

Isotopic evidence for palaeowaters in the British Isles.

W G Darling, W M Edmunds and P L Smedley

British Geological Survey, Wallingford, OX10 8BB, UK

Abstract:- Before the 20th century, groundwater circulation in the aquifers of the British Isles had largely adjusted to the temperate maritime climate and sea levels established over the past 10 ka since the end of the Pleistocene. However, in the last 100 years this natural regime has been disturbed by abstraction of water for public supply and industrial use, and palaeowaters from earlier recharge episodes are now becoming a factor to be considered in water balance estimates. This paper presents a synthesis of the existing palaeowater distribution in the British Isles, based on isotopic evidence ($\delta^{18}\text{O}$, $\delta^2\text{H}$ and ^{14}C). As such, it has relevance to palaeoclimatic studies in addition to the water resource implications.

The Triassic basins of England and Northern Ireland contain saline waters beyond the range of ^{14}C dating (>40 ka). Stable isotopic ratios show enrichment in some basins and depletion in others, without an overall pattern that would explain all the observed compositions. The results for the Wessex basin suggest recharge in pre-Quaternary times, but for the other basins some flushing by Pleistocene or Holocene meteoric waters is indicated. Isolated occurrences of apparently long-residence waters are found elsewhere throughout the British Isles, for example from Carboniferous and Lower Palaeozoic strata. In such cases, environmental isotopes are more useful as constraints on hydrogeological models than as indicators of palaeoconditions.

Major water supply aquifers are restricted almost entirely to England. The two sandstone formations (Triassic Sherwood Sandstone and Cretaceous Lower Greensand) have a greater range of stable isotopic values between phreatic and confined conditions than the two carbonate formations (Jurassic Lincolnshire Limestone and Cretaceous Chalk). This indicates that the sandstone aquifers are better archives of information on palaeoconditions than the carbonate aquifers. They show that atmospheric circulation patterns over Britain have probably remained the same since the late Pleistocene. However, ^{14}C data from all four of the major aquifers emphasise the hiatus in recharge during periglacial conditions which occurred between the late Pleistocene and early Holocene.

INTRODUCTION

The residence times of groundwaters in actively circulating systems may range from tens to thousands of years. Present-day circulation patterns may have originated as far back as the Tertiary, but have reached their present state mainly since the late Pleistocene, about 10 ka ago, following ice withdrawal, rise in sea level and climate change. In some low-permeability strata and large basins, transient conditions may persist where adjustment to post-glacial conditions could still be taking place (Custodio, 1992). Palaeowaters are defined here as waters which are remnants of former hydrogeological regimes and are largely unaffected by natural circulation at the present day. In particular they include deep formation waters, and the waters in the deeper confined parts of water-supply aquifers. The latter may be difficult to distinguish from modern waters during hydraulic testing except by using hydrochemical or isotopic methods.

The size of British sedimentary aquifers is small when considered on a global scale. However, palaeowaters are recognised in a wide range of environments, including hard-rock formations, mainly through the use of isotopic techniques. It is only during the past 100 years, with the exploitation of aquifers for water supply, that any disturbance of the natural flow regimes has occurred. Thus, the flow between natural recharge and discharge has been intercepted, the original flow directions may have been reversed and upconing of isolated palaeowaters may have occurred. It is therefore important for water resource management to be able to distinguish palaeo-groundwaters from those which form part of the present circulation regime. An overestimation of the amount of renewable resources will be obtained unless this is taken into account in the calculation of water balance. An additional benefit from the study of palaeowaters is a better understanding of past climatic conditions as a key to planning for the future, which is of particular importance to long-term applications such as the construction of waste repositories.

In this paper we bring together the existing (often scattered) evidence on palaeowaters in the British Isles, derived mainly from stable O and H isotope and radiocarbon evidence. Because of their relationship with the temperature of rainfall, stable isotopes are a proven method for the identification of palaeowaters recharged under different climatic conditions (Fontes, 1981). However, factors such as latitudinal differences mean that stable isotopes can only be relative indicators of temperature and therefore approximate age. Radiocarbon, although itself subject to various restrictions (principally its limitation to ages of less than 40 ka, and difficulties in interpretation), provides the residence-time dimension with which to compare stable isotopic data (Mook, 1980). Therefore it is essential for the study of late-Pleistocene and Holocene groundwaters to consider both kinds of data in order to obtain the maximum amount of palaeowater information.

This paper combines a synthesis of relevant published information with new data for the deep Triassic basins and the Lincolnshire Limestone (Jurassic) and Lower Greensand (Cretaceous) aquifers. All the data are brought together to establish common features that may be used more widely in water source evaluation across the country, and to note any important differences between aquifers.

SAMPLING AND ANALYSIS

The data reported here were derived from samples obtained by a variety of techniques and at various

intervals during the past 20 years. From deep boreholes, samples were obtained by drill stem tests, production tests, porewater extraction by centrifugation of core material, and (occasionally) gas lifting. Samples from water-supply boreholes were normally collected as pumped samples, with the likelihood that at least some of the samples are mixtures of water from different levels in the aquifer. Waters for stable isotope analysis were stored without pre-treatment in McCartney glass bottles. For radiocarbon analysis, dissolved inorganic carbon was precipitated from 120 litres of water by the addition of alkaline BaCl₂, though more recent analyses using accelerator mass spectrometry (AMS) techniques required collection of only 1 litre of untreated water in a glass bottle.

Following preparation by the methods of Epstein and Mayeda (1953) and Coleman et al (1982), stable isotope analyses were carried out on VG 602E and Optima mass spectrometers at BGS Wallingford. Precisions for most waters are considered to be within $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$, and $\pm 2\text{‰}$ for $\delta^2\text{H}$, although for the more saline basin brines could fall slightly outside this range. Isotope ratios are expressed in the normal way in permil relative to VSMOW:

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

Radiocarbon contents were measured by conventional counting techniques at the NERC Radiocarbon Laboratory (RCL), East Kilbride, or by AMS following target preparation at RCL. Measurement precisions for both techniques were better than 1% relative at high ¹⁴C activities down to around 5% at low activities. These are expressed as percent modern carbon (pmc).

RESULTS AND REVIEW

Trends rather than site-specific aspects are addressed. New results are considered together with existing data in three categories: (i) saline formation waters, (ii) freshwater aquifers and (iii) minor aquifers.

