit a study of the British Isles as a whole.

## Sampling and analysis

Unfiltered water samples were collected and stored in glass bottles with rubber-lined metal caps, usually of 7 ml or 28 ml capacity to provide adequate volume for the separate analysis of  $^{18}\text{O}/^{16}\text{O}$  and  $^2\text{H}/^1\text{H}$ . Analysis was carried out using standard preparation techniques followed by isotope ratio measurement on VG-Micromass 602E or Optima mass spectrometers. All data considered in this paper are expressed in ‰ with respect to Vienna Standard Mean Ocean Water (VSMOW) on the delta scale:

$$\delta = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 10^3 \quad (1)$$

where  $R_{\text{sample}}$  is the  $^{18}\text{O}/^{16}\text{O}$  or  $^2\text{H}/^1\text{H}$  ratio of the sample, and  $R_{\text{standard}}$  the corresponding ratio in VSMOW. Analytical precisions are better than  $\pm 0.2\text{‰}$  for  $\delta^{18}\text{O}$  and  $\pm 2\text{‰}$  for  $\delta^2\text{H}$ .

## Results and discussion

### SURFACE WATERS

#### *General background*

Surface waters may originate more or less directly from rainfall by runoff, or via groundwater discharge, or by some combination of both. Runoff is likely to suffer less ‘damping’ of rainfall isotopic variability than aquifer discharge, though the effects are still fairly pronounced (e.g. Ogunkoya and Jenkins, 1991). Once these waters are exposed to the atmosphere in waterways or lakes, they are potentially subject to modification by evaporative fractionation (e.g. Clark and Fritz, 1997). The kinetic processes involved tend to cause isotopic ratios to deviate in a correlated way from values approximately consistent with the World Meteoric Line (WML) of Craig (1961), which has a  $\delta^2\text{H}$  versus  $\delta^{18}\text{O}$  slope of 8, to values that define a lower slope. Slope values

depend critically on atmospheric humidity, with the lowest slopes produced by lowest humidity. The amount of evaporation on the other hand is indicated by the displacement of the sample along the evaporative line, which in extreme cases can result in positive  $\delta$ -values (e.g. Clark and Fritz, 1997). Clearly, lakes are more likely than rivers to suffer evaporative modification since residence times will normally be longer, thus allowing time for more contact and exchange with the atmosphere.

Because the isotopic values of surface waters may change over time owing to evaporation, their measurement is often seen as being of limited use in practical terms. In general they are measured only for specific purposes such as characterising local sources of leakage (e.g. from dams) or for identifying larger-scale hydraulic links between surface waters and groundwater. As the climate of NW Europe is seldom sufficiently warm and dry to impart large evaporative isotope shifts to surface waters, such applications are constrained in the region. Accordingly, little has been published on the stable isotopic composition of surface waters in the British Isles.

The compositional range of surface waters is always liable to exceed that of groundwaters in a particular area, partly because of the evaporative effects outlined above, but also because those surface waters resulting more or less directly from rainfall can, under certain conditions, reflect the extremes of individual rainfall events. In Britain, the most enriched sample found during this survey had a  $\delta^{18}\text{O}$  value of  $-1.3\text{‰}$ , while the most depleted value reported is  $-10.6\text{‰}$  (Soulsby *et al.*, 1999). This range of  $\sim 9\text{‰}$  is about double that measured for groundwaters (see below).

The available data from samplings of surface waters in the British Isles are shown in Fig. 1 in the form of a delta-plot ( $\delta^2\text{H}$  v.  $\delta^{18}\text{O}$ ), where lakes and canals are included under the ‘standing’ and rivers under the ‘flowing’ categories. (Isotope ratios in upland streams are not considered here; their use in hydrograph separations is beyond the scope of this paper.) It is apparent that, taken as a whole, surface waters lie along a lower slope than the WML, exhibiting the signs of evaporative enrichment in heavy isotopes under a generally high-humidity climate. The correlation is not particularly good but the samples come from a wide area of the British Isles at different dates and are likely to have had different original compositions along the WML or its local variants. Predictably, standing (more accurately slow-moving) waters show more evidence of evaporation than rivers. The most enriched compositions were found in waters from small lochs on the Scottish islands, the ‘heaviest’ sample of all (Loch of Watlee, Unst, Shetlands) coincidentally being the most northerly sample of the present survey. The major factor in these enrichments may be that

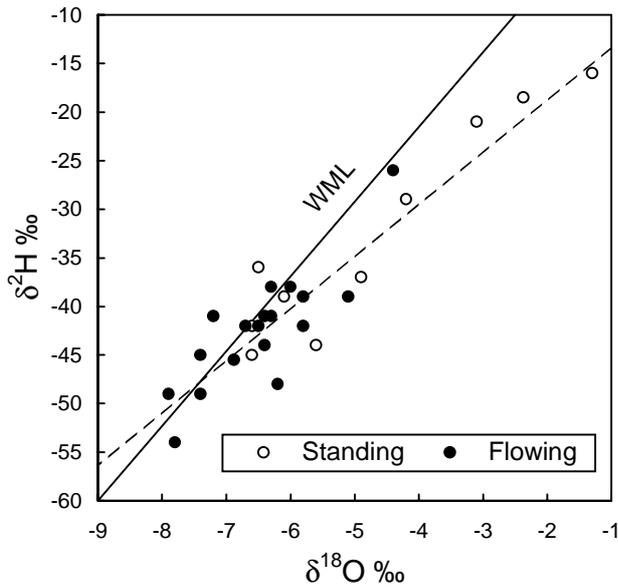


Fig. 1.  $\delta$ -plot for surface waters from the British Isles (BGS unpublished data). The datapoints are arrayed along a lower slope than that of the World Meteoric Line (WML) of Craig (1961), indicating the effects of evaporative fractionation. Standing waters exhibit these effects more strongly because they have more time to evaporate.

high average wind velocities in the Scottish islands lead to relatively large evaporation/inflow ratios in the smaller basins.

### River variations

Most rivers have two main sources of water: runoff and baseflow. At any one time, the balance between these depends partly on the geology of the catchment and partly on the season of the year. Thus, for example, rivers at the end of a typical British summer contain a low flow (baseflow) which primarily represents the discharge from the aquifer(s) over which the river passes. In an attempt to discover to what extent river waters may vary in isotopic composition over the course of a year, monthly samples were collected from the River Thames at Wallingford from December 1997 to December 1998. The results are shown in Figs. 2 and 3.

Several points about these data should be noted: (i) the river isotope values are spot samples taken during the month concerned and do not represent mean or weighted mean values; (ii) the flowrates are based on measurements taken at a weir a few km up-river from the collection point; (iii) the rainfall data refer to the Wallingford collection station (Darling and Talbot, 2003) but are assumed to be reasonably indicative of conditions further up the catchment.

Figure 2 shows that there was little variation in the isotopic composition of the river water over much of the year. Only in late summer and early autumn was there much change. After two months of low flow at the end of August there was some isotopic enrichment, which judging by the displacement from the WML (Fig. 3) may have been due to