Saline formation waters

Basins containing significant thicknesses of Permo-Triassic sediments have been a target of geothermal exploration in the British Isles (Downing and Gray, 1986). These basins are restricted to England and Northern Ireland (Fig 1) and were regarded as the only areas where aquifers of reasonable transmissivity might reach depths of 1500-3000 m below surface, thereby allowing waters to reach temperatures from

50°C upwards (Wheildon and Rollin, 1986). Deep boreholes were drilled for geothermal exploration at Marchwood and Western Esplanade, situated on either side of Southampton Water in the Wessex Basin, at Cleethorpes in the East Yorkshire and Lincolnshire Basin, and at Larne in Northern Ireland. In addition to samples collected from these wells, further samples were obtained from boreholes drilled for hydrocarbon exploration mostly in the Wessex Basin, but also in the Worcester Basin. In the East Midlands, where the Permo-Triassic is too shallow to be of geothermal potential, numerous oil company production wells and a few coal exploration boreholes provided access to formation waters in Carboniferous strata.

Oxygen and hydrogen stable isotope analyses of basinal waters are reported in Table 1, together with their chloride concentrations. Waters collected by different techniques did not usually differ significantly. Where they did, the porewater values were considered to be the most reliable indicators of conditions at depth (Edmunds et al, 1985). While not all technically brines (Cl > seawater), most are at least as saline as seawater and some have TDS values of up to 300 g l⁻¹. In all cases the salinity is primarily due to Na and Cl, a composition that does not require the conversion of measured $\delta^{18}\text{O}$ values from the activity to concentration scales (Horita et al, 1993).

Wessex Basin. The pattern of isotopic data from the Wessex Basin sites is typical of basin brines found elsewhere (e.g. Kharaka and Carothers, 1986). Fig 2a shows a δ -plot which reveals an array of data points defining a trend with a slope of 1.4. This trend is clearly unrelated to simple freshwater-seawater mixing (confirmed by Cl concentrations well above that of seawater, Fig 2b), and reflects a possibly complex diagenetic history (Edmunds, 1986; Darling and Edmunds, 1987). However, the trend probably does indicate a mixing of some kind, and intercepts the WMWL (world meteoric water line - Craig, 1961) at around $\sim 5.5\text{‰}$ $\delta^{18}\text{O}$. This is isotopically rather heavier than the present value of recharge for the Wessex Basin area, which is in the range -6 to -7‰ (Darling et al, 1996).

Downing and Penn (1992) considered that the brines are a mixture of Triassic meteoric water, made saline by halite dissolution, with Jurassic seawater and further influxes of meteoric waters in the early Cretaceous and Tertiary. Dating by ⁴He accumulation gave a tentative median age of ~ 15 Ma (Edmunds, 1986), which would indicate a Miocene (Tertiary) bulk age for the brine. The intercept value of -5.5‰ $\delta^{18}\text{O}$ could be reflecting the warmer climatic conditions of that time, but since much of Triassic-Tertiary time was warmer than the present, the $\delta^{18}\text{O}$ value is merely indicative of pre-Quaternary recharge.

Worcester Basin. Waters from the Triassic formations at Kempsey in the northern part of the Worcester basin (Fig 1), have O and H stable isotopic values (Table 1, Fig 2c) slightly more depleted than would be expected for shallow waters in the area (Darling et al, 1996). Permian formation waters from the same borehole plot at around the modern values, but Fig 2d indicates that their Cl values approach that of seawater. In the Guiting Power borehole further south in a separate sub-basin, waters from the Triassic are isotopically enriched (Fig 2c) and could be substantially the product of simple mixing between meteoric water and ancient seawater (Fig 2d). Little is known regarding the age of these waters; the fact that depleted, relatively low-Cl waters exist in the Triassic strata at Kempsey implies a Quaternary rather than Tertiary recharge, and therefore much younger water than in the Wessex Basin.

East Yorkshire-Lincolnshire Basin. The Cleethorpes geothermal exploration borehole is the only source of Permo-Triassic data in the onshore part of this basin, which is effectively part of the North Sea Basin. Fig 2e shows a δ -plot which includes data from the Triassic and Permian sandstones in this 2100 m deep well. It is evident that the waters residing in the two formations are very different. Despite their high salinity (Table 1), the Triassic waters have an isotopic composition only slightly enriched compared to that expected for shallow groundwaters in the region (Darling et al, 1996). The Permian waters, however, have an even higher salinity and a much-enriched isotopic composition, falling in the region of SMOW, though quite clearly from their Cl concentration unrelated to simple seawater mixing. The addition of halite appears to have taken place at some point during their evolution. Upper Carboniferous formation waters sampled from exploratory and producing oil wells mainly in Lincolnshire are also shown in Fig 2e. These are isotopically enriched up to half the extent of the Permian waters.

When Cl is plotted versus $\delta^{18}\text{O}$, a possible relationship between the various waters becomes apparent (Fig 2f). On this plot, mixing lines are shown between the Permian brine and modern and Pleistocene meteoric waters in the East Midlands (range of values from Bath et al, 1979 and Andrews et al, 1984). The Triassic and Carboniferous waters fall close to or within the putative ternary mixing zone, and it is therefore inferred that the Permian waters are the remnants of a basin brine which has undergone flushing by meteoric waters since at least the late Pleistocene. The Triassic and Carboniferous waters would then represent intermediate stages of flushing. The work of Downing et al (1987) offers support for this view.

At a higher stratigraphic level in the southern part of the basin, porewaters from the Trunch deep borehole in the Chalk of NE Norfolk showed a marked enrichment in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ with increasing

depth. The trends in salinity are consistent with dilution by diffusion of an original, slightly modified connate water still present in the Chalk at 450-500 m below OD (Bath and Edmunds, 1981). The stable isotope ratios in these waters (around -3.7‰ $\delta^{18}\text{O}$ and -17‰ $\delta^2\text{H}$) support this conclusion on the assumption that the diffusion rate for water exceeds the rates for ionic species .

Cheshire Basin. Unlike the examples above, the Triassic infill of the Cheshire Basin is not overlain by younger rocks. It therefore has hydrogeological characteristics intermediate between those of the 'concealed' basins and the freshwater aquifers to be considered below.

Waters from the edge of the Cheshire Basin have a range of stable isotopic values from meteoric to close to seawater in composition (Howell and Sedgwick, 1978; Lucey, 1987; Fig 2g). A simple mixing with seawater is apparent (Fig 2h), with the highest Cl contents found near the present coastline. However, the plot also shows that while minimum Cl values are found close to the expected $\delta^{18}\text{O}$ values of -7 to -8‰ for modern recharge (Darling et al, 1996), there are more-depleted waters with a higher Cl content. This implies that the longer-residence groundwaters, probably recharged in the late Pleistocene by analogy with the East Midlands equivalents (Bath et al, 1979), have acquired their elevated Cl contents by dissolution of the halite known to exist in the Basin. Since it is not a simple trend, there may be some ternary mixing between palaeowaters and waters on the (presumably more modern) meteoric-seawater mixing trend.

There are no isotopic data for thermal waters in the deeper, more central part of the basin, and so it is unknown to what extent the Cheshire basin brines resemble those from any of the other basins.

Larne Basin. In the Larne Basin of Northern Ireland, formation waters were sampled from the Ballymacilroy and Larne exploration boreholes, respectively inland and on the coast. At Ballymacilroy both Triassic and Permian waters are isotopically similar to present-day meteoric waters (Fig 2i), despite the fact that Cl concentrations are around three times higher than seawater (Fig 2j). The Permian waters at Larne are still more saline and have an enriched isotopic composition, but remain near the WMWL.

Freshwater aquifers

Although groundwater supplies are used throughout the British Isles, exploitation on a large scale occurs only in England. Here, isotopic results from the major sedimentary aquifers have helped to demonstrate the extent of modern recharge and the presence of palaeowater. Four aquifers (Fig 3) are important: the

Sherwood Sandstone (Triassic), the Lower Greensand (Lower Cretaceous), the Middle Jurassic limestones, and the Chalk (Upper Cretaceous). The first and second are respectively redbed and glauconitic sandstones, while the last two are carbonates. Outcrops are shown on the map in Fig 3. The aquifers are treated in stratigraphic order.

Sherwood Sandstone. The Sherwood Sandstone consists of aeolian and fluvial deposits of varying porosity and permeability, in which intergranular flow is usually significant. It outcrops in eastern, central and northwestern England (Fig 3). In each area, the aquifer becomes confined beneath the Mercia Mudstone and younger strata. Isotopic studies indicating the existence of palaeowaters have been conducted in the West and South Midlands and in the Cheshire Basin (Lloyd, 1976; Jackson and Lloyd, 1983; Lucey, 1987). However, the most comprehensive study has been carried out in the East Midlands, where the application of a series of dating techniques has proved beyond reasonable doubt that waters of late Pleistocene age are found in the deeper parts of the confined aquifer (Bath et al, 1979; Andrews et al, 1984). Available stable isotopic data are plotted in Fig 4a, with the WMWL for reference. Ratios range from around -7.5 to almost -10‰ $\delta^{18}\text{O}$, with some evidence of two separate populations separated by residence time. Radiocarbon values range from ~80 to <1 pmc.

Noble gas measurements indicate that waters furthest from outcrop were recharged at temperatures on average 5-7°C lower than those at or near outcrop, with a strong bimodality between the ancient and modern waters (Bath et al, 1979). Such a temperature drop is consistent with the isotopic evidence of a late-Pleistocene time for recharge. Accumulation of ^4He suggests ages about twice as great as those indicated by ^{14}C and other isotopes, perhaps due to diffusion of He from the overlying Mercia Mudstone (Andrews and Lee, 1979).

Middle Jurassic limestones. The Lincolnshire Limestone, an oolitic, very fissured limestone, crops out only in Eastern England (Fig 3). It has been the target of several published isotopic investigations (Lawrence et al, 1976; Downing et al, 1977; Bishop and Lloyd, 1990, 1991), and further new stable isotopic and radiocarbon data are reported in Table 2. The confined aquifer in the southeast of the region is saline and probably mixed with seawater (Andrews and Kay, 1982; Bath, 1983), the age of which is uncertain. With the exception of saline samples, Fig 4b shows that the range of isotopic depletion across the area is small, at barely 1‰ $\delta^{18}\text{O}$, although ^{14}C values decline from around 70 to <1 pmc.

Noble gas measurements by Andrews and Lee (1980) suggested a drop in average recharge temperature of about 1.6°C between outcrop waters and those at depth, a significantly smaller range than for the Sherwood Sandstone but consistent with the smaller stable isotope difference exhibited by groundwaters in the Lincolnshire Limestone. Accumulation of ^4He was interpreted to indicate a minimum age of 4 Ma for the saline part of the aquifer, but an age of 170 Ma if extrapolated to seawater salinity. The Sr isotope data of Smalley et al (1988) were used to discount this suggestion of a truly connate water, indicating instead a Pliocene maximum age for the saline zone on the assumption that the water had a marine origin. Such an influx would have to have occurred by leakage through overlying formations, since the last inundation of the Lincolnshire Limestone outcrop is likely to have been in the late Cretaceous (Bennison and Wright, 1969).

Limited radiocarbon data for groundwaters from the Corallian and Great and Inferior Oolite (the lateral equivalents of the Lincolnshire Limestone) of southern Oxfordshire show very low pmc values downgradient in the confined zone, accompanied by somewhat-depleted O and H stable isotope ratios after the onset of confinement (Alexander and Andrews, 1984). However, at the deepest sampling point, some 7 km from outcrop, stable isotope ratios and Cl concentrations were enriched relative to modern shallow groundwater, indicating mixing with a formation water component of unknown age.

Lower Greensand. The Lower Greensand, a glauconitic marine sandstone with predominantly intergranular flow, is restricted to southeast England (Fig 3), where the most significant outcrops are in the Cambridgeshire area in the north of the region, and around the London Basin and north Kent in the south. Radiocarbon data have been interpreted to give groundwater residence times up to 29 ka (Mather et al, 1973; Evans et al, 1979). Data from the present study are given in Table 3. A δ -plot (Fig 4c) of these data plus those of Evans et al (1979) shows a range from around -6.5 to -9‰ $\delta^{18}\text{O}$, with a bimodal distribution, though the situation is complicated by the slightly depleted range of the "northern" relative to the "southern" samples, presumably a consequence of the geographical location of the respective recharge areas.

Radiocarbon values range from about 85 to <1 pmc between outcrop and confinement, the lowest values being found in the axial region of the western London Basin. Noble gas measurements show that an average recharge temperature difference of around 6°C is observed between outcrop and depth, and that the distributions are markedly bimodal (Haran 1994). This drop in temperature for the older recharge is similar to that observed for the Sherwood Sandstone of the East Midlands, and indicates an origin in the late Pleistocene.