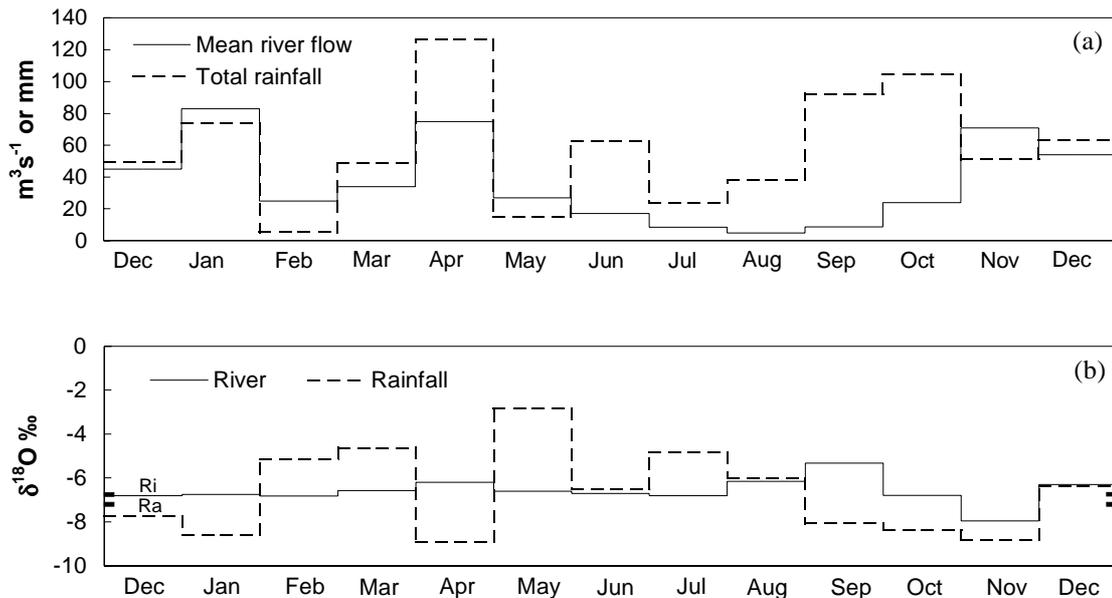


Fig. 2. The River Thames at Wallingford during 1998 in its isotopic and hydrological context: (a) mean monthly river flow (measured at the nearby Day's Lock site of the Environment Agency) is compared with total monthly rainfall, (b)  $\delta^{18}\text{O}$  values for monthly spot samples of river water are compared to weighted mean monthly values of rainfall from the Wallingford meteorological site (Darling and Talbot, 2003).

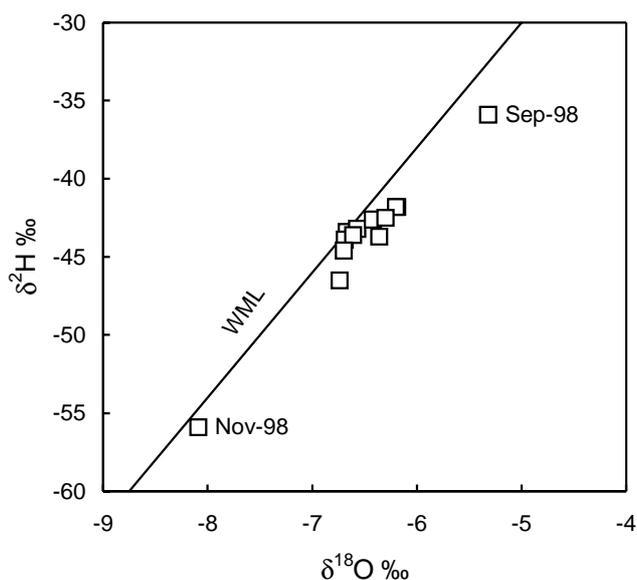


Fig. 3.  $\delta$ -plot of River Thames monthly spot sampling during 1998. Note that the largest variation occurs over the autumn months (Sep–Nov).

evaporation. In November the situation was reversed with high flow and a depleted isotopic composition. The isotopic composition of October and November’s rainfall as measured at Wallingford was relatively depleted, and runoff from these events seems likely to have contributed to the river’s composition. However, isotopically depleted rainfall and high river flow the previous January had no marked effect on river composition. At the beginning of autumn there may be insufficient soil moisture left after summer evapotranspiration to buffer the isotopic signature of water from the first few rainfall events of the ‘winter’ period as it moves via infiltration to feeding the river, while later on

there is enough mixing to result in a near-average river composition.

Two lesser rivers, the Darent and Stour, were studied more recently, again over approximately one year. The Darent was sampled a few km above Dartford, Kent, while the Stour was sampled in its upper course near Haverhill, Suffolk. Both can be regarded as Chalk rivers in their respective sampling areas and therefore have important baseflow components, though the Stour flows through a catchment dominated by boulder clay drift. Plots of  $\delta^{18}\text{O}$  v. time are shown in Fig. 4. These show an offset in isotopic composition for much of the year with apparently unrelated fluctuations in values, and a convergence over the course of the winter of 2002–03. These features are provisionally attributed as follows: the isotopic offset is due partly to different degrees of rainout affecting Kent and Suffolk, but rather more to the existence of extensive gravel workings on the Darent upstream, particularly in the Sevenoaks area, which promote evaporative enrichment for much of the year. The convergence is caused by the notably wet autumn flushing away any evaporated water from the Darent (the  $\delta^{18}\text{O}$  value for November rainfall at Wallingford, the largest monthly total for 25 years, is shown in Fig. 4). Other variations are the consequence of the balance between baseflow and runoff: even though both rivers are likely to be subject to basically similar rainfall isotope inputs, the drift cover in the Stour valley is likely to promote a different response to rainfall from that of the largely uncovered Chalk of the lower Darent.

The variations observed in the Darent and Stour tend towards the very small range of compositions noted by Lawler (1987) during investigations of the rivers Lambourn and Winterbourne in Berkshire. These are spring-fed streams

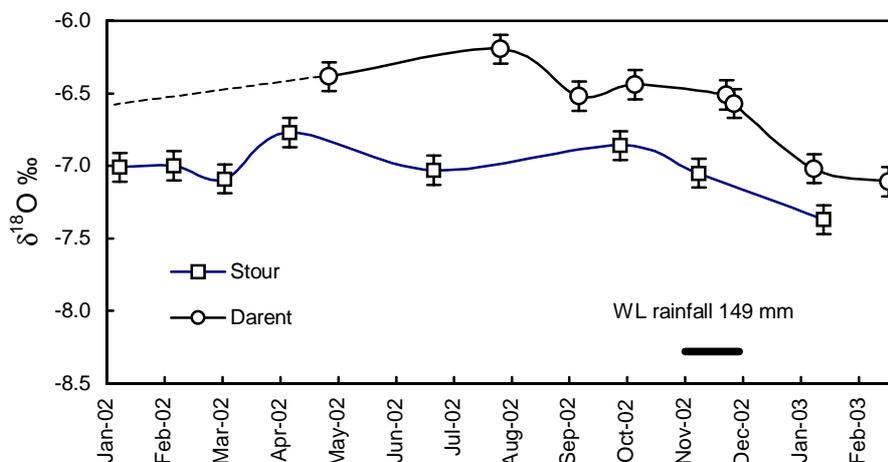


Fig. 4. Plots of  $\delta^{18}\text{O}$  v. time for the rivers Darent (Kent) and Stour (Suffolk). Error bars as shown. The rivers respond rather differently to what is likely to be a similar rainfall isotope input. The composition of the somewhat isotopically-depleted heavy rainfall at Wallingford during November 2002 is also shown for reference.

in Chalk valleys and therefore consist overwhelmingly of groundwater discharge from the Chalk aquifer. In general, groundwaters are well-mixed and would therefore be expected to give rise to uniform stream compositions, except in markedly karstic units such as the Carboniferous Limestone (Lawler *ibid*).

## GROUNDWATER

### *The relationship between rainfall and groundwater*

Even in the more humid-temperate areas of the world, only a relatively small proportion of total rainfall will ever reach the underlying aquifer. The remainder will, apart from any direct runoff, be lost to evaporation or transpiration; since these reach their peak in summer, it is reasonable to assume that most recharge occurs in the winter. Indeed, Darling and Bath (1988) noted that drainage at the base of a 5 m deep Chalk lysimeter at Fleam Dyke in eastern England occurred only from around November to May.

Part 1 of this study (Darling and Talbot, 2003) shows that in Britain there is a tendency for winter rainfall to be more isotopically depleted than summer rainfall; this is a normal pattern for many regions of the world (Clark and Fritz, 1997). It might therefore be expected that the bulk isotopic composition of winter half-year rainfall (September–February) would be close to that of groundwater. Table 1 gives typical local groundwater isotopic compositions compared with the bulk compositions of winter, summer

and annual rainfall collected at three main stations: Wallingford (Oxfordshire), Keyworth (Nottinghamshire) and Valentia (Co Kerry).