Chalk. Environmental isotopes were first measured on confined Chalk groundwaters by Smith et al (1976) in the London Basin. They found slightly depleted O and H isotopic compositions towards the centre of the basin compared with the margins, and they attributed these to a late-Pleistocene palaeowater component. Similarly depleted values have been found near the centre of the basin by Kinniburgh et al (1994) and Dennis et al (this volume), and in Berkshire towards the western end of the basin by Edmunds et al (1987), though here there was less of a consistent pattern of depletion with distance from outcrop than was found in the central part of the basin by Smith et al (1976). Fig 4d shows a δ -plot of data from the main London Basin. These cover a relatively restricted range, between approximately -6.5 and -8‰ $\delta^{18}\text{O}$ and lying along the WMWL. Radiocarbon values in and around the London Basin range from about 70 in the unconfined aquifer to <1 pmc in the centre of the basin (Smith et al, 1976; Edmunds et al, 1987; Dennis et al, this volume).

The relatively few other isotope measurements from confined Chalk groundwaters do not usually show significant O and H isotope depletion. Some radiocarbon measurements have been made in Chalk groundwaters away from the London Basin: Lloyd and Howard (1979) in Lincolnshire, Bath et al (1985) in Suffolk and Hiscock (1993) in North Norfolk. While these studies identified a few low-pmc values, there were too few accompanying stable isotope data to determine the existence of age-related depletion, except in the case of North Norfolk. Here, an apparent depletion of about 0.5‰ $\delta^{18}\text{O}$ is recorded (Hiscock et al, 1996), with the most depleted samples as negative as those from the London Basin. In the confined Chalk of the Wessex Basin, where relatively high Cl contents (~2000 mg l⁻¹) are present, isotope values are close to those of modern recharge (Edmunds, 1986). Assuming a basically marine origin for the salinity, this may indicate mixing with a slightly-depleted freshwater end member. Reference has already been made to porewaters from the Chalk of the Trunch deep borehole, which suggest a diffusional profile between meteoric recharge and connate seawater (Bath and Edmunds, 1981).

Noble gas measurements in the Berkshire sector of the London Basin suggested an average temperature drop of only about 0.5°C between outcrop and greatest confinement, though a range of several degrees is seen on traverses into the central sector of the Basin beneath London (Dennis et al, this volume). On the basis of accumulation of ⁴He, Edmunds et al (1987) calculated a residence time of 2.5 Ma, far in excess of either ¹⁴C ages or the early Holocene age suggested by recharge temperatures. Diffusion of He from beneath the Chalk was suggested as the cause of this discrepancy, but equally it could be due to a small upward leakage of deep groundwater.

Minor aquifers

The waters considered in this section are isolated occurrences where there is evidence of a palaeowater component. The locations of most of the sites referred to are shown in Fig 1.

Carboniferous strata. At Bath (SW England), thermal waters derived from the Carboniferous Limestone were studied by Andrews et al (1982). They found low radiocarbon values (around 4 pmc), but noted that the interpretation of age based on this was hindered by the unquantifiable effect of the hot water (46°C) on carbonate dissolution. Stable isotope ratios and noble gas recharge temperatures were only slightly depleted compared to shallow groundwaters in the area, supporting the interpretation of an early-Holocene rather than a late-Pleistocene age for recharge. However, high concentrations of ⁴He indicated a contribution from very old waters, perhaps originating in the underlying Old Red Sandstone. The Buxton and Matlock springs of Derbyshire in the north Midlands also issue from Carboniferous Limestone, though their temperatures are significantly lower (maximum 27.5°C). At Buxton, Evans et al (1979) measured a radiocarbon value of 20 pmc, which they modelled to give an age of 3 ka. Stable isotope measurements were consistent with modern local recharge.

Springs with cooler but still above-ambient temperatures issue from the Carboniferous Limestone to the west of Dublin and to the north of Cork, and these were investigated using a variety of geochemical techniques. While the Cork springs showed no isotopic or noble gas evidence for a palaeowater component, some of the Dublin springs had clear evidence. The most isotopically-depleted water, at Leixlip, gave a noble gas recharge temperature of 5°C (compared to the present 11°C), and contained a relatively large amount of ⁴He (Burdon et al, 1985).

Colliery waters from the Upper Carboniferous have yielded stable isotope values indicating various processes at work. Sheppard and Langley (1984) found stable isotopic evidence of both depletion and enrichment relative to shallow groundwater in mine waters of northeast England. In the Kent Coalfield, samples from mines showed no enrichment (compared to shallow groundwaters) at 500 m below surface at Betteshanger on the coast, but inland at 900 m in Snowdown were enriched in $\delta^{18}\text{O}$ by about 1‰ $\delta^{18}\text{O}$ (Darling and Edmunds, 1987). Chloride concentrations indicate that this change is not due directly to seawater dilution, with the implication that these are palaeowaters of considerable age.

Shales and mudrocks. At Llandrindod Wells in central Wales, where waters from Silurian strata have been exploited for curative purposes, some of the spa waters have a chemical content which implies they

must have been in residence for a considerable time (Edmunds et al, submitted). The relatively low ^{14}C value of ~20 pmc in the Chalybeate Spring confirms this, and some of the stable isotope analyses are slightly depleted, notably for the Saline and Chalybeate Springs.

A study to characterise the hydrogeology of younger, less consolidated mudrocks in eastern and southeastern England used squeezing methods to extract porewaters from borehole cores for geochemical analysis (Bath, 1995). While the interpretation of results was not always straightforward, including the possibility of analytical artefacts arising from the squeezing process, there was sufficient evidence of stable isotope depletion from different profiles to suggest that recharge from the Pleistocene was preserved at depth.

Igneous and metamorphic rocks. In the extreme southwest of England, the Hercynian granites of Cornwall contain mineworkings with thermal waters with temperatures similar to those of the Bath springs, but much higher salinities (Edmunds, 1986). Although this might suggest a long residence, measurable tritium was found in the waters, implying the drawdown of modern water, and their stable isotope values were typical of current recharge in the area. However, the amount of ^4He in the waters indicated a considerable age for the saline component, perhaps as much as 1 Ma.

At Sellafield on the Cumbrian coast (NW England), investigations to characterise the hydrogeology of a potential nuclear waste repository site in rocks of the Borrowdale Volcanic Group (Ordovician) have yielded chemical and isotopic data indicating that there is an interface between relatively recent recharge and very old saline waters from the East Irish Sea Basin (Bath et al, 1996). Since this basin developed in Triassic times and is comparable in size to those shown in Fig 1, formation brines with ages considerably beyond radiocarbon measurement (i.e. >40 ka) would be expected.

At the Dounreay site of the UK Atomic Energy Authority in Caithness (northern Scotland), two deep boreholes drilled to characterise the hydrogeology of the Moine metasediments beneath the site provided some evidence of palaeowaters at depth, when compared with the regional average for shallow groundwaters reported by Kay et al (1984). Although many of the samples obtained may have been contaminated to various degrees by drilling fluid, some samples with low- ^{14}C activities were collected which, accompanied by a relatively low contamination index (based on Li concentration), suggest that these consist largely of palaeowater (data of UK Nirex Ltd). Fig 5a shows clearly that there is an accompanying depletion in stable isotopes, while Fig 5b shows that there is apparently an increase in palaeowater content with depth.

DISCUSSION

Pre-Quaternary

It is likely that pre-Quaternary waters are present in at least some of the Triassic basins. These waters could be of meteoric or marine origin. Significant remnants of presumed ancient, possibly true connate waters appear to exist in the Wessex, East Yorkshire-Lincolnshire, Irish Sea and Larne basins, but these are of peripheral interest to this study. There is rather little evidence of pre-Quaternary meteoric recharge: only the Wessex basin has provided any consistent data. Here, the inferred $\delta^{18}\text{O}$ value of the palaeorecharge is some 1‰ heavier than present-day recharge, implying a warmer temperature (Dansgaard, 1964), but difficult to quantify without further palaeogeographical evidence. Otherwise, while there is evidence of palaeorecharge in the Worcester, East Yorkshire-Lincolnshire and Cheshire basins, and some of the minor aquifers, stable isotopic evidence indicates that most of this is of Quaternary age.

The late Pleistocene-Holocene

As shown earlier, the major freshwater aquifers are the best hydrological archives for records of conditions over this period of time. An effective way of comparing the quality of information from the four aquifers is to obtain a "fingerprint" of each based on the relationship between $\delta^{18}\text{O}$ and radiocarbon (Fig 6a-d). (Uncorrected ^{14}C values are used throughout this section because a detailed treatment of age modelling for the different aquifers concerned is beyond the scope of this paper.) To obtain points suitable to fit a straight-line regression, ^{14}C has been plotted on a logarithmic scale. While it could be argued that fitting such a line is not strictly justifiable if two independent populations are present, there is no evidence from Fig 6a-d that ^{14}C - $\delta^{18}\text{O}$ gradients differ significantly with time, and in any case the process must be regarded as empirical in approach.

The figure indicates that (i) lower maximum ^{14}C values are measured in groundwaters of the carbonate aquifers, (ii) groundwaters in the Sherwood Sandstone and Lower Greensand exhibit considerable scatter while the two carbonate aquifers show much less, and (iii) bimodality is evident in all of the aquifers, though more pronounced in the sandstone than in the carbonate aquifers.

The observed features can be explained in various ways. The lower maximum ^{14}C values in the carbonate aquifers suggest a lithological control: there is so much scope for solution-precipitation processes in the carbonate aquifers, even during recharge, that ^{14}C is significantly more diluted by "dead" rock carbon. Indeed, maximum ^{14}C values are lowest for the Chalk, which has the most reactive matrix. The scatter of data points in each aquifer reflects input variations and the amount of reaction with carbonate minerals. The fairly uniform availability of carbonate coupled with the amount of mixing in carbonate aquifers promoted by extensive fissuring leads to a smaller scatter for Lincolnshire Limestone and Chalk groundwaters than for those in the sandstones, which undergo less mixing and have less uniform and abundant carbonate with which to interact. The existence of bimodality (i.e. a time gap) in results from each of the aquifers reinforces the suggestion first made on the basis of early isotopic studies of the aquifers that there was a hiatus in recharge under glacial or periglacial conditions (Smith et al, 1976; Downing et al, 1977; Bath et al, 1979).

If the regression lines from Fig 6a-d are combined (Fig 7), some further features are seen. The two sandstone lines are almost parallel, thereby implying the same amount of isotopic depletion over the same amount of time. The reason they are displaced relative to one another is almost certainly related to geographical effects. Long-term (~10-yr) weighted means for $\delta^{18}\text{O}$ in rainfall at Wallingford and Keyworth (W and K on Fig 3) were given by Darling et al (1996) and are shown on Fig 7 for reference. The Wallingford value can be taken as broadly applicable to recharge to the Lower Greensand and southeastern Chalk, while the Keyworth value applies to the Sherwood Sandstone and Lincolnshire Limestone. Because the sandstone aquifer differential remains consistent back to the late Pleistocene, it implies that the same direction of atmospheric moisture movement has been maintained, but with a greater distance to the ocean in the past, a concept consistent with the conclusions of Andrews et al (1994) based on studies of ^{36}Cl . Supporting evidence is provided by the waters of the Cheshire Basin, which at around the same latitude show about the same maximum depletion as the East Midlands waters. Unconfined, recently recharged water in each pair of aquifers would be expected to be similar in stable isotopic content, and Fig 7 shows this to be the case. (Slight discrepancies between rainfall and groundwater values will depend on local climatic conditions and mode of aquifer recharge.)

The carbonate aquifers diverge both from the sandstone trend and to some extent from each other. The Lincolnshire Limestone is a relatively thin aquifer, extensively exploited for water supply (Downing et al, 1977) and therefore likely to be more mixed than the other aquifers. Therefore any original signature of palaeorecharge (i.e. stable isotope depletion or noble gas temperatures) will have been degraded. This has also occurred for the Chalk, though to a rather smaller extent, certainly regarding the stable

isotope depletion and probably also the noble gas temperatures. This may be due to the much greater primary porosity of the Chalk or the greater thickness of the aquifer, or a combination of both. While radiocarbon minimum values in both carbonate aquifers are of the same order as those in the sandstones and therefore appear to argue against the mixing suggested by the stable isotopes, this presumably reflects a greater input of dead rock carbon rather than the preservation of unmixed waters of a similar "age".

Clearly, the non-carbonate aquifers are superior to the carbonate aquifers as archives of information on palaeoconditions. At the same time, it demonstrates that if calibration of stable isotope ratios (relative) against noble gas temperatures (absolute) is going to be carried out, it needs to be done on the basis of individual aquifers because of the significant effects of geographical location.