Table 1 shows that water pumped from the Chalk in the vicinity of Wallingford has a  $\delta^{18}\text{O}$  composition very close to the weighted mean of rainfall, implying that winter and summer rainfall alike are contributing to recharge. Groundwaters from the Triassic Sherwood Sandstone aquifer in the vicinity of the Keyworth station show a bias in favour of winter rainfall. Since the climate of Keyworth is little different from that of Wallingford, especially in terms of rainfall amount, the bias seems likely to be attributable to differences in the physical properties between chalk (coccolith limestone) and sandstone. The sandstones forming major UK aquifers (Sherwood Sandstone and Lower Greensand) tend to have freely-draining unsaturated zones, in which infiltrating rainfall, if not intercepted for plant transpiration, will flow downwards as recharge to the aquifer. This would favour recharge of winter rainfall. In contrast, owing to an extremely fine texture, chalk porespace are commonly close to saturation throughout the unsaturated zone (Barker and Foster, 1981). This means that infiltrating rainfall is likely to be buffered by mixing with existing porewater. Only a proportion of the mixed water will be transpired, the remainder eventually becoming recharge with a composition at or near the weighted mean.

In apparent contrast to the case of the Sherwood Sandstone, Table 1 suggests that spring waters in the Valentia region are the result of rather greater recharge in summer,

*Table 1.* Averaged  $\delta^{18}\text{O}$  compositions of rainwater at collection stations compared to local groundwater compositions. Data from this study except where indicated.

	Wallingford	Keyworth <sup>1</sup>	Valentia <sup>2</sup>
RAINFALL			
$\delta^{18}\text{O}$ winter (Sep-Feb)	-7.81	-8.27	-5.91
$\delta^{18}\text{O}$ summer (Mar-Aug)	-6.63	-6.99	-4.92
$\delta^{18}\text{O}$ whole year	-7.28	-7.67	-5.51
Collection period	1982–2001	1985–96	1960–99
GROUNDWATER			
Average $\delta^{18}\text{O}$	-7.20	-7.99	-5.20
Std dev	0.06	0.15	0.08
Sample source (No)	Tap (8)	B/h (7)	Spr (4)
Aquifer	Chalk	Sherwood Sst	Peat <sup>3</sup>
Collection period	1978–2001	Early 1990s	Jun 1993

<sup>1</sup> groundwater data from Edmunds *et al.* (1996)

<sup>2</sup> rainfall data from GNIP (2002)

<sup>3</sup> overlying Old Red Sandstone

but this seems unlikely since winter rainfall accounts for some 60% of annual rainfall in the region. The springs were sampled in June 1993; the low storage of the peaty deposits typical of the area favours relatively short residence times and therefore the spring compositions may have reflected a substantial contribution from the previous winter's rainfall which was atypically enriched (GNIP, 2002).

Although sparse, the available time-sequence data for groundwaters points to considerable homogeneity in isotopic composition below the level of circulation in superficial deposits. On a seasonal scale neither the shallow test boreholes at Altnabreac, Scotland (Kay *et al.*, 1984) nor a borehole at Malham, North Yorkshire (Lawler, 1987) showed any convincing evidence of variation (Fig. 5a, 5b), despite both the formations concerned (granite and Carboniferous Limestone respectively) being dominated by relatively rapidly-responding fracture permeability. Figures 5b and 5c also demonstrate that groundwaters pumped from the Chalk of southern England show little variation either

on the seasonal or longer-term timescales, but this may reflect the buffering effects of chalk's high porosity. In aquifers where intergranular permeability predominates, such as the Sherwood Sandstone, waters would be expected to be well-mixed resulting in a similar degree of isotopic homogeneity.

Taken as a whole, the evidence suggests that the stable isotopic composition of groundwaters over the British Isles is close (i.e. within 0.5‰  $\delta^{18}O$ ) to the bulk composition of rainfall. This is presumably the result of mixing between new rainfall and older soil water, which must occur so rapidly that evapotranspiration does not use exclusively new water; transpiration would in any case be derived from a range of rooting depths. (An alternative view is that spring and summer rainfall is wholly, or almost wholly, used up by evapotranspiration, and that recharge consists effectively of a mixture of 'heavy' autumn and 'light' winter rainfall that happens to approximate the annual average. However, examination of the Wallingford record from Darling and

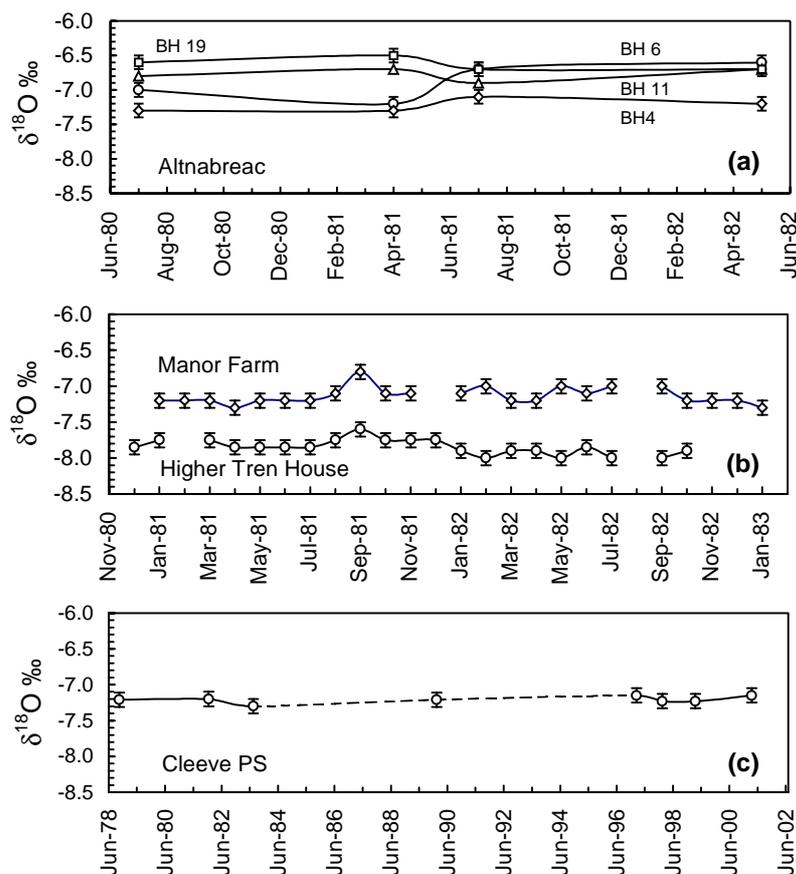


Fig. 5. Plots of  $\delta^{18}O$  v. time showing the general lack of significant seasonal or decadal change in typical pumped shallow groundwaters: (a) Altnabreac shallow test boreholes from Kay *et al.* (1984), (b) domestic supplies from the Carboniferous Limestone (Higher Tren House, Malham, W Yorks) and Chalk (Manor Farm, Lambourn, Berks) from Lawler (1987) and (c) mains supply from the Chalk (Cleeve Pumping Station, Oxon) from this study. Datapoints are shown with measurement precision error bars.

Talbot (2003) shows that all combinations of months between September and May give weighted averages more depleted than local groundwaters.) The evidence further implies that groundwaters preserve a good record of rainfall integrated over the last tens of years or more. Accordingly, groundwater and bulked rainfall isotope values are to a great extent interchangeable, in that one can be reasonably well predicted from the other.

#### Groundwater isotope maps

Two contour maps showing the compositions of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  respectively for 'recent' groundwaters in the British Isles are presented in Fig. 6. The maps are based primarily on BGS studies, but also use data from Hiscock *et al.* (1996) and Kimblin (1995). All the points chosen are in unconfined aquifers and are known or believed to represent groundwaters recharged well within the Holocene (0–10 ka BP), and therefore unlikely to contain any groundwater from Glacial times ('palaeowater'). Additionally, all the waters are considered to have suffered little or no modification by

processes such as evaporation which might otherwise have affected isotopic compositions.