Age stratification in aquifers

The example of Dounreay considered earlier raises the question of the extent to which aquifers are age-stratified. Available evidence, though limited, suggests that sampling by conventional pumping from boreholes may mix waters with different residence times, possibly leading to the attribution of an average "age" which may be hydrologically meaningless. The pumping of discrete horizons between packers, or depth-sampling of strong inflows are ways around this problem. In the Hayton (Fig 8) and Boston Park boreholes in the Sherwood Sandstone of the East Midlands, differences of up to 1.4‰ $\delta^{18}\text{O}$ are seen between the top and bottom of the water columns in the boreholes (Edmunds and Smedley, in prep; Smedley et al, submitted). In neither case is the trend of depletion with depth particularly uniform; since the boreholes were depth-sampled rather than pumped over discrete intervals separated by packers, this may be a function of differing strengths of flow at various horizons. The Stanlow Borehole in the Sherwood Sandstone of the Cheshire basin also shows a certain amount of age-related stratification (Fig 8). The magnitude of $\delta^{18}\text{O}$ depletion appears significantly greater than for Hayton, but the CI data for the borehole suggest that the sample values more enriched than about -7.5‰ are due to mixing with seawater (Lucey, 1987) and that the age-related depletion is only slightly greater than for Hayton. Although no ^{14}C data are available for either of the boreholes in Fig 8, the indications are that waters with quite different residence times could be present in each aquifer.

Such age stratification would presumably reach its maximum development in aquifers without extensive fissuring. Evidence for stratification in carbonate aquifers is also sparse. Various Chalk boreholes in N Norfolk show signs of stratification, but isotopic depletion gradients are generally lower than for the

sandstones, albeit over more restricted depth ranges (Hiscock et al, 1996; Feast et al, this volume). Other factors being equal, this would be consistent with the evidence reviewed above that waters in carbonate aquifers are more extensively mixed. However, in certain circumstances, notably the Corpusty borehole (Hiscock et al, 1996), gradients may be comparable to those seen in the sandstone aquifers.

CONCLUSIONS

This paper has presented the isotopic evidence for the occurrence of long-residence groundwaters in the British Isles, and has considered both published and new data for a variety of aquifers. Meteoric water of pre-Quaternary age characterised by enriched stable isotopic ratios may be present at depth in the Wessex basin. Otherwise, although most of the Triassic basins probably contain some pre-Pleistocene seawater, the available evidence indicates that Quaternary meteoric recharge has obliterated evidence of any pre-Pleistocene recharge under warmer climatic conditions. The minor aquifers include a range of rather poorly-characterised groundwaters in a wide variety of lithologies. Both isotopically-depleted and -enriched waters are found, the former indicating Pleistocene-Holocene recharge, and the latter suggesting mixing between Holocene meteoric water and connate seawater rather than the presence of pre-Quaternary recharge.

Aquifers exploited for water supply on a large scale are restricted to England. Here, the Sherwood Sandstone, Lincolnshire Limestone, Lower Greensand and Chalk all contain evidence of confined late-Pleistocene or early Holocene waters at depth. While isotopic methods provide useful information about the hydrogeology of all the aquifers, palaeowater signals are better preserved in the sandstone than the carbonate aquifers, because in the latter the signals are degraded by mixing due to the more pronounced dual porosity. Geographical effects on the stable isotopic content of rainfall appear to have maintained the same relationships at least as far back as the Pleistocene, implying that air-mass movements have remained much the same over this period, while distance to the ocean has changed, presumably due to lowering of sea level. Limited stable isotopic evidence of depletion with depth in a variety of aquifer settings demonstrates the need for a better understanding of age-related stratification.

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Table 1. Stable isotope values for formation waters extracted from basins in England and Northern Ireland.

Borehole	NGR	Formation	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	Cl mg l ⁻¹	Borehole	NGR	Formation	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	Cl mg l ⁻¹
EAST YORKSHIRE AND LINCOLNSHIRE											
Cleethorpes (a)	TA302071	Triassic	-6.3	-46	30200	Ballymacilroy (f)	IJ306398	Triassic	-7.0	-52	58000
Cleethorpes	TA302071	Triassic	-6.7	-47	30200	Ballymacilroy	IJ306398	Triassic	-7.3	-49	68000
Cleethorpes	TA302071	Triassic	-6.5	-47	30200	Ballymacilroy	IJ306398	Triassic	-8.5	-50	66000
Cleethorpes	TA302071	Triassic	-6.9	-51	30200	Ballymacilroy	IJ306398	Triassic	-6.9	-51	51000
Cleethorpes	TA302071	Triassic	-6.7	-51	30200	Ballymacilroy	IJ306398	Triassic	-7.1	-49	59000
Cleethorpes	TA302071	Permian	+0.4	-12	135000	Ballymacilroy	IJ306398	Triassic	-7.0	-47	59000
Cleethorpes	TA302071	Permian	+0.4	-12	135000	Ballymacilroy	IJ306398	Triassic	-7.8	-55	71000
Cleethorpes	TA302071	Permian	-0.4	-14	135000	Ballymacilroy	IJ306398	Triassic	-7.0	-55	71000
Cleethorpes	TA302071	Permian	-0.6	-15	135000	Ballymacilroy	IJ306398	Triassic	-7.4	-54	72000
Beckingham 22 (b)	SK776910	U Carb	-5.3	-30	70700	Ballymacilroy	IJ306398	Triassic	-7.8	-53	72000
Beckingham 30 (b)	SK770902	U Carb	-4.5	-28	71300	Ballymacilroy	IJ306398	Triassic	-7.8	-49	72000
Broughton 1 (b)	SE946108	U Carb	-5.4	-33	61000	Ballymacilroy	IJ306398	Permian	-7.3	-50	69000
Cropwell Butler 2 (b)	SK680382	U Carb	-9.1	-63	3000	Ballymacilroy	IJ306398	Permian	-7.7	-51	69000
Farley's Wood 4 (b)	SK705720	U Carb	-8.2	-56	17800	Larne (a)	ID556569	Permian	-4.0	-28	115000
Farley's Wood 5 (b)	SK705719	U Carb	-8.0	-54	11000	Larne	ID556569	Permian	-2.3	-24	115000
Gainsborough 5 (b)	SK811897	U Carb	-4.6	-36	55000	WORCESTER BASIN					
Glentworth 1 (b)	SK826904	U Carb	-4.3	-24	54700	Guiting Power (g)	SP086245	Triassic	-5.3	-42	11200
Henswell 1 (b)	SK954898	U Carb	-6.1	-41	60800	Guiting Power	SP086245	Triassic	-6.3	-46	9850
Ironville 5 (b)	SK430514	U Carb	-7.8	-51	140	Guiting Power	SP086245	Triassic	-5.7	-42	11200
Rolleston 3 (b)	SK750512	U Carb	-8.0	-50	19200	Kempsey (a)	SO861493	Triassic	-8.1	-54	3460
Stainton 1 (b)	IF062785	U Carb	-5.2	-39	51600	Kempsey	SO861493	Triassic	-8.4	-55	3540
Welton A4 (b)	IF036768	U Carb	-7.2	-49	17000	Kempsey	SO861493	Triassic	-8.2	-57	3270
Welton C4 (b)	TF042752	U Carb	-8.3	-58	26300	Kempsey	SO861493	Triassic	-8.0	-55	3130
Welton C7 (b)	TF042752	U Carb	-7.0	-50	22100	Kempsey	SO861493	Triassic	-7.9	-53	2840
WESEX BASIN											
Marchwood (a)	SZ399112	L Jurassic	-4.1	-34	38100	Kempsey	SO861493	Permian	-7.0	-48	16300
Shrewton (a)	SU031420	L Jurassic	-3.2	-29	48500	Kempsey	SO861493	Permian	-7.1	-50	17100
Wyth Fm (c)	SY980854	L Jurassic	-4.8	-34	52000	Kempsey	SO861493	Permian	-7.0	-49	15500
Yarnbury (d)	SU034411	L Jurassic	-3.8	-32	45000	Kempsey	SO861493	Permian	-6.7	-50	14600
Bournemouth Offshore (c)	SZ130839	Triassic	+0.5	-23	135000	Kempsey	SO861493	Permian	-7.4	-50	12000
Bushey Fm (c)	SY969831	Triassic	-3.2	-30	165000						
Chilworth (e)	SU392180	Triassic	-1.4	-31	88000						
Marchwood (a)	SZ399112	Triassic	-3.1	-33	63800						
Mappowder (d)	SI729058	Triassic	-4.7	-30	170000						
Waddock Cross (c)	SY804913	Triassic	-2.5	-30	150000						
W Esplanade (a)	SZ416120	Triassic	-2.1	-31	74000						
Winterborne Kingston (a)	SY847979	Triassic	-3.7	-27	179500						