The inset to Fig. 6 shows that the density of the groundwater sampling on which the maps are based is variable, with lowest densities in Scotland, Wales and Ireland largely because these countries depend more on surface waters to meet their needs. The contouring on the maps is therefore more speculative in these areas. No account of sampling altitude has been taken because correcting to sea level values is not a viable option. Over much of the British Isles this is unlikely to be a significant issue, but in areas of high relief the isotopic contouring is more of a compromise and it is in these areas that some groundwaters are likely to have isotopic compositions outside the contour interval, most probably on the depleted side.

As would be expected, both maps show essentially similar features. The spread of isotopic compositions is relatively large, covering ranges of almost 4‰ in  $\delta^{18}\text{O}$  and 30‰ in  $\delta^2\text{H}$ . Despite the complexity of their weather patterns, the British Isles receive most of their rainfall from the southwest, and this basically controls the areal isotopic distribution.

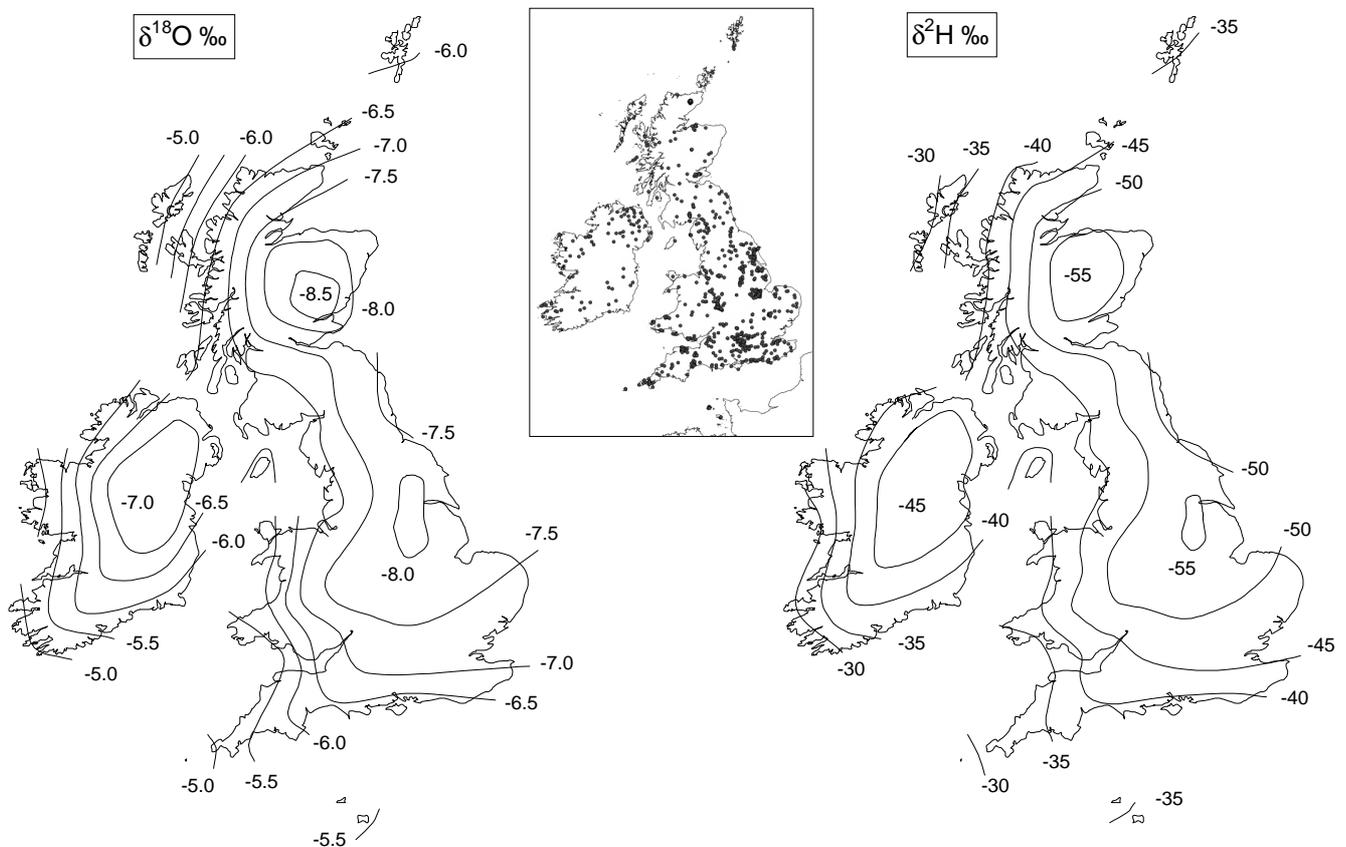


Fig. 6. Contour maps of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in recent groundwaters of the British Isles. Inset: the distribution of dots indicates the density of sampling, which in turn indicates the reliability of contouring in a particular area.

However, the topography of the islands exerts some influence, particularly the Pennines of England and the Highlands of Scotland where sizeable isotopic depletions take place between the western and eastern sides of the country owing to the orographic patterns of rainfall distribution. Conversely, in flat-lying areas such as the Midlands of Ireland and England there is relatively little change. Proximity to the sea can have a profound effect: for example, although the distance from Land's End to the northern Outer Hebrides is some 1000 km there is little isotopic change. Indeed, there are some indications from the database that all peri-coastal areas, even on eastern leeward coastlines, have groundwaters rather more enriched than those inland. However, the database is not yet comprehensive enough to demonstrate such an 'edge effect' convincingly.

As might be expected, the pattern in variation of groundwater stable isotope ratios resembles to an extent that of average rainfall amount (Fig. 7). Basically, the lower the amount of rainfall the greater the depletion in the heavier

isotopes  $^{18}\text{O}$  and  $^2\text{H}$ . However the equivalence is not unconditional because of altitude effects: for example, the large amounts of rainfall depicted for the Scottish Highlands would be expected to have a relatively depleted weighted average composition at higher elevations because of temperature effects. Air temperature might also be expected to show some relationship; Fig. 8 shows that the similarity

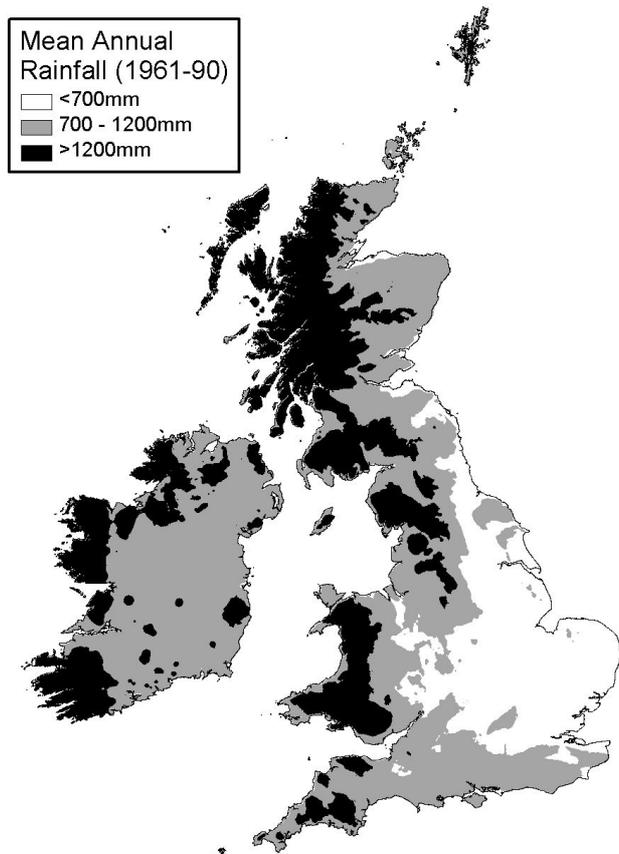


Fig. 7. Thirty-year average rainfall distribution for the British Isles over the period 1961–1990, based on UK Meteorological Office and Met Eireann data.

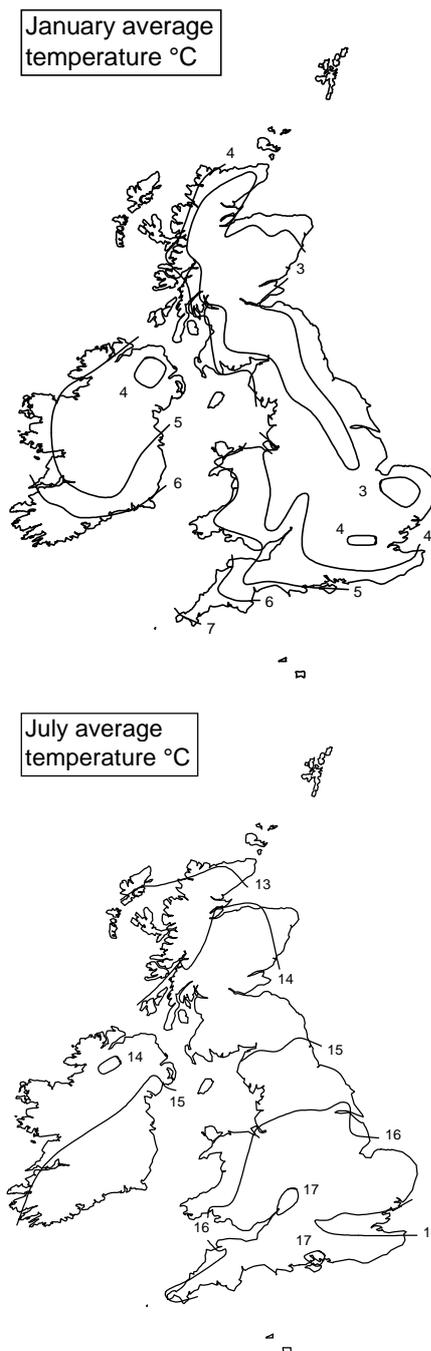


Fig. 8. Thirty-year average January and July temperatures for the British Isles, based on UK Meteorological Office and Met Eireann data.

is much more marked for the January rather than the July means. This is slightly surprising given that it has been shown above that groundwater isotopic values are by no means controlled exclusively by winter half-year rainfall. Clearly the three-way relationship between rainfall, temperature and groundwater isotopic composition is complex.

#### *Altitude effects*

Most of the groundwaters measured were obtained from lowland areas where the effects of altitude on rainfall compositions will have been either small or minimal. However, Darling and Talbot (2003) show that these effects can be significant in areas of high relief. Accordingly in mountainous areas the contouring of Fig. 6 only represents groundwater composition in broad terms, though this is perhaps of limited practical concern because in general such areas do not have significant groundwater reserves.

There are a few instances in Scotland where high-level spring data are available against which to test the altitude effect of approximately  $-0.25\text{‰}$   $\delta^{18}\text{O}$  per 100 m ascent which was observed for rainfall in the Monachyle catchment at Balquhiddy (Darling and Talbot, 2003). A sample collected for the present study from a spring at 850 m aod (above ordnance datum) on Sgurr Beag (NGR 19970 81080), Northwest Highlands, had a  $\delta^{18}\text{O}$  composition of  $-7.1\text{‰}$  compared to  $-5.7\text{‰}$  for a groundwater seepage at 150 m aod in nearby Barrisdale (NGR 18620 80450). Assuming the low discharge rate reflected an essentially locally recharged water, an altitude effect of  $-0.20\text{‰}$  per 100 m is indicated, consistent with the Monachyle rainfall data.

In the Grampian Highlands to the east, a spring in Dalvorar Corrie (NGR 30407 78856) near Braemar had a  $\delta^{18}\text{O}$  value of  $-9.4\text{‰}$  for an altitude of 700 m aod, while a spring in the Drumtochty Forest at 300 m aod (NGR 30703 78154) had a value of  $-8.2\text{‰}$ . This equates to an altitude effect of  $-0.30\text{‰}$  per 100 m. While the magnitude of the altitude effect in both localities is similar, the groundwaters in the Grampian Highlands are much more depleted owing to the distance from the Atlantic coast and consequent operation of rainout effects (Darling and Talbot, 2003).

In Part 1 of this study (Darling and Talbot, 2003) it was explained that snow often has a highly depleted isotopic composition because the frozen water cannot re-equilibrate with air at higher temperatures during its fall. The fact that the higher mountains of Scotland in particular receive a sizeable part of their precipitation in the form of snow suggests that some very negative groundwater values should be found due to the infiltration of snowmelt. However, as

the Sgurr Beag and Dalvorar examples show, this does not seem to occur, presumably because most snowmelt leaves the catchments as surface water. Even on the high massif of the Cairngorm Mountains to the north of Braemar, where up to 40 percent of precipitation may fall as snow, the most depleted composition sampled from a spring at 970 m was  $-9.7\text{‰}$  (Soulsby *et al.*, 1999), which conforms reasonably well with the Braemar altitude effect quantified above. This suggests the most depleted, reasonably well-mixed groundwater that could be expected in the British Isles under today's climatic conditions would have a  $\delta^{18}\text{O}$  no more negative than about  $-10\text{‰}$ .

#### *Secular changes*

While the groundwater maps shown in Fig. 6 reflect bulk rainfall isotope values integrated over periods probably averaging tens to hundreds of years, in the longer term there have been changes in bulk rainfall composition across the British Isles. Radiocarbon dating of residence times of older waters in the confined zones of the principal aquifers indicates that waters from the late Pleistocene (i.e. ages of 10 ka and upwards) are of the order of  $1.5\text{‰}$  more depleted in  $\delta^{18}\text{O}$  (and concomitantly in  $\delta^2\text{H}$ ) compared to present-day compositions (e.g. Darling *et al.*, 1997). These differences are related primarily to the lowering of recharge temperature (RT) under peri-glacial climatic conditions. The  $\delta^{18}\text{O}$  seasonal temperature effect of  $0.23\text{‰}$  per  $^{\circ}\text{C}$  noted for rainfall at Keyworth (Darling and Talbot, 2003) can be compared with noble gas RT and isotopic data from the local Triassic sandstone aquifer which yield a depletion of approximately  $1.5\text{‰}$  in  $\delta^{18}\text{O}$  for a temperature drop of  $5\text{--}6^{\circ}\text{C}$  (Bath *et al.*, 1979). However, because ocean waters would have been up to  $1\text{‰}$  more enriched in  $\delta^{18}\text{O}$  during glacial periods (Schrag *et al.*, 1996), the real isotopic depletion in the palaeowaters is closer to  $2.5\text{‰}$ . This would amount to a secular temperature effect of around  $0.45\text{‰}$  per  $^{\circ}\text{C}$ . This difference indicates that while the seasonal temperature effect to a degree mimics climate change insofar as it goes through summer and winter extremes (Siegenthaler and Matter, 1983), there are additional factors affecting the long-term  $\delta^{18}\text{O}/\text{RT}$  relationship. These might include changes in temperature difference between source and recharge areas, changes in sea level and therefore land area, and changes in seasonality of recharge.