Analyses are expressed in permil relative to VSMOW. NGR - national grid reference.

Wells drilled by: a - BGS; b - BP Petroleum Dev. Ltd; c - Carless Exploration Onshore; e - Amoco; f - Geol. Surv. N. Ireland; g - Bearcat Exploration (UK).

Table 2. Stable isotope and radiocarbon values for waters pumped from the Lincolnshire Limestone aquifer. Data from this study unless otherwise indicated.

Borehole	NGR	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	A^{14}C pmc	Borehole	NGR	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	A^{14}C pmc
Aslackby	TF144304	-7.7	-54		Kate's Br	TF106150	-7.7 (b)	-49 (b)	60.0 (b)
Aslackby Fen	TF141303	-7.9	-53		Kloridyke	TF087193	-7.7	-54	
Barron's Fen	TF182113	-8.1	-54	1.1 (a)	Langtoft Fm	TF119129	-7.8 (b)	-50 (b)	46.3 (a)
Baston Fen	TF140160	-8.2 (b)	-53 (b)	2.3 (b)	Leggat's Fm	TF213341	-8.1	-47	
Bertie Fen	TF221278	-8.0	-56		Lenton	TF056313	-7.7	-52	
Billingborough	TF112340	-8.1	-54		Momington Hse	TF173317	-7.8	-54	
Black Hole Drove	TF178252	-8.2	-57		Moulton W Fen	TF288157	-7.0	-40	
Boston Tractors	TF093202	-7.6	-53		New Inn Hse	TF125346	-7.8	-54	
Bourne	TF100202	-7.7	-52		Newlands Fm	TF221241	-8.6	-58	67.3 (c)
Car Dyke	TF125279	-7.8	-55	50.6 (c)	Northorpe	TF109179	-7.8	-55	
Cheal Bridge	TF226294	-7.9	-51		Northorpe Fen Fm	TF114183	-7.6	-51	
Crowland	TF240106	-7.3	-42		Orchard Villa	TF214159	-8.6	-58	
Crowland Bridge	TF231106	-7.3	-44	0.3 (a)	Peakirk	TF169069	-8.1	-54	
Cuckoo Bridge	TF202197	-8.5	-57	2.3 (b)	Pepper Hill	TF184180	-8.0	-56	1.4 (a)
Dean's Farm	TF134292	-8.0	-55		Pinchbeck W	TF205250	-8.0	-53	
Deeping Fen	TF188163	-8.1	-55		Rigbolt Ho	TF195283	-7.8	-53	
Deeping St James	TF165095	-8.3	-56		Rippingale	TF147281	-8.1	-54	
Deeping St Nicholas	TF223180	-8.2	-53	2.3 (a)	Ropsley Lodge	SK983355	-7.9	-54	61.6 (c)
Digby Fen	TF118547	-7.9	-55	47.2 (c)	Ryhall	TF035108	-7.0	-46	
Donington Caythorpe	TF221363	-8.8	-57		Ryland	TF032768	-8.1	-52	
Donington Westdale	TF176355	-8.1	-55	17.5 (c)	Sixscore	TF166141	-8.4 (b)	-54 (b)	0.6 (a)
Dorrington Fen	TF114539	-8.4	-54	1.2 (c)	South Fen Fm	TF133190	-8.2	-52	
Dorrington	TF085530	-8.1	-52		South Moulton	TF293138	-6.3	-40	
Dowsby	TF108293	-7.8	-54		Spalding Bulb	TF231219	-8.5	-58	
Dunholme Rd	TF037764	-8.0	-55		Stow 4	TF072711	-8.1	-54	2.9
Dyke Fm	TF137224	-7.7	-54		Stow 5	TF063705	-7.9	-53	61.1
Dyke Fen	TF129224	-7.7	-52		Stow 6	TF074699	-8.1	-55	2.4
Elm Fm	TF152129	-7.9	-54		Surfleet	TF248280	-8.2	-57	
Engine Fm	TF114639	-7.8	-52		Swaton	TF162364	-7.9	-55	25.7 (c)
Eton	TF142066	-8.0	-50		Tallington	TF097087	-7.7 (b)	-51 (b)	45.9 (b)
Fory Foot Fm	TF162312	-7.1	-47		Timberland	TF130586	-8.2	-54	1.9 (c)
Gibbs Fm	TF142127	-7.9	-54		Tongue End Fm	TF170177	-8.2 (b)	-53 (b)	1.1 (b)
Gosberton	TF245315	-8.4	-53		Vicarage Fm	TF176283	-7.7	-54	
Horseshoe Br	TF219212	-8.4	-56		Walcott	TF130565	-7.9	-54	6.5 (c)
Jockey	TF172264	-8.0	-53		Wilthorpe	TF096137	-8.1	-48	

Analyses expressed in permil relative to VSMOW (stable isotopes) and in percent modern carbon (radiocarbon). NGR - national grid reference. Data sources: (a) - from Lawrence et al (1976), (b) - from Downing et al (1977), (c) - from Bishop and Lloyd (1991).