The maps in Fig. 9 attempt to show the isotopic composition of what would have been late-Quaternary unconfined groundwaters immediately prior to the Pleistocene-Holocene transition at some 10 ka BP. Information is most plentiful for the main aquifers of England but elsewhere the reconstruction is more

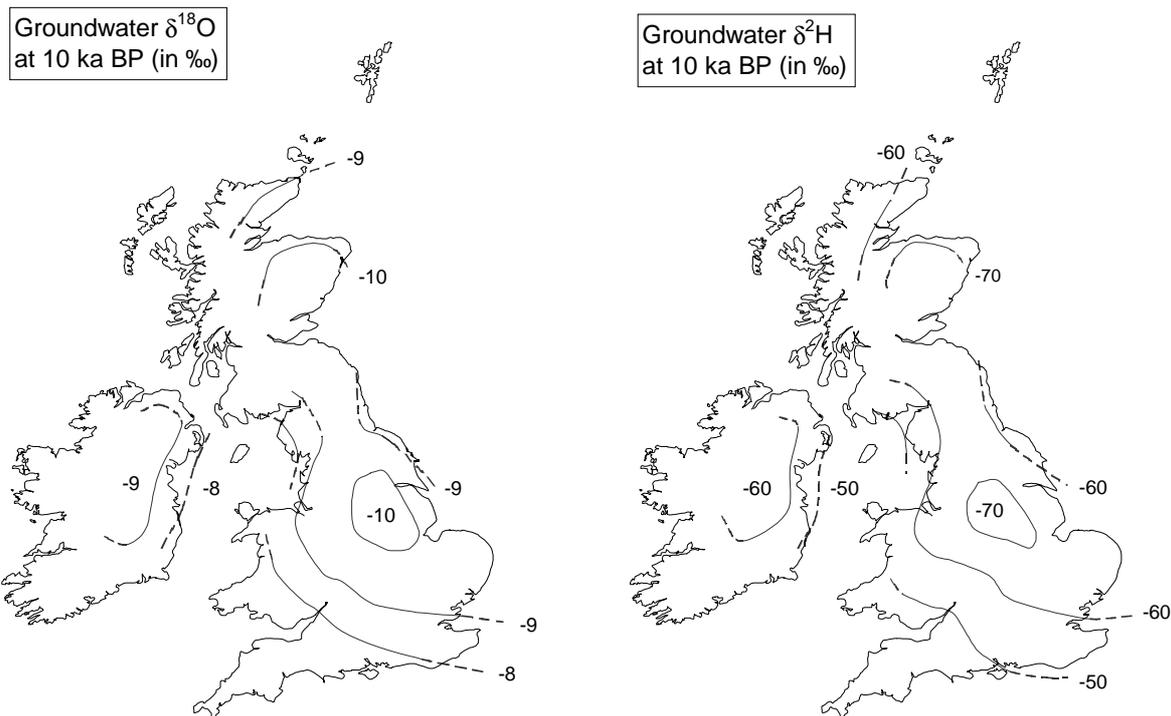


Fig. 9. Tentative contour maps of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  in unconfined groundwaters of the British Isles at the end of the Pleistocene prior to 10 ka BP. Based mainly on data from Alexander and Andrews (1984), Bath (1983), Bath et al. (1979), Bath et al. (1987), Bath et al. (1996), Bruck et al. (1986), Burdon (1985), Darling et al. (1997), Edmunds et al. (1998), Edmunds et al. (2001), Evans et al. (1979), Kay et al. (1984), Lucey (1987), and Tellam (1995).

speculative. At least in southern Britain, the present pattern of geographical differentials in isotopic composition appears to have been largely retained from the Quaternary, indicating that air-mass trajectories have remained substantially similar since at least the late Pleistocene. (This supports the view of Rozanski (1985) that European atmospheric circulation has been unchanged for at least 35 ka.) Beyond the Quaternary, the little evidence available from the British Isles is much more difficult to interpret (Darling *et al.*, 1997).

#### SOURCES OF WATER SUPPLY

Where water is supplied from unconfined aquifers in the vicinity, the stable isotopic composition of piped water ('tapwater') will be representative of local groundwater because there is no significant opportunity for fractionation to occur. Under other circumstances, tapwater may not be representative of local shallow groundwater. It may have been brought in from elsewhere (for example the use of lakes in Cumbria to supply the Manchester conurbation), or subject to evaporation in lowland rivers and reservoirs, or derived from upland impoundments, or obtained from palaeowaters in confined aquifers.

The results of a limited survey of tapwaters in Great Britain

are shown in Fig. 10. They show that for many lowland areas agreement between tapwater values and shallow groundwater  $\delta^{18}\text{O}$  contours is reasonably good. Larger differences occur in areas where supplies are likely to be obtained from mountain lakes, or where open reservoirs are an important element in meeting water demands. In the former case tapwater would be more depleted, and in the latter case more enriched, than would be anticipated on the basis of the groundwater contouring. Fig. 10 shows some examples of depletion in the Scottish Highlands, and both enrichment and depletion in SW England where water supplies may be derived from reservoirs of different sizes and elevations. It also shows that Central London tapwater has a composition isotopically heavier than would be expected from local shallow groundwater. In fact, much of London's mains water supply is abstracted from the Thames; by the time it reaches Wallingford some 70 km to the west, the river has already acquired a somewhat enriched average composition (Fig. 3).

#### THE BRITISH ISLES IN WIDER CONTEXT

To put the British Isles in its northeastern Atlantic maritime context, weighted means of rainfall from the Valentia, Lista

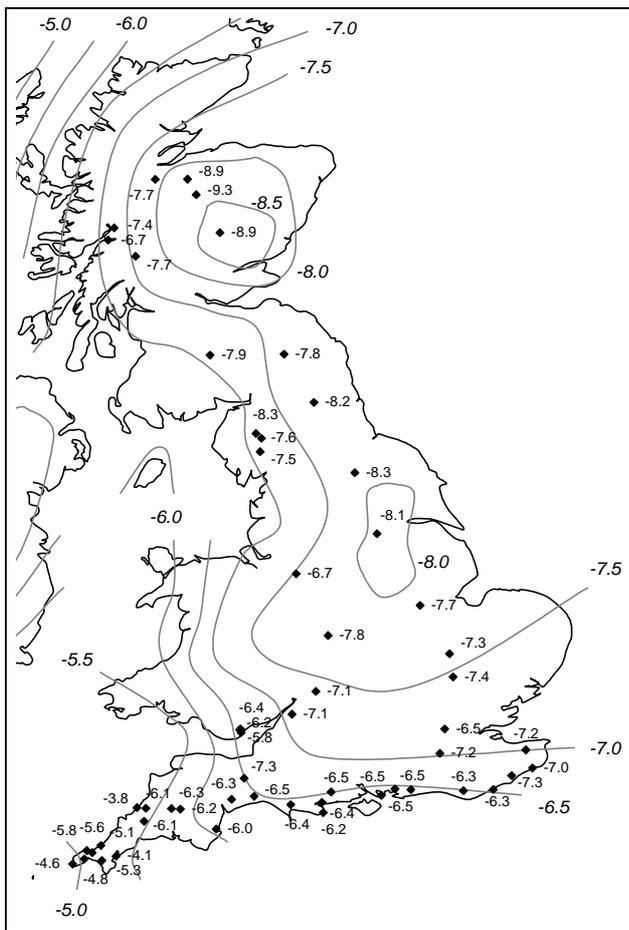


Fig. 10. Tapwater  $\delta^{18}\text{O}$  compositions superimposed on the recent groundwater contour map from Fig 6. Agreement is reasonably good except for some northern and south-western localities (most tapwater data by courtesy of C Sonntag).

(Norway) and Gröningen (Netherlands) stations of the IAEA-WMO Global Network for Isotopes in Precipitation (GNIP) are shown in Fig. 11 together with groundwater isotopic contours in the vicinity of the Channel coast of France (Lecolle, 1985; Chery *et al.*, 2000) and representative water compositions in the Shetland and Faeroe Islands. The results from the Faeroes (Fig. 12) are notable for the amount of isotopic depletion between the south (Suðuroy) and the north (Kunoy and Borðoy), presumably due to rainout effects over the islands which reach altitudes in excess of 800 m. The value used in Fig. 11 is the average for the two sites on Suðuroy, the most isolated island and with a relatively low relief, where rainfall should be least modified by topographic interactions.

On the basis of the rainfall-groundwater relationship considered above, it is assumed that average groundwater compositions are comparable with weighted mean rainfall for a particular location. The data in Fig. 11 confirm that

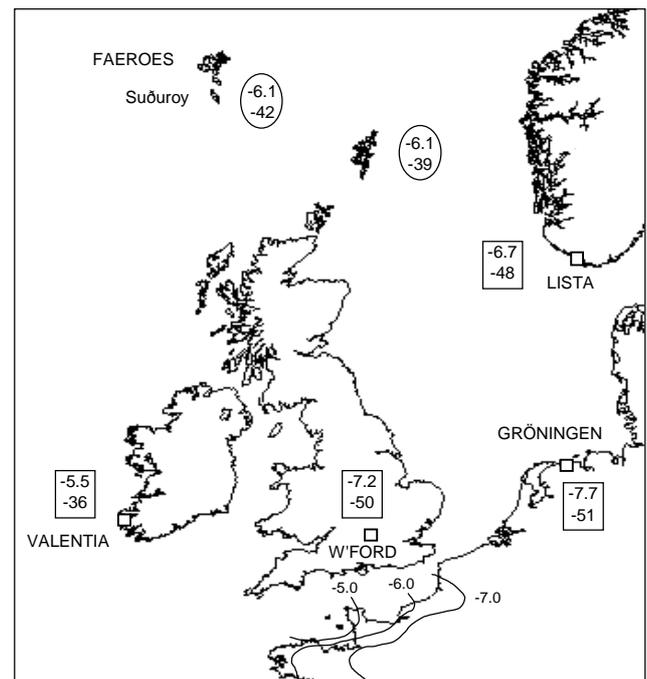


Fig. 11. The wider perspective for the northeast Atlantic: long-term weighted means of  $\delta^{18}\text{O}$  (above) and  $\delta^2\text{H}$  (below) for the rainfall collection stations at Valentia, Wallingford, Gröningen and Lista (rectangles, data from GNIP, 2002), plus representative water compositions from the Shetland and Faeroe Islands (ovals, data from this study). French contours for  $\delta^{18}\text{O}$  in rainfall from Chery *et al.* (2000) after Lecolle (1985).

proximity to the ocean can have a profound effect on isotopic compositions. Although the Faeroe Islands lie some 10 degrees in latitude to the north of Valentia Island, isotopic depletion is small: there is, for example, significantly more depletion between Land's End and Wallingford, only 350 km apart (see Fig. 6). However, isotope values do not always depend directly on proximity to the ocean; predominant wind and ocean current directions are also important. Thus waters found at Lista are isotopically heavier than those at Gröningen several hundred km to the south, because the latter experiences more of the 'continental effect'. The rainfall  $\delta^{18}\text{O}$  contours from the Channel coastal zone of France match up only approximately with the English groundwater contours of Fig. 6, but the French database is at a preliminary stage (Chery *et al.*, 2000).

## Conclusions

Surface waters show evidence of evaporative fractionation but, given the temperate nature of the climate of the British Isles, isotopic enrichments are generally small. Monthly sampling from the Upper Thames indicates that its isotopic composition is a complex balance between surface

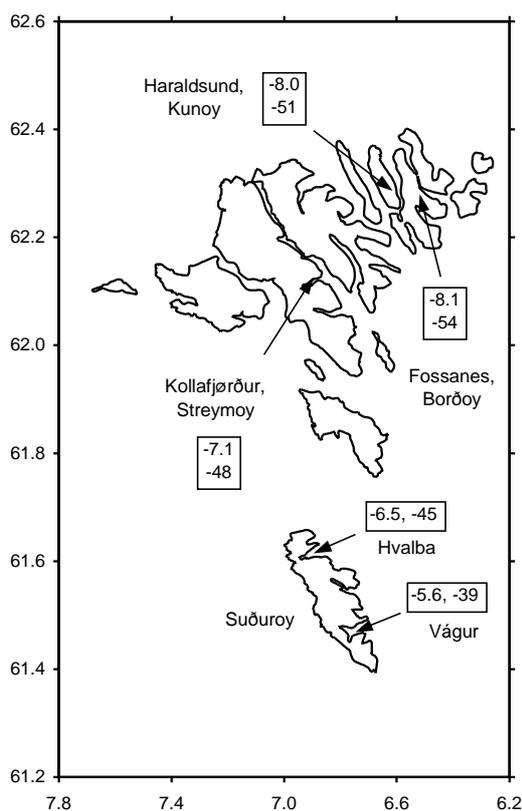


Fig. 12. Map of the Faeroe Islands showing water compositions ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ) at selected sites. The northern islands reach altitudes of over 800 m, resulting in the observed SW to NE isotopic depletions.

contributions and groundwater inflow, modified by soil conditions and evaporative effects. Periodic sampling from lesser Chalk rivers has so far revealed a lower amplitude of variation.

Comparison of bulk rainfall at Wallingford, Keyworth and Valentia with local groundwaters shows some differences between the areas, probably due to local soil physical or hydrogeological factors. Nevertheless, long-term rainfall and groundwater isotopic values appear to be reasonably representative of each other.

Maps of the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  composition of recent, unconfined groundwaters in the British Isles have been compiled largely from survey data. These show depletions consistent with the continental effect. The influence of the altitude effect is less obvious but, where explored on the local scale, agrees broadly with that observed for rainfall in Part 1 of this study (Darling and Talbot, 2003).

The groundwater maps are considered to represent isotopic compositions basically at the present day in geological terms (perhaps decades or possibly centuries old in some cases). On a longer timescale, there is evidence

mainly from the old groundwaters presently found confined in major aquifers that isotopic compositions were more negative beyond ~10 ka ago. Maps reconstructing unconfined groundwater compositions at around this time suggest that there has been relatively little change in air-mass trajectories since then.

Consideration of the countries and islands around the British Isles reveals that proximity to the ocean often has a profound effect, with islands more than 10 degrees apart in latitude possessing waters with similar isotopic compositions.

## Acknowledgments

Most of the groundwater data considered in this paper have come from studies carried out by staff of the British Geological Survey over the past quarter-century. Several colleagues helped to 'fill in the gaps' on and off duty — in this regard the authors are particularly grateful to Dave Buckley, Chris Milne and Pauline Smedley. Samples from Shetland, the Outer Isles of Scotland and parts of western Ireland were kindly provided by the local councils (Shetland Islands, Western Isles Regional, Sligo and Mayo County Councils), and in the case of the Faeroes by the Food and Environmental Agency (Heilsufrøðiliga Starvsstovan). CEH Wallingford is thanked for the Thames sampling and flow data, and Prof C Sonntag, University of Heidelberg, for the donation of his tapwater data. Helpful reviews were provided by Tim Atkinson and Kazimierz Rozanski. This paper is published with the permission of the Executive Director, British Geological Survey (NERC).

## References

- Alexander, J. and Andrews, J.N., 1984. Hydrogeological investigations in the Harwell region: the use of environmental isotopes, inert gas contents and the uranium decay series. *British Geological Survey Report FLPU 84-7*, Keyworth, UK.
- Andrews, J.E., Riding, R. and Dennis, P.F., 1997. The stable isotope record of environmental and climatic signals in modern terrestrial microbial carbonates from Europe. *Palaeogeogr. Palaeoclimatol.*, **129**, 171–189.
- Barker, J.A. and Foster, S.S.D., 1981. A diffusion exchange model for solute movement in fissured porous rock. *Quart. J. Eng. Geol.*, **14**, 17–24.
- Bath, A.H., 1983. Stable isotope evidence for palaeo-recharge conditions of groundwater. In: *Palaeoclimates and Palaeowaters: a Collection of Environmental Isotope Studies*, IAEA, Vienna, Austria. 169–186.
- Bath, A.H., Edmunds, W.M. and Andrews, J.N., 1979. Palaeoclimatic trends deduced from the hydrochemistry of a Triassic sandstone aquifer, United Kingdom. In: *Isotope Hydrology 1978*, Vol II, IAEA, Vienna. 545–566.
- Bath, A.H., Darling, W.G., George, I.A. and Milodowski, A.E., 1987. *Geochim. Cosmochim. Acta*, **51**, 3113–3118.