Table 3 Stable isotope and radiocarbon values for waters pumped from the Lower Greensand aquifer. Data from this study unless otherwise indicated.

Borehole	NGR	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	A ¹⁴ C pmc	Borehole	NGR	$\delta^{18}\text{O}$ ‰	$\delta^2\text{H}$ ‰	A ¹⁴ C pmc
NORTHERN-CENTRAL									
AC Delco 1	TL007113	-7.3	-47	54.1	SOUTH				
AC Delco 2	TL006223	-7.4	-46	47.4	Bourne	SU846145	-7.3	-48	37.1
Battlesden	SP960281	-7.5	-49	63.4	Boxall's Lane	SU864493	-7.7	-52	1.2
Birchmore	SP944348	-7.6	-46	86.5	Mousehill	SU939417	-7.0	-46	37.2
Great Shelford*	TL462517	-8.8	-58	8.6	Netley Mill	TQ077476	-7.3	-45	72.5
Harston*	TL418508	-8.9	-60	2.0	Oakhanger	SU736361	-6.6	-40	35.1
Horlicks	SU950817	-8.7	-56	2.1	Tilford Meads	SU875143	-7.3	-45	24.4
Kingston*	TL345553	-7.7	-48	37.3	Tongham Moor	SU884494	-7.6	-49	0.5
Lord's Bridge*	TL397546	-8.1	-51	21.0	Tongham	SU877148	-8.2	-56	3.1
Pulloxhill	TL080336	-7.5	-48	42.6					
Sandhouse	SP939302	-7.3	-42	39.2	KENT				
Slough Est 7	SU947182	-8.3	-57	0.1	Bowaters*	TQ625745	-8.6	-56	2.8
Slough Est 10	SU947182	-8.2	-56	2.4	Luddesdown*	TQ669663	-7.4	-42	39.0
Slough Est 12	SU949182	-8.3	-56	0.1	Northfleet*	TQ625712	-7.5	-46	32.2
Slough Ind Est*	SU950817	-8.5	-53	1.3	Ryarsh*	TQ670598	-7.3	-47	71.2

Analyses expressed in permil relative to VSMOW (stable isotopes) and in percent modern carbon (radiocarbon). NGR - national grid reference.
* all data for these sites from Evans et al (1979)

Figure captions

- Fig 1 Map of the major Permo-Triassic sedimentary basins of southern Britain and Northern Ireland (after Downing and Gray, 1986.), showing the location of deep borehole sampling points. Also shown are the locations of sites in the *Minor aquifers* category to be discussed below: 1 - Cornish granites; 2 - Bath; 3 - Kent coalfield; 4 - Llandrindod Wells; 5 - Buxton and Matlock; 6 - Sellafield; 7 - Dounreay; 8 - Leixlip
- Fig 2 Plots of $\delta^2\text{H}$ vs $\delta^{18}\text{O}$ and Cl vs $\delta^{18}\text{O}$ for deep brines from geothermal and hydrocarbon exploration wells in the Triassic basins. M - modern groundwaters; P - Quaternary palaeowaters; S - seawater; solid line - world meteoric water line. Plots are as follows: (a) and (b) - Wessex Basin; (c) and (d) - Worcester Basin; (e) and (f) - East Yorkshire and Lincolnshire Basin; (g) and (h) - Cheshire Basin; (i) and (j) - Larne Basin. Plot (a) shows the regression line for Wessex Basin brines. Plot (f) shows the compositional envelope assuming ternary mixing between formation waters as found in the Permian of the Cleethorpes Borehole with modern and Pleistocene meteoric waters of the East Midlands. Plot (h) shows the mixing line between modern recharge and seawater.
- Fig 3 Outcrops of the four main water supply aquifers of England: Permo-Triassic sandstones, Jurassic limestones and the Cretaceous Lower Greensand and Chalk. Principal study areas referred to in the text are 1 - West Cheshire Trias, 2 - East Midlands Trias, 3 - Lincolnshire Limestone, and 4 - London Basin Chalk and Greensand. K -Keyworth, W - Wallingford rainfall isotope stations.
- Fig 4 Plot of $\delta^2\text{H}$ vs $\delta^{18}\text{O}$ for the four main water supply aquifers of England: (a) Triassic of the East Midlands, (b) Lincolnshire Limestone, (c) Lower Greensand, and (d) Chalk of the main London Basin. The world meteoric water line is shown on each plot. Data from Bath et al (1979) and Andrews et al (1984) for the Triassic, Evans et al (1979) and this study for the Lower Greensand, Downing et al (1977), Bath (1983) and this study for the Lincolnshire Limestone, and Smith et al (1976) and Dennis et al (this volume) for the Chalk.
- Fig 5 (a) Plot of $\delta^2\text{H}$ versus depth and (b) plot of radiocarbon activity vs $\delta^2\text{H}$ for water samples from the Dounreay (DN) boreholes, Caithness, northern Scotland. Samples have been selected on the basis of showing least contamination from drilling mud, but may not represent the truly natural compositions. Data of UK Nirex Ltd. Regional shallow groundwater composition from Kay et al (1984).
- Fig 6 Plots of radiocarbon activity ($A^{14}\text{C}$) in percent modern carbon vs $\delta^{18}\text{O}$ for groundwaters in (a) the Sherwood Sandstone of the East Midlands, (b) the Lincolnshire Limestone, (c) the Lower Greensand, and (d) the Chalk of the main London Basin. Regression lines through the data are shown. Data sources as for Figs 4, plus Lawrence et al (1976) and Bishop and Lloyd (1990, 1991) for radiocarbon data from the Lincolnshire Limestone.
- Fig 7 Comparison of the regression lines from Fig 6. K and W represent the long-term weighted mean annual isotopic content of rainfall at the Keyworth and Wallingford collection stations (locations - Fig 3).
- Fig 8 Variation of $\delta^{18}\text{O}$ with depth for two boreholes in Sherwood Sandstone aquifers, showing apparently age-related layering: Hayton, East Midlands, and Stanlow, Cheshire. Some of the variation in the upper part of the Stanlow Borehole is due to mixing with seawater. M - $\delta^{18}\text{O}$ value of modern recharge; P - increasing palaeowater content; S - mixing with seawater. Data from Edmunds and Smedley (in prep.) for Hayton, and from Lucey (1987) for Stanlow.