- Bath, A.H., McCartney, R.A., Richards, H.G., Metcalfe, R. and Crawford, M.B., 1996. Groundwater chemistry in the Sellafeld area: a preliminary interpretation. *Quart. J. Eng. Geol.*, **29**, S39–57.
- Bruck, P.M., Cooper, C.E., Cooper, M.A., Duggan, K., Goold, L. and Wright, D.J., 1986. The geology and geochemistry of the warm springs of Munster. *Irish J. Earth Sci.*, **7**, 169–194.
- Burdon, D.J., 1985. Geothermal investigations in Ireland. In: *European Geothermal Update*, A.S. Strub and P. Ungemach (Eds.), Reidel, Dordrecht, The Netherlands. 350–360.
- Butler, M.J. and Verhagen, B.T., 1997. Environmental isotope tracing of water in the urban environment of Pretoria, South Africa. In: *Groundwater in the Urban Environment, Vol 1: Problems, processes and Management*, J. Chilton *et al.* (Eds.), Balkema, Rotterdam, The Netherlands. 101–106.
- Chery, L., Michelot, J.L., Blavoux, B. and Dray, M., 2000. Project of French isotopic data base. In: *Isotope Techniques in Water Resources Development and Management*, IAEA, Vienna, Austria. Poster Session 2, 9–11.
- Clark, I.D. and Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*, Lewis Publishers, Boca Raton, USA, 328pp.
- Craig, H., 1961. Isotopic variations in meteoric waters. *Science* **133**, 1702–1703.
- Darling, W.G. and Bath, A.H., 1988. A stable isotope study of recharge processes in the English Chalk. *J. Hydrol.*, **101**, 31–46.
- Darling, W.G. and Talbot, J.C., 2003. The O and H stable isotopic composition of fresh waters in the British Isles: 1, Rainfall. *Hydrol. Earth Syst. Sci.* **7**, 163–181.
- Darling, W.G., Edmunds, W.M. and Smedley, P.L., 1997. The isotopic composition of palaeowaters in the British Isles. *Appl. Geochem.*, **12**, 813–829.
- Edmunds, W.M., Smedley, P.L. and Spiro, B., 1996. Controls on the geochemistry of sulphur in the East Midlands Triassic aquifer, United Kingdom. In: *Isotopes in Water Resources Management*, Vol 2, IAEA, Vienna, Austria. 107–122.
- Edmunds, W.M., Robins, N.S. and Shand, P., 1998. Origins of the saline waters of Llandrindod and Builth, Central Wales. *J. Geol. Soc. London*, **155**, 627–637.
- Edmunds, W.M., Buckley, D.K., Darling, W.G., Milne, C.J., Smedley, P.L. and Williams, A.T., 2001. Palaeowaters in the aquifers of the coastal regions of southern and eastern England. In: *Palaeowaters in Coastal Europe: Evolution of Groundwater Since the Late Pleistocene*, W.M. Edmunds and C.J. Milne (Eds.), Geological Society of London Special Publication No 189. 71–92.
- Evans, G.V., Otlet, R.L., Downing, R.A., Monkhouse, R.A. and Rae, G., 1979. Some problems in the interpretation of isotope measurements in United Kingdom aquifers. In: *Isotope Hydrology 1978*, Vol II, IAEA, Vienna. 679–706.
- Förstel, H. and Hütten, H., 1983. Oxygen isotope ratios in German groundwater. *Nature*, **304**, 614–616.
- GNIP, 2002. IAEA-WMO Global Network for Isotopes in Precipitation. Website <http://isohis.iaea.org>
- Heathcote, J.A. and Lloyd, J.W., 1986. Factors affecting the isotopic composition of daily rainfall at Driby, Lincolnshire. *J. Climatol.*, **6**, 97–106.
- Hiscock, K.M., Dennis, P.F., Saynor, P.R. and Thomas, M.O., 1996. Hydrochemical and stable isotopic evidence for the extent and nature of the effective Chalk aquifer of north Norfolk, UK. *J. Hydrol.*, **180**, 79–107.
- Hoffmann, G., Jouzel, J. and Masson, V., 2000. Stable water isotopes in atmospheric general circulation models. *Hydrol. Process.*, **14**, 1385–1406.
- Iacumin, P. and Longinelli, A., 2002. Relationship between  $\delta^{18}\text{O}$  values for skeletal apatite from reindeer and foxes and yearly mean  $\delta^{18}\text{O}$  values of environmental water. *Earth Planet. Sci. Lett.*, **201**, 213–219.
- Iacumin, P., Bocherens, H. and Mariotti, A., 1997. An isotopic palaeoenvironmental study of human skeletal remains from the Nile Valley. *Palaeogeogr. Palaeoclimatol.*, **126**, 15–30.
- Kay, R.L.F., Andrews, J.N., Bath, A.H. and Ivanovich, M., 1984. Groundwater flow profile and residence times in crystalline rocks at Altnabreac, Caithness, UK. In: *Isotope Hydrology 1983*, IAEA, Vienna, Austria. 231–248.
- Keenleyside, A., Bertulli, M. and Fricke, H.C., 1997. The final days of the Franklin expedition: new skeletal evidence. *Arctic*, **50**, 36–46.
- Kimblin, R.T., 1995. The chemistry and origin of groundwater in Triassic sandstone and Quaternary deposits, northwest England and some UK comparisons. *J. Hydrol.*, **172**, 293–311.
- Lawler, H.A., 1987. Sampling for isotopic responses in surface waters. *Earth Surf. Process. and Landf.*, **12**, 551–559.
- Lecolle, P., 1985. The oxygen isotope composition of landsnail shells as a climatic indicator: applications to hydrogeology and palaeoclimatology. *Chem. Geol. (Isotope Geoscience Section)* **58**, 157–181.
- Longinelli, A. and Selmo, E., 2003. Isotopic composition of precipitation in Italy: a first overall map. *J. Hydrol.* **270**, 75–88.
- Lucey, P.A., 1987. *The Hydrochemistry of Groundwaters in the West Cheshire Aquifer of NW England*. MPhil Thesis (unpubl), Univ. Lancaster.
- Maréchal, J.C. and Etcheverry, D., 2003. The use of  $^3\text{H}$  and  $^{18}\text{O}$  tracers to characterize water inflows in Alpine tunnels. *Appl. Geochem.*, **18**, 339–351.
- Ogunkoya, O.O. and Jenkins, A., 1991. Analysis of runoff pathways and flow contributions using deuterium and stream chemistry. *Hydrol. Process.*, **5**, 271–282.
- Rauert, W., Wolf, M., Weise, S.M., Andres, G. and Egger, R., 1993. Isotope-hydrogeological case study on the pollution into the deep Tertiary aquifer in the area of Munich, Germany. *J. Contam. Hydrol.*, **14**, 15–38.
- Rozanski, K., 1985. Deuterium and oxygen-18 in European groundwaters—links to atmospheric circulation in the past. *Chem. Geol. (Isotope Geoscience Section)* **52**, 349–363.
- Rozanski, K., Araguas-Araguas, L. and Gonfiantini, R., 1993. Isotopic patterns in modern global precipitation. In: *Climate Change in Continental Isotopic Records*, American Geophysical Union, Geophysical Monograph 78. 1–37.
- Schrag, D.P., Hampt, G. and Murray, D.W., 1996. Pore fluid constraints on the temperature and oxygen isotopic composition of the Glacial ocean. *Science*, **272**, 1930–1932.
- Siegenthaler, U. and Matter, H.A., 1983. Dependence of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in precipitation on climate. In: *Palaeoclimates and Palaeowaters: A Collection of Environmental Studies*. IAEA, Vienna, Austria. 37–51.
- Smith, D.B., Downing, R.A., Monkhouse, R.A., Otlet, R.L. and Pearson, F.J., 1976. The age of groundwater in the Chalk of the London Basin. *Water Resour. Res.*, **12**, 392–404.
- Soulsby, C., Malcolm, R., Helliwell, R.C., Ferrier, R.C. and Jenkins, A., 1999. Hydrogeochemistry of montane springs and their influence on streams in the Cairngorm Mountains, Scotland. *Hydrol. Earth Syst. Sci.*, **3**, 409–419.
- Tellam, J.H., 1995. Hydrochemistry of the saline groundwaters of the lower Mersey Basin Permo-Triassic sandstone aquifer, UK. *J. Hydrol.*, **165**, 45–84.
- White, C.D., Spence, M.W., Stuart-Williams, H.L.Q. and Schwarcz, H.P., 1998. Oxygen isotopes and the identification of geographical origins: the Valley of Oaxaca versus the Valley of Mexico. *J. Archaeol. Sci.*, **25**, 643–655.

